WATER ENCYCLOPEDIA

Domestic, Municipal, and Industrial Water Supply and Waste Disposal

Edited by

JAY H. LEHR

JACK KEELEY

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DOMESTIC, MUNICIPAL, AND INDUSTRIAL WATER SUPPLY AND WASTE DISPOSAL

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PREFACE

No one really questions that water is the life blood of humankind. We all remain amazed that the existence of water separates our planet from every other we have thus far viewed in our universe. We can arguably do without every naturally occurring molecule on the earth except water. Life was clearly formed within water and exists in one way or another on water.

Few people in the developed world give this simple fact of life much thought. We have an abundance of water for most of our needs, although some agricultural areas, a few municipalities, and some rural families, at times are strapped for the full amount of water they desire. In the developing world, however, in some locations, the collection and distribution of water is a critical part of every day life, with many women devoting the major portion of their day to the provision of water for their family. In other villages, the construction and protection of a single well can be the primary focus of community needs.

In general, the actual delivery of water for a myriad of uses followed by its disposal is taken for granted by all but the individuals charged with carrying out these often amazing tasks. In this volume of the *Water Encyclopedia*, a collaborative effort of hundreds of people from dozens of countries, we have tried to cover every conceivable topic of interest to people in every walk of life, be they students, researchers, professionals, or just plain folks with an intellectual curiosity about our elixir of life.

We are concerned in this volume with the actual delivery of water to the home by the home owner (subjects include disinfection, corrosion control, nitrates, gray water, septic tanks, and windmills), from the municipal supplier (and their challenges, including distribution, filtration, zebra mussels, reverse osmosis, cryptosporidium, arsenic, and public confidence), to industry and its special needs (such as microfiltration, effluent discharge, reuse, energy, nuclear reactor coolants, and even golf course irrigation), and of course the disposal of our used water in a safe and efficient manner (subjects such as air stripping, bioassays, flotation, sludge, bioavailability, and wetlands). We hope that no reader can stump the experts, which means that we have covered every area of interest. However, we know that this goal is not currently possible, but in coming years and in coming editions on paper and on the World Wide Web, we will more closely approach it. Let us know on our website where our information may be incomplete, and we will be sure to follow-up and fill in the gap in the future.

The contributors to this volume have freely offered their expertise to this project. Some have focused their information on those in need of complete and often complex detail of their subject matter. Others have followed a middle road for a wider audience, and still others believed that a very simple approach to conveying information on their subject was best.

The reader may find all approaches on the same subject matter because the editors frequently sought overlapping information presented from different points of view. We are confident that most people will find their needs met.

Through this encyclopedia, which is the most comprehensive effort ever undertaken on behalf of this most important subject, we hope that we will collectively make a contribution that will enhance the distribution and use of our water supplies in ever safer and more efficient ways.

Jay Lehr
Jack Keeley

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Stuart A. Smith, *Smith-Comeskey Ground Water Science LLC, Upper Sandusky, Ohio,* Evaluation of Microbial Components of Biofouling

Mervyn Smyth, *Centre for Sustainable Technologies, Newtownabbey, United Kingdom,* Domestic Solar Water Heaters

Muhammad Sohail, *Loughborough University, Leicestershire, United Kingdom,* Domestic Water Supply—Public–Private Partnership

Ludovico Spinosa, *National Research Council, BARI, Italy,* Sludge Treatment and Disposal

Fiona M. Stainsby James C. Philp Sandra Dunbar, *Napier University, Edinburgh, Scotland, United Kingdom,* Microbial Foaming and Bulking in Activated Sludge Plants

Bradley A. Striebig, *Gonzaga University, Spokane, Washington,* Sewerage Odors—How to Control

Patrick Sullivan, *Forensic Management Association, San Mateo, California,* Chemical Drinking Water Standards, Past, Present, and Future

Bryan R. Swistock, *Pennsylvania State University, University Park, Pennsylvania,* Methods of Reducing Radon in Drinking Water

David J. Tonjes, *Cashin Associates, PC, Hauppauge, New York,* New York City Harbor Survey

Jack T. Trevors, *University of Guelph, Guelph, Ontario, Canada,* Molecular-Based Detection of *Cryptosporidium Parvum* in Water

Konstantinos P. Tsagarakis, *University of Crete, Rethymno, Greece,* Wastewater Management for Developing Countries

Izrail S. Turoviskiy, *Izrail S. Turoviskiy,* Jacksonville, FloridaProcessing of Sludge, Biosolids, Wastewater Sludge

U.S. Environmental Protection Agency—Office of Wastewater Management, *What Wastewater Utilities Can Do Now to Guard Against Terrorist and Security Threats,*

U.S. Geological Survey, *Estimated Use of Water in The United States in 1990 Industrial Water Use, Source Water Assessment,*

Miguel A. Valenzuela, *Instituto Politecnico Nacional—ESIQIE. MEXICO,,* Wastewater Treatment Techniques—Advanced

G. van der Velde, *Radboud University Nijmegen, Nijmegen, The Netherlands,* Chlorine and Chlorine Residuals

D.V. Vayenas, *University of Ioannina, Agrinio, Greece,* Nitrification of Potable Water Using Trickling Filters

Raghuraman Venkatapathy, *Oak Ridge Institute for Science and Education, Cincinnati, Ohio,* Health Effects of Microbial Contaminants and Biotoxins in Drinking Water, Health Effects of Commonly Occurring Disinfection Byproducts in Municipal Water Supplies, Disinfectants

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Uruya Weesakul, *Thammasat University, Pathumthani, Thailand,* A Real-Time Hydrological Information System for Cities

Janice Weihe, *American Water, Quality Control and Research Laboratory, Belleville, Illinois,* Potential Risks of Waterborne Transmission of *Escherichia coli* O157:H7

June Weintraub, *City and County of San Francisco, Department of Public Health, San Francisco, California,* Disinfectants

Andy Whiteley, *Centre for Ecology and Hydrology, Oxford, United Kingdom,* Molecular Biology Tools for Monitoring Biodiversity in Wastewater Treatment Plants

Dan Wolz, *City of Wyoming, Michigan, Wyoming, Michigan,* Getting Our Clean Water Act Together

Don J. Wood, *University of Kentucky, Lexington, Kentucky,* Design of Water Distribution Systems

Grant Wright, *Heriot-Watt University, Edinburgh, Scotland, United Kingdom,* Roof Drainage Hydraulics

J. Michael Wright, *Harvard School of Public Health, Boston, Massachusetts,* Disinfectants

W. Zachritz II, *New Mexico State University, Las Cruces, New Mexico,* Land Applications of Wastewater in Arid Lands: Theory and Case Studies

B. Zani, *University of Fort Hare, Alice, South Africa,* Key Causes of Drinking Water Quality Failure in a Rural Small Water Supply of South Africa

Grietje Zeeman, *Wageningen University and Research Center, Wageningen, The Netherlands,* Anaerobic Sewage Treatment

Anastasios Zouboulis, *Aristotle University of Thessaloniki, Thessaloniki, Greece,* Landfill Leachates: Part 2: Treatment, Landfill Leachates, Part I: Origin and Characterization, Solidification/Stabilization of Hazardous Solid Wastes, Municipal Storm Water Management, Combined Sewer Overflow Treatment, Technologies for Arsenic Removal from Contaminated Water Sources

THE ARSENIC DRINKING WATER CRISIS IN BANGLADESH

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INTRODUCTION

Although the incidence of arsenic poisoning in groundwater is worldwide and includes Bangladesh and India, Taiwan, Vietnam, Chile, China, North America, and Finland, the area of the highest demand for a resolution of the problem is Bangladesh. The source seems to be geological, for arsenic has been found in tube well water used for drinking and irrigation, although the geochemistry is not completely understood. As many thousands of boreholes have been produced to support modern irrigation systems, the underground aquifers are aerated, which causes transformation of anaerobic conditions to aerobic conditions. The presence of oxygen in this way decomposes arsenopyrite-releasing arsenic acid. At low pH, this arsenic dissolves in water and hence leads to water contamination. The arsenic content of sediments is high relative to crustal concentrations. The biogeochemical cycling of arsenic and iron are coupled in deltaic systems; iron oxyhydroxides act as a carrier for the deposition of arsenic in sediments. From there, it can be mobilized by bicarbonate, which can extract arsenic from sediments under both aerobic and anaerobic conditions.

Arsenic also becomes a pollutant as a result of various industrial uses and activities. Arsenic is a metalloid, and its primary usage has been in agriculture, in formulating herbicides, especially for controlling weeds in cotton fields. Sodium arsenite has been used as an insecticidal ingredient in sheep-dips. In industry, arsenic has found use in glass manufacture and a new role in the semiconductor industry. Copper smelting releases significant amounts into soils.

ARSENIC AND THE GEOGRAPHY OF BANGLADESH

Bangladesh, 85% of which is deltaic and alluvial plain, is situated in the lower end of three large river systems, the Ganges, the Brahmaputra, and the Meghna, whose catchment area is about 600,000 square miles (Fig. 1). The sediments produced in the catchment areas are very high and expose the underlying rocks, including arsenic-bearing rocks.

Arsenic pollution became a live issue in Bangladesh as recently as 1993, following a warning by the World Health Organisation (WHO) that levels of arsenic in groundwater above the permissible limit of 0.05 mg/L had been reported in seven districts of adjoining West Bengal in India. The Department of Public Health Engineering of Bangladesh was invited to test water samples from the adjoining eight Bangladeshi districts that have the same geographical continuity and aquifers as the West Bengal districts; this yielded the result that slightly more than 20% of the samples contained arsenic at levels ranging from 0.01 to 0.4 mg/L. Ten million people populate these areas and hence are at risk of arsenic toxicity.

Figure 1. The geography of Bangladesh.

Since that time, it has been shown that there is groundwater contamination in more than 40 districts that endanger in excess of 50 million people. The problem has been described in *The Lancet* as the world's worst episode of arsenic poisoning; more than 220,000 people reportedly suffer from arsenic-related diseases. In a recent study of 27 districts in Bangladesh, 58% of the water samples were unsuitable for drinking. The worst case was in Nawabganj district, where one well contained 60 times the WHO maximum permissible level.

TOXICITY AND DISEASE

Arsenic occurs principally in the forms of organic arsenic (methyl arsonic acid, dimethyl arsonic acid, arsenobetaine, and arsenocholine) and inorganic arsenic (trivalent and pentavalent arsenic). Of these, the trivalent form is the most toxic to humans (20 times more so than the pentavalent form) and is the most difficult to remove chemically from water.

Arsenic is a suspected carcinogen and has many acute effects on human health. But at the concentrations present in drinking water, it has no immediate side affects. The latency (i.e., the time from first exposure to manifestation of disease) for arsenic-caused skin lesions, in particular keratoses, is typically of the order of 10 years, and so a major increase in the number of cases of arsenic-caused diseases can be projected into the future (Fig. 2).

Figure 2. Common manifestations of long-term, chronic arsenic poisoning.

Exposure to arsenic in this way can lead to latent or manifest clinical symptoms through even low-level exposure over a period of time. This can result in an accumulation of this toxicant in various organs and systems, affecting their normal functioning, including the kidney and nervous system. Arsenic causes skin cancers and internal cancers such as lung and bladder cancer. The most common manifestations in afflicted people in Bangladesh are melanosis (93.5%), keratoses (68.3%), hyperkeratosis (37.6%), and dipigmentation (leucomelanosis) (39.1%). Cancers are found in 0.8% of the afflicted population. Preliminary work indicates that there may be several factors triggering arsenic-related diseases, but experts generally feel that poor nutrition may be a primary cause. Studies in Taiwan have shown that there is an increased occurrence of diabetes in the population exposed to arsenic via drinking water.

Recent studies have shown that arsenic is also a teratogen. Further, at the *5th International Conference on Arsenic* held in Dhaka, 2004, one of the key messages and cause for increased concern is that there is very good evidence that the environmental contaminant is getting into the food chain, thus putting even more lives at risk.

DRINKING WATER STANDARDS

The World Health Organisation has set 10 μg/L as the allowable level for arsenic in drinking water. On January 22, 2001, the U.S. EPA adopted this standard, and public water systems must comply by January 23, 2006.

DETECTING ARSENIC IN DRINKING WATER

In the modern analytical laboratory, arsenic is quantified by soluble arsenic assaying, preferable with GF-AAS (graphite furnace-atomic absorption spectrometry) for detection levels of less than 50 μg/L. However, given the highly dispersed nature of tube wells in Bangladesh, the transport of the many samples to central laboratories is logistically impossible. Field techniques are more important, so that samples can be processed as they are taken. In Bangladesh, this requires inexpensive and completely portable techniques. At present, a chemical test kit is being used (Fig. 3). The disadvantage of this approach is that the sensitivity of the chemistry (poor below 100 μg/L) is not compatible with the levels of contamination that need to be detected (50 μg/L and less). Often, at best, the presence or absence of arsenic can be inferred, but not the level of contamination. In addition, such testing is slow and can take about 6 months to cover some 2000 villages in a district.

Bioavailability Biosensors for Detecting and Quantifying Arsenic

A few strains of bacteria are resistant to arsenate, arsenite, and antimonite through the action of the gene products of the *ars* operon. The *ars* operon consists of five genes that code for three structural and two regulatory proteins. Two structural genes in the *ars* operon, *ars*A and *ars*B, code for proteins that form an efflux pump that transports arsenite and antimonite out of cells.

A means of measuring available arsenicals would be to construct a gene fusion plasmid in which part of the *ars* operon is fused upstream of a reporter gene system, such as the bacterial *lux* operon, which results in the production of light. A transcriptional gene fusion has been done (1) that consists of *E. coli ars*B :: *lux*AB. The detection limit of arsenic is of the order of 10 μg/L. Moreover, bioluminescence may be inducible in a concentration-dependent manner (Fig. 4) by arsenic salts; high concentrations result in higher bioluminescence, so that such biosensors may be able to

- Quantify arsenic within the required range of drinking water in Bangladesh
- Provide a measure of the bioavailability of the arsenic for risk assessment

REMOVAL OF ARSENIC FROM DRINKING WATER

Coprecipitation of arsenate with ferric (Fe^{3+}) ion is currently the most effective and practical method of arsenic removal. Optimum stability of the $FeAsO_4$ precipitate occurs at Fe/As molar ratios of >4; this ratio increases significantly, in practice, depending on water turbidity, slime levels, dissolved solids, and the presence of

Figure 3. Testing for arsenic in drinking water using test kits at a village.

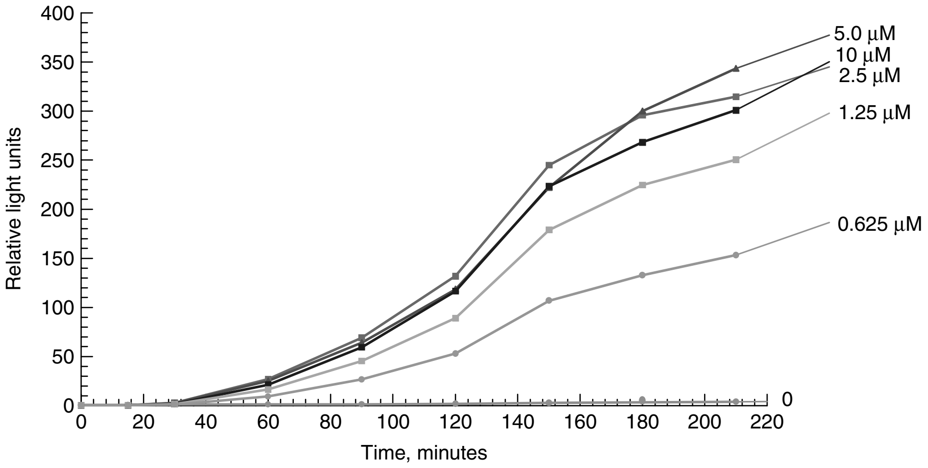

Figure 4. The response of a bacterial whole-cell bioavailability biosensor to increasing concentrations of arsenic.

iron-consuming species. However, Fe^{3+} ion coprecipitation of arsenite ($AsO_3{}^{3-}$) is moderately effective at pH ~7.0. The trivalent As(III) species must be oxidized to As(V) for complete precipitation with Fe^{3+} ion. Oxidation may be achieved through aeration or by adding oxidizers such as hypochlorite, permanganate, peroxide, and ozone. The application of other technologies, including alum and lime precipitation together with activated alumina adsorption, are not fully effective.

In Bangladesh, for geographical and financial reasons, there is likely to be a preference for local treatment rather than large-scale treatment plants. The ideal solution would be to modify each tube well at low cost for arsenic removal by, for example, ion exchange.

BIBLIOGRAPHY

1. Cai, J. and DuBow, M.S. (1997). Use of a bioluminescent bacterial biosensor for biomonitoring and characterization of arsenic toxicity of chromated copper arsenate (CCA). *Biodegradation* **8**(2): 105–111.

READING LIST

Akhtar, S.A. et al. (1997). Arsenic contamination in ground water and arsenicosis in Bangladesh. *Int. J. Environ. Health Res.* **7**: 71–276.

Anawar, H.M., Akai, J., and Sakugawa, H. (2004). Mobilization of arsenic from subsurface sediments by effect of biocarbonate ions in groundwater. *Chemosphere* **54**: 753–762.

Dave, J.M. (1997). Arsenic contamination of drinking water in Bangladesh. *WHO SEA/EH/Meet.3/6.17*.

Dipankar, D. et al. (1996). Arsenic in groundwater in six districts of West Bengal, India. *Environ. Geochem. Health* **18**: 5–15.

Karim, M.D.M. (2000). Arsenic in groundwater and health problems in Bangladesh. *Water Res.* **34**: 304–310.

Tareq, S.M., Safiullah, S., Anawar, H.M., Majibur Rahman, M., and Ishizuka, T. (2003). Arsenic pollution in groundwater: a self-organizing complex geochemical process in the deltaic sedimentary environment, Bangladesh. *Sci. Total Environ.* **313**: 213–226.

Wadud Khan, A. et al. (1997). Arsenic contamination in ground water and its effect on human health with particular reference to Bangladesh. *J. Preventative Soc. Med.* **16**: 65–73.

SOME OTHER ARSENIC LINKS

Harvard University Arsenic Project Website

Natural Resources Defense Council—FAQs: Arsenic in drinking water

U.S. Agency for Toxic Substances and Disease Registry—ToxFAQs: Arsenic

U.S. Environmental Protection Agency—Arsenic Standard pages and Q & A's: Occurrence of Arsenic in Ground Water

West Bengal and Bangladesh Arsenic Crisis Information Centre

World Health Organisation http://www.who.int/mediacentre/factsheets/fs210/en/

BOTTLED WATER

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INTRODUCTION

Bottled water sales in the United States have increased dramatically during the past decade. Total domestic and imported sales rose 142% from almost 2.5 billion gallons (9.4 billion liters) in 1992 to more than 6 billion gallons (22.8 billion liters) in 2002. Bottled water revenues rose nearly 190% from \$2.66 billion in 1992 to \$7.7 billion in 2002. Using the same 11-year period from 1992 to 2002 (1), per capita consumption in the U.S. increased more than 119% from 9.8 to 21.5 gallons (37.1 to 81.4 liters).

The global water market also shows comparable increases. For example, the world total consumption of bottled water rose nearly 63% from 21.3 billion gallons (80.6 billion liters) in 1997 to 34.7 billion gallons (131.3 billion liters) in 2002. Using the same 6-year period from 1997 to 2002, global per capita consumption increased 107% from 5.7 to 11.8 gallons (21.6 to 44.7 liters). Italy, Mexico, and France were the top three countries in per capita consumption in 2002 at 44.2, 37.7, and 37.1 gallons (167.3, 142.7, and 140.4 liters), respectively. In per capita consumption, the United States rose from a rank of 15 in 1997 to a rank of 11 in 2002 (1).

The rising consumption in the United States is attributed to an increasingly effective advertising campaign that touts bottled water as a safer and better tasting alternative to tap water. Packaging labels that show massive glaciers and springs in alpine settings have also helped.

HISTORICAL USES OF BOTTLED OR MINERAL WATER

The presumed reason for drinking mineral water and more recently bottled water is for the purported therapeutic effects and associated health benefits. Using mineral waters as a form of therapy was discussed by the ancient Egyptians and Greeks. Based on legend, the thermal springs of Bath, England, date to 800 B.C. Hannibal's army (and elephants) was reputed to have refreshed itself in the pools of Vergeze in southern France in 218 B.C. while enroute to attack Rome. Later on, the spring waters at Vergeze became known as the source of Perrier Water. The mineral waters from 12 springs at Vichy, France, date back to Roman times. Spring water from Fiuggi near Rome, Italy, was used by Michaelangelo. Another Italian luminary from the fifteenth century, Leonardo da Vinci, used the mineral waters from the three deep springs (396 m; 1300 ft) at San Pellegrino. Famous spas and watering holes, such as Hot Springs in Arkansas and Saratoga Springs in New York and many others in Europe, developed near mineral springs during the late 1800s and early 1900s (2).

Poland Spring water from Maine began to be distributed during the mid-1800s. Bottled water from Mountain Valley near Hot Springs, Arkansas, goes back to 1871. Commercial bottling of San Pellegrino water from Italy began in 1899, and export of Evian water from France to the United States began in 1905 (2).

TYPES OF BOTTLED WATER

Bottled water can be grouped into the following several categories depending upon the nature of the water and its source.

Nonsparkling Water

This includes spring water, artesian water, mineral water, and purified water. Domestic production of this type of water in the United States made up more than 95% of the bottled water market in 2002 (1).

1. Spring water is ground water. It comes from a water-bearing subsurface geologic formation known as an aquifer from which water flows naturally to the earth's surface. Water of this type can be collected only at the spring or from a well that taps the aquifer that feeds the spring.
2. Artesian water is derived from a well in an aquifer that is under pressure due to overlying confining layers. Artesian or confined well water can be collected with external pumps that supplement the natural underground pressure. The word "artesian" was derived from the first deep wells that were drilled into confined aquifers in the province of Artois in northern France from about 1750 (3).
3. Mineral water naturally contains at least 250 ppm of mineral salts such as calcium, chloride, sulfate, carbonate, and bicarbonate. No minerals can be added artificially, and it cannot come from a municipal source.
4. Purified (or demineralized) water may come from a municipal source and is treated by one or more of the following water treatment processes:
   a) Distillation: heating of water to produce water vapor which is then condensed and collected;
   b) reverse osmosis, where water is filtered by passing it though a membrane;
   c) deionization: a process where minerals are drawn to particles of the opposite electrical charge and then removed.

Sparkling Water

Sparkling water may include any type of naturally carbonated water. In addition, if the water is treated, CO_2 can be added to the product as long as the water has the same amount of CO_2 as it had when it emerged from its source.

Domestic and imported sparkling water made up about 2.6% and 2.1% of the U.S. bottled water market in 2002, respectively (1).

Beverages that contain certain ingredients or additives, such as sugar, fall into a separate category called soft drinks. Thus, tonic water, soda water, and seltzer are not considered bottled waters and are regulated differently.

REGULATORY AGENCIES

Public potable water supplies in the United States are regulated by the Environmental Protection Agency (EPA) under the federal Safe Drinking Water Act (SDWA). This means that all public water systems that operate under either public or private investor-owned companies that serve 25 or more people must be tested regularly for up to 118 chemicals and bacteria that are specified by the SDWA.

In contrast, bottled water in the United States is regulated as a packaged food product by the federal Food and Drug Administration (FDA). By law, the FDA must follow the same water quality standards as outlined in the Safe Drinking Water Act. In addition, bottled water companies are required to comply with FDA's quality standards, labeling rules, and good manufacturing practices. Finally, bottlers that are members of the International Bottled Water Association (IBWA) may opt to receive random, unannounced site inspections annually by a third-party organization. However, not all bottled water companies comply with the standards of the IBWA. To compound the regulatory issues associated with bottled water, the standards of the IBWA are not legally enforceable (4). Also, the results of any water quality tests that are made by the bottled water companies need not be released to the public (5). This stands in sharp contrast with the water quality reports that all United States public water supply purveyors must furnish each year to their customers.

The EPA states that bottled water is not inherently safer than tap water distributed by public water systems (6). Although tap water and bottled water must meet the standards set by their respective regulatory agencies, the FDA requires testing only once a year for bottled water, whereas the EPA requires much more frequent, often daily, testing. Another factor worth noting is that the FDA rules apply only to water sold in interstate commerce. The Natural Resources Defense Council (7) estimates that about 60% of all bottled water is sold in the same state where it is bottled; thus, FDA rules do not apply.

State regulations and industry standards affect bottled water at the state level. Some states abide by the FDA standards; others are even more stringent. For example, the State of New Jersey requires that the labels of all bottled water products must contain an expiration date of 2 years from the date of bottling (8). However, about 20% of the states have either very limited enforcement powers or no regulations at all.

Fluorides

It is well known that fluorides are a key factor in reducing tooth decay, particularly in children. Drinking water that has been adjusted to optimal fluoride levels prevents cavities and thereby improves dental health. The consumption of fluoridated water is more effective than the use of fluoridated toothpastes or mouth rinses as the latter is only on the teeth for a short time, whereas fluoridated water can be delivered to the teeth continuously through the bloodstream and saliva (5). Most bottled water does not have an optimal fluoride level. Although some bottlers provide fluoride information on their labels, they are not required to do so.

Safety of Plastic Bottles

For reasons of convenience and nonbreakability, most bottled waters are sold in plastic containers that contain phthalates. Water is a universal solvent, so phthalates can be leached from a plastic bottle. It is still not known if there are any negative health effects from human exposure to phthalates. However, rodents have experienced adverse effects from the chemical in some studies. It is apparent that additional research is needed on this issue (5).

COST TO THE CONSUMER

One thing is very clear about the differences between bottled water and tap water: the former is orders of magnitude more expensive (240–10,000 times greater). Bottled water packaged in convenient sizes of plastic containers costs about $6.60/gallon ($1.74/liter) compared to average costs of 1/100 of a cent/gallon for municipal tap water.

Is the difference warranted by taste, quality, and convenience in carrying, or does the explosive growth in bottled water sales reflect the success of mass marketing appeals to a more affluent generation that follows current fashion trends in beverage types? Time will tell, but for the forseeable future, bottled water sales continue to increase, even though the EPA states on its website that bottled water is not necessarily safer than regular tap water.

BIBLIOGRAPHY

1. Beverage Marketing Corp. (2003). *Bottled Water*. New York.
2. LaMoreaux, P.E. and Tanner, J.T. (Eds.). (2001). *Springs and Bottled Waters of the World: Ancient History, Source, Occurrence, Quality and Use*. Springer-Verlag, New York.
3. Todd, D.K. (1980). *Groundwater Hydrology*, 2nd Edn. John Wiley & Sons, New York.
4. International Bottled Water Association. www.bottledwater.org.
5. Minnesota Department of Health. (2003). *Bottled Water: Questions and Answers*. St. Paul, MN.
6. U.S. EPA (Environmental Protection Agency). *Ground Water and Drinking Water*. www.epa.gov/safewater.
7. Natural Resources Defense Council. (1999). *Bottled Water: Pure Drink or Pure Hype?* New York, NY.
8. New Jersey Department of Health and Senior Services. (2002). *Report to the New Jersey Legislature Summarizing Laboratory Test Results on the Quality of Bottled Drinking Water for the period January 1, 2001 Through December 31, 2001*. Trenton, NJ.

CORROSION CONTROL IN DRINKING WATER SYSTEMS

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CORROSION IN DISTRIBUTION SYSTEM

Corrosion Process and Corrosion Cell

Corrosion can be defined as the wearing away or deterioration of a material because of chemical reaction with its environment. When iron or steel is exposed to water, rust (oxidized iron) forms (1). Water that promotes corrosion is defined as aggressive or corrosive. The corrosion processes consist of a series of electrochemical reactions occurring at the metal surface in contact with water and its constituents. Corrosion is an extremely complex chemical and electrochemical phenomenon. During oxidative reactions, local galvanic couples form on the surface of the metal, in which the metal is oxidized, while the oxidant is reduced. Each couple is a microbattery where the corrosion reaction proceeds with a flow of electric current between anodic and cathodic sites on the metal (Fig. 1). The electrochemical corrosion corresponds to the destruction of a metal by electron transfer reaction. All the components of an electrochemical cell must be present for this type of corrosion to occur. The components include an anode and a cathode (which are sites that have a different electrical potential on the metal), an electrical path between the anode and cathode for electron transport (internal circuit), an electrolyte solution that will conduct ions between the anode and cathode (external circuit), and an oxidizing agent to

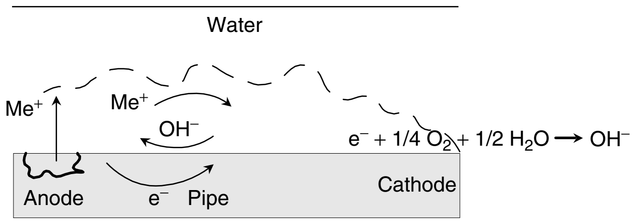

Figure 1. Pipe corrosion in water.

be reduced at the cathode (2). As metallic plumbing materials are not completely homogeneous, anodic and cathodic sites occur on the pipe surface. Oxidation and dissolution of the metal occur at the anode (Fig. 1). Electrons generated at the anode migrate to the cathode, where they are accepted by an electron acceptor, such as oxygen, after chemical reduction. Consequently, the positive ions generated at the anode migrate through the solution to the cathode and negative ions generated at the cathode tend to migrate to the anode. The mechanisms of corrosion are extremely complex and depend on the interactions of physical and chemical factors and the material itself. Table 1 shows different materials, their use in distribution systems, and corrosion-associated problems. Generally, inert and nonmetallic materials like concrete or plastic are more corrosion resistant than metallic pipes.

Scale Formation

The formation of a scale on the pipe surface protects the pipe from corrosion by separating the corrodible metal from the water. Scale is formed when the divalent metallic cations associated with hardness (calcium and magnesium) combine with other minerals contained in water and precipitate to coat the pipe wall. Scale generally includes calcium carbonate ($CaCO_3$), but also magnesium carbonate ($MgCO_3$), calcium sulfate ($CaSO_4$), or magnesium chloride ($MgCl_2$). Water can hold a certain amount of a given chemical in solution. If more is added, it will precipitate instead of dissolve. The point at which no more chemical can be dissolved is the point of saturation. The saturation point depends on water quality, including pH, temperature, and total dissolved solids (TDS) (1).

Types of Corrosion

Different types of corrosion exist, which can be divided into two broad classes: uniform or localized, depending on the material to be corroded, system construction, and water characteristics. Localized corrosion resulting in pitting is produced after galvanic corrosion and concentration cell corrosion. Uniform corrosion takes place in an equal rate over the entire surface (3). The different types of corrosion are summarized in Table 2.

Microbial Corrosion

Bacteria adhere to the pipe surface and form a biofilm (4). Microbes can promote corrosion by creating areas with different concentrations in oxygen, hydrogen ions, minerals, and metals. These concentration differentials promote corrosion. Some microorganisms also catalyze reactions associated with the corrosion process. Iron precipitating bacteria (such as *Gallionella*) can convert Fe (II) to Fe (III) and influence the structure of Fe (III) precipitates (2,5). Organisms involved in the sulfur cycle in water also affect the corrosion process. Sulfate reducers have been found in tubercles under anoxic conditions. Bacteria involved in the nitrogen reaction affect the concentration of oxygen, leading to oxygen concentration cells that produce localized corrosion and pitting. Corrosion also protects bacteria from disinfection. Corrosion products offer a large surface area for microbial attachment. One corrosion product

Table 1. Different Material Types and Corrosion-Associated Problems in the Distribution Network

Material	Sources	Corrosion Problems
Iron and steel	Most common material in water systems	–Buildup of corrosion products on pipe walls and release or iron oxide products
Galvanized pipe	Oldest and most common plumbing material, quality varies	–Better service in hard water –Subject to galvanic corrosion –Leaching of zinc, iron, cadmium, and lead (impurities)
Lead	Lead service lines, lead pipe joints, gaskets	–Corrodes in soft water with pH<8 and hard water with high alkalinity levels –Leaching of lead
Copper	Most commonly used since World War II, excellent characteristics including good corrosion resistance, low cost, and ease of installation	–Subject to uniform corrosion, erosion, and pitting –Attacked by high velocities, soft water, chlorine, oxygen, low pH, and high alkalinity water –Copper leaching
Brass	Alloy of copper and zinc, in meters and plumbing fixtures	–Dezincification (selective removal of zinc) –Good corrosion resistance
Cement/asbestos	Asbestos/cement mains	–Release of asbestos fibers –Calcium can be leached from cement in contact with aggressive water –Increase of pH –Good corrosion resistance
Plastic	PVC pipes	–Resistant to corrosion

Table 2. Different Types of Corrosion

Type of Corrosion	Characteristics
Uniform corrosion	–Corrosion of a single metal –A site is anodic one instant and cathodic the next –Metal loss is uniform over the metal surface
Galvanic corrosion	–Occurs between 2 different types of metals in contact –One metal serves as anode and deteriorates, whereas the other acts as cathode and is protected (Anode: Zinc>aluminum>iron>cast iron>lead>brass>copper: cathode)
Pitting corrosion	–Localized attack, pitting may occur if imperfections in the metal or regions of high stress exist –Imperfection or high-stress area is anodic and surrounded by cathodic area –Corrosion occurs rapidly at point of failure –Chloride is associated with pitting
Tuberculation	–Occurs when pitting corrosion leads to a product buildup at the anode next to a pit
Crevice corrosion	–Form of localized corrosion caused by changes in acidity, decrease in oxygen, or dissolved iron
Erosion corrosion	–Removal of protective films and the pipe metal as well –Results from high flow velocities and turbulence
Cavitation corrosion	–Type of erosion corrosion –Water pressure drops, causing water to form water vapor bubbles that collapse with an explosive effect –Removal of protective coating on metal –Occur in pump impellers, partially closed valves, and reducers
Selective leaching	–Preferential removal of one metal
Stay-current corrosion	–Localized corrosion caused by grounding of home appliances to water pipes
Concentration cell corrosion	Occurs when concentrations of aqueous species (like oxygen) differ between two parts of the metal

(goethite, α–Fe–O–OH) quickly reacts and consumes chlorine. Chlorine is consumed before it can diffuse to the core of corrosion tubercles. The microorganisms within the tubercles are not exposed to lethal concentrations of disinfectant and thus are allowed to grow in the distribution systems. Corrosion products including iron oxides are also capable of adsorbing natural organic matter (NOM) from the bulk fluid (6). NOM accumulates on the surface of corrosion products. It was found that heterotrophic microorganisms found in drinking water supply could readily extract the NOM from the corrosion products for cell growth (7,8). In highly corroded environments, biofilm microorganisms can cause many problems such as bad taste and odor, slime formation, or coliform occurrences.

Consequences of Corrosion

Corrosion is one of the main problems in the drinking water industry. It can affect public health, water aesthetics, and operations. Corrosive water can leach toxic metals from distribution and household plumbing systems. Lead and cadmium may occur in tap water. US EPA promulgated the lead and copper rule in 1991 in order to reduce lead and copper levels in drinking water (9). The methods to reduce lead and copper are the following: removal of these metals from the source water (if present), implementation of a corrosion control program, replacement of lead service lines, and public education. The lead and copper rule defines an action level for the tap concentration of lead and copper higher than 15 ppb and 1.3 ppm, respectively (for the 90th percentile of the samples). Periodic sampling is required to monitor lead and copper concentrations at the customer's tap after leaving the water stagnant in the service lines for 6–8 hours. Moreover, optimal corrosion control water parameters (pH, calcium, alkalinity, temperature, inhibitor level) are defined for the plant effluent and distributed waters. When the lead or copper concentration is above the action level, the water utility has to implement a corrosion control program (9).

Copper in water can cause blue stains and a metallic taste, whereas zinc leads to a metallic taste. Corrosion of cast iron pipes can cause the formation of iron deposits called tubercles in the mains. Red water problems occur when iron is dissolved from cast iron by corrosive water. Iron stains plumbing fixtures, laundry, and makes water appear unappealing for drinking. Responding to customer complaints of colored water or bad taste is expensive in terms of money and public relations. Corrosion-caused problems that add to the cost of water include increased pumping costs after a buildup of corrosion products (tuberculation), uncontrolled scale deposit that can seriously reduce pipeline capacity, and increased resistance to flow. Aggressive water reduces the life of valves and can shorten the service life of plumbing fixtures and hot water heaters. Water leaks lead to loss of water and water pressure (1,3,10).

FACTORS IMPACTING CORROSION

The corrosion rates depend on many site-specific conditions and their interactions, including water characteristics and pipe conditions (2,3,10). The following section describes major factors impacting corrosion. Table 3 shows the effects of some chemicals present in water.

Table 3. Effects of Chemicals on Corrosion

Parameter	Effect on Corrosion
Hardness (measures calcium and magnesium)	Hard water is less corrosive than soft water because of the formation of a film of calcium carbonate ($CaCO_3$) on the pipe wall
Chloride (Cl^-)	Leads to pitting by causing the metal to stay in solution
Sulfate ($SO_4{}^{2-}$)	Leads to pitting by causing the metal to stay in solution
Hydrogen sulfide (H_2S)	Accelerates corrosion
Ammonia (NH_3)	Increases corrosion rates
Organic Matter	Can increase or decrease corrosion rates

Temperature

Corrosion generally increases with temperature as temperature accelerates chemical reactions. Temperature changes the solubility constants and can favor the precipitation of different substances or transform the identities of corrosion products. These changes result in either more or less protection of the pipe surface, depending on the conditions. Temperature also affects the dissolving of $CaCO_3$. $CaCO_3$ tends to precipitate and form a protective coating more readily at higher temperatures. Temperature can affect the nature of corrosion. Corrosion that can be of pitting type at cold temperatures can become uniform at hot temperatures (2,3,10).

Flow/Velocity

The velocity of water increases or decreases corrosion rates depending on the conditions. When water is corrosive, higher flow velocities bring dissolved oxygen to the corroding surface more rapidly. For water with protective properties or containing corrosion inhibitors, high flow velocities aid in the formation of a protective film. At low velocities, the slow movement does not aid the effective diffusion of protective ingredients to the metal surface. High velocities can lead to the erosion of pipes, especially in copper lines. Stagnant waters in water main and house plumbing have been shown to promote tuberculation accompanied with biological growth (4).

Metal and Manufacturing Process

A metal that easily gives up electrons will corrode easily. When dissimilar metals are connected together, the metal corroding easier becomes an anode, whereas the metal resistant to corrosion becomes a cathode (defined as galvanic corrosion). The anode metal will corrode rapidly, whereas the cathode is protected. Manufacturing process can also impact the durability of the pipe, especially for galvanized piping.

Electrical Current

Corrosion is accelerated when an electrical current is passed through the metal. Improper grounding of household electrical systems or electric railway systems leads to electrical current in water pipes.

Dissolved Oxygen (DO)

Corrosion rate increases with increasing DO concentrations. Oxygen is the molecule accepting the electrons given up by the corroding metal. Oxygen also reacts with soluble ferrous iron ions to form ferric iron, which precipitates and forms a tubercle.

Total Dissolved Solids (TDS)

TDS levels are critical because electrical flow is necessary for corrosion to occur. Corrosion rates increase with increasing concentrations of TDS because water becomes a better conductor.

pH

pH is a measure of hydrogen ions (H^+). H^+ is a substance accepting the electrons given up by the metal. Generally, corrosion rate decreases as pH increases.

Alkalinity and Dissolved Inorganic Carbon (DIC)

Alkalinity measures the ability of water to neutralize acids or bases. The corrosion rates decreases as alkalinity increases.

Chlorine Residual

Gaseous chlorine lowers the pH of water by reacting with water to form hypochlorous acid (HOCl), hydrogen ion, and chloride ion. This reaction makes the water more corrosive. For low alkalinity water, the problem is greater because water has less ability to resist pH changes.

MEASUREMENT OF CORROSION

A comprehensive corrosion control program should include several techniques to monitor corrosion, because no single technique provides all the information on corrosion. The corrosion rates are expressed in mils (1/1000 inch) per year (MPY). Corrosion rates can be determined by weight loss method or electrochemical methods. Physical observations of a pipe exposed to water can be conducted, and corrosion indexes can be determined for given water (2,3,10). Table 4 presents different methods to monitor corrosion.

Coupon Weight Loss Method

A metallic coupon is inserted inside a main. The coupon method determines the average corrosion rate over a period of exposure, which is accomplished by weighing the coupon before and after exposure. The corrosion rate is calculated from the weight loss, initial surface area of the coupon, and time of exposition.

Loop System Weight Loss

This method uses a pipe loop or sections of a pipe for determining the effect of water quality on pipe material. Water flows through the loop under a continuous or intermittent flow to simulate the flow patterns of a

Table 4. Different Methods to Assess Corrosion Levels

Method	Advantages	Disadvantages
Coupon weight loss	–Provides corrosion over a specific period –Economical –Coupons placed in system	–Takes a long time –Does not show variations occurring during test –Analytical error because of weighing –Coupon may not be representative of system material
Loop system weight loss	–Actual pipe sections used –Loops placed in the system –Loop can be used to test different chemicals	–Takes a long time –Does not show variations occurring during test
Electrochemical rate measurements	–Simple and reliable –Instantaneous readings –Continuous monitoring possible –Gives uniform and pitting corrosion	–Relatively expensive –Gives corrosion rates for a particular material
Microscopic techniques	–Examination of particles in water and films on pipes –Determination of the morphology of corrosion products	–Require equipment
X-ray analysis and diffraction	–Identification of the elements or class of compounds present in corrosion products and films with possible quantification depending of the technique	–Require equipment
Corrosion indices	–Various indices available	–Have some limitations, can be misapplied –Useful after the fact but not to predict corrosion problems

household. Pipe sections are removed for weight loss measurement and inspection.

Electrochemical Methods

Several instruments are based on the electrochemical nature of metal corrosion in water. They are based on electrical resistance, linear polarization, or galvanic current. Electrical resistance probes measure the resistance of a thin metal probe; as corrosion causes metal to be removed from the probe, its resistance increases. Linear polarization resistance (LPR) is an electrochemical technique that measures the DC current through the metal/fluid interface, which results from polarization of one or two electrodes of a material after application of a small electrical potential. The corrosion current density, which corresponds to the current flowing in a corrosion cell per unit area, is related to the DC current. The galvanic current method measures corrosion of dissimilar alloys of metals.

Radiography Methods

X-ray emission spectroscopy and X-ray diffraction help characterize the corrosion scales.

Microscopic Methods

The deterioration of pipe surface can be evaluated using optical or scanning electron microscopes.

Chemical Analysis of Water and Corrosion Indexes

Water quality data can be used to calculate stability indexes or indicators of water corosivity (Table 5) (10–14). The Langelier Saturation Index (LSI) indicates whether a given water is likely to form or dissolve a protective film of calcium carbonate (11). The calcium carbonate precipitation potential (CCPP) estimates the quantity of $CaCO_3$ that can be precipitated from oversaturated water and the amount that can be dissolved by unsaturated water (12). Larson and Skold (13) studied the effects of chloride and sulfate ions on iron and proposed two indices. In general, it is very difficult to find a relationship between these indices and potential corrosion problems in the system.

METHODS OF CORROSION CONTROL

The complete elimination of corrosion is almost impossible. However, it is possible to reduce corrosion. As corrosion depends on both water quality and pipe characteristics, optimal corrosion control methods are site specific. Three basic approaches to control corrosion exist: (a) modify water quality so that it is less corrosive to the metal, (b) place a protective barrier between the water and pipe, and (c) use pipe material and design the system so that it is not corroded by water. Methods used to achieve corrosion control involve modifying water quality (changing pH and alkalinity), forming a calcium carbonate coating, using corrosion inhibitors, providing cathodic protection, and using a corrosion-resistant coating (3,10).

pH Adjustment

Adjusting the pH is one of the most common methods of corrosion control. As most metals used in the distribution system tend to dissolve more readily at lower pH (presence of H^+), an increase in pH and alkalinity levels can reduce corrosion by reducing the solubility of metals. The optimum pH is related to water and system characteristics; it is generally above 7.0. Various chemicals can be used in corrosion control treatment (Table 6). For example, lime is commonly used to increase both pH and alkalinity. It is less expensive than the other chemical products. However, lime softening can cause severe scale problems

Table 5. Indexes of Water Corrosion

Index	Formula
Langelier Saturation Index (LSI)	$LSI = pH_{actual} - pH_s$ pH_{actual} : pH of water sample $pH_{s:}$ Theorical pH at which water is saturated with calcium carbonate LSI = 0: stable water, LSI < 0: corrosive water, calcium carbonate dissolves, LSI > 0: calcium carbonate precipitates
Calcium carbonate precipitation potential (CCPP)	$CCPP = 50{,}000\ (Talk_i - Talk_{eq})$ (in mg of $CaCO_3$/L) $Talk_i$: initial total alkalinity $Talk_{eq}$: Total alkalinity at equilibrium
Larson Index	$LI_1 = \dfrac{2[SO_4{}^{2-}] + [Cl^-]}{[HCO_3{}^-]}$ The brackets indicate the concentration in mole/L $LI_2 = \dfrac{[Cl^-]}{[HCO_3{}^-]}$
Ryznar Stability Index (RSI)	RSI = pHs-pH RSI = 6.5–7: water at saturation RSI < 6.5: Scale forming water RSI > 7: Undersaturated water

Table 6. Various Chemicals Used to Adjust pH

Chemical	Effect	Addition Equipment
Lime, $Ca(OH_2)$	Increases pH, alkalinity, and calcium levels	Dry storage, gravimetric or volumetric dry feeders, slurry feed
Caustic soda, NaOH	Raises pH and converts CO_2 to alkalinity species	50% solution, metering pumps
Soda Ash, Na_2CO_3	Increases alkalinity with moderate pH increase	Dry storage with solution feed
Sodium bicarbonate, $NaHCO_3$	Increases alkalinity	Dry storage with solution feed
Sulfuric acid, H_2SO_4	Lowers pH	Metering pumps
Carbon dioxide, CO_2	Lowers pH, converts hydroxyls to bicarbonate and carbonate	Pressurized gas feeder

when it is not stabilized. Stabilization after softening can be accomplished by feeding carbon dioxide or sulfuric acid to decrease pH so that calcium carbonate does not precipitate in the distribution system (1).

Formation of a Calcium Carbonate Coating

Protective coating can be applied by controlling the chemistry of water. A common protective coating technique is to adjust the pH of water to a level just above the saturation of calcium carbonate. This process has to be closely controlled because a pH that is too low may result in corrosion and a pH too high may lead to precipitation and cause plugging of the lines.

Corrosion Inhibitors

Some waters do not contain enough calcium or alkalinity to lead to the formation of a coating. Corrosion inhibitors used in potable water act by forming a protective scale over anodic or cathodic sites. These films are commonly inorganic precipitates containing the ions added as inhibitors. They provide a barrier between the water and the pipe. Chemical inhibitors include phosphates and silicates. The success of an inhibitor in controlling corrosion depends on three requirements. First, when treatment is initiated by adding two to three times the normal concentration of inhibitor to build up a protective film rapidly. Several weeks are required for the film to develop. Second, the inhibitor must be fed continuously at a proper concentration. An interruption in chemical addition can lead to the dissolution of the film. Third, water flow rates must be adequate to transport the inhibitor to all parts of the system, otherwise the protection film will not form (3).

Several types of phosphates are used for corrosion control, including linear and cyclic polyphosphates, orthophosphates, glassy polyphosphates, and bimetallic phosphates. It is also possible to use zinc along with polyphosphates and orthophosphates, or blends of ortho and polyphosphates (15). The choice of a particular phosphate product depends on the water and the distribution system characteristics as well as the utility treatment goals. Some phosphates work better than others for a given system (3). It is recommended to conduct laboratory and pilot testing to evaluate the effectiveness of different products. Phosphate inhibitors need particular pH, alkalinity, and concentrations to be effective; the balance required is poorly understood. Orthophosphates seem to be very effective for a wide range of plumbing materials (15). It can be used alone (phosphoric acid, H_3PO_4) or in combination with zinc. Commercial formulations of orthophosphates exist that contain various levels of zinc. Zinc orthophosphate products are used primary in water where the potential for formation of $CaCO_3$ scale is low (soft and slightly acidic water). When using zinc phosphates, limitations of metal levels in wastewaters can limit the use of products with a high zinc content. Zinc orthophosphate leads to the formation of a zinc phosphate scale (16). When zinc is not available with phosphates, a protective scale still forms, such as ferrous or ferric phosphate scale on iron pipes.

Phosphate is most effective in the absence of prior scale formation because phosphates must be part of the precipitate to be effective. When fed into the system, phosphates soften the previously formed scales, causing red water and bacteriological problems as the scale washes out of the system. Orthophosphates can reduce corrosion rate of iron, lead, zinc, and galvanized pipes; although it is not considered to be very effective in preventing copper corrosion (15,17).

A distinction should be made between orthophosphates and polyphosphates (10). Polyphosphates have been used to control corrosion in cast iron pipes; however, little evidence exists of any beneficial effects of polyphosphates on lead corrosion. Some studies (18,19) showed that lead levels could increase in water after solubilization of protective films on the pipes. Some polyphosphates can be used as sequestering agents to keep in solution scale-forming ions (calcium and magnesium) and iron. These polyphosphate products tie up with iron and prevent red water (3).

Inorganic silicates have also been used to reduce corrositivity; they lead to the formation of a protective film onto various metal surfaces. Silicates inhibit corrosion in asbestos cement pipes, where its effectiveness may be attributed to a surface catalyzed conversion to quartz (20). Soluble silicates are adsorbed onto the metal pipe surface at the anodic area and form a thin film. High dosages (20 mg/L) are required during the first 30–60 days of treatment. Then, doses of 4–8 mg/L are added in the system. Silicates have not been widely used because their effects on corrosion are debatable (21,22).

Cathodic Protection

This process limits corrosion of metallic structures. It is used to prevent internal corrosion in water storage tanks. It consists of using an inert electrode (such as high silicon cast iron or graphite) powered by an external source of current. The current forces the inert electrode to act as an anode, preventing the metal to be protected to become an anode and corrode. Another method involves a magnesium or zinc electrode acting as a galvanic anode. The electrode produces a galvanic action with iron; it is sacrificed and corrodes, whereas the iron is protected from corroding.

Lining, Coating, and Paints

A protective coating can keep corrosive water away from the pipe surface and storage tanks. Some linings include coal tar enamels, epoxy paint, cement mortar, polypropylene, or vinyl. These linings are applied when pipes are manufactured or in the field.

UTILITY EXPERIENCE WITH CORROSION CONTROL

Figure 2 shows corrosion rates as a function of temperature and corrosion inhibitor levels in two pilot systems (23). The first system received a constant dose of phosphate over the entire study (system fed after conventional treatment of the Mississippi water, IL-American Water, E. St. Louis), whereas the second system received changing inhibitor levels (test system to optimize treatment). Corrosion rates were strongly related to water temperature (and/or other seasonal factors). For the plant condition system, corrosion rates could vary up to 7 mpy, even when the plant was feeding a corrosion inhibitor (constant doses of 0.86 mg PO_4/l over the year). Higher phosphate levels in the test reactor resulted in low corrosion rates, especially in the summer. Corrosion rates were maintained below 3 mpy when phosphate dosages were slightly increased (between 1.5 and 2 PO_4/l), especially during warm periods. For this site, a seasonal corrosion control strategy was developed that would require slightly higher corrosion inhibitor concentrations during the summer and possibly lower dosages during winter months, rather than using a constant concentration over the entire year (23).

CONCLUSION

As distribution system pipes are in place for long periods of time ($\gg$50 years), corrosion control is critical to maintain microbial and aesthetic water quality and pipe integrity. Water utilities should set corrosion control goals and monitor corrosion rates on a regular basis to determine seasonal changes in corrosivity and adjust corrosion control programs to prevent excessive corrosion.

BIBLIOGRAPHY

1. American Water Works Association (AWWA). (1995). *Water Treatment*, 2nd Edn. AWWA, Denver, CO.
2. AWWA Research Foundation. (1996). Internal Corrosion of Water Distribution Systems. *AWWARF-DVGW-TZW Cooperative Research Report*. Denver, CO, p. 586.
3. Schock, M. (1990). Internal corrosion and deposition control. In: *Water Quality and Treatment*, 4th Edn. McGraw-Hill, New York.
4. Geildreich, E.E. (1996). *Microbial Quality of Water Supply in Distribution Systems*. CRC Press, Boca Raton, FL.
5. Kolle, W. and Roshe, H. (1980). *Von Wasser.* **55**: 159–167.
6. Tipping, E. and Cooke, D. (1982). *Geochimica et Cosmochimica Acta.* **46**: 75–80.
7. Chang, Y., Li, C., and Benjamin, M.M. (1997). *J. Amer. Water Works Assoc.* **89**: 100–113.
8. Abernathy, C.G. and Camper, A.K. (1997). Interactions between pipe materials, disinfectants, corrosion inhibitors, organics and distribution biofilms. *Proc. AWWA WQTC.* Denver, CO.
9. U.S. EPA. (1991). Maximum Contaminant Level Goals and NPDWR for Lead and Copper. *Federal Register*.
10. Faust, S.D. and Aly, O.M. (1999). *Chemistry of Water Treatment*, 2nd Edn. Lewis Pubilsher, Boca Raton, FL.
11. Langelier, W.F. (1936). *J. Amer. Water Works Assoc.* **28**(10): 1500–1505.
12. Rossum, J.R. and Merrill, D.T. (1984). *J. Amer. Water Works Assoc.* **76**(8): 72–82.
13. Larson, T.E. and Skold, R.V. (1957). *J. Amer. Water Works Assoc.* **49**(10): 94–97.
14. Ryznar, J.W. (1944). *J. Amer. Water Works Assoc.* **36**: 472–479.
15. Benjamin, M.M., Reiber, S.H., Fergusson, J.F., Van der Werff, E.A., and Miller, M.W. (1990). *Chemistry of Corrosion Inhibitors in Potable Water*. AWWA Research Foundation, Denver, CO.
16. Swayze, J. (1983). *J. Amer. Water Works Assoc.* **75**: 101–102.

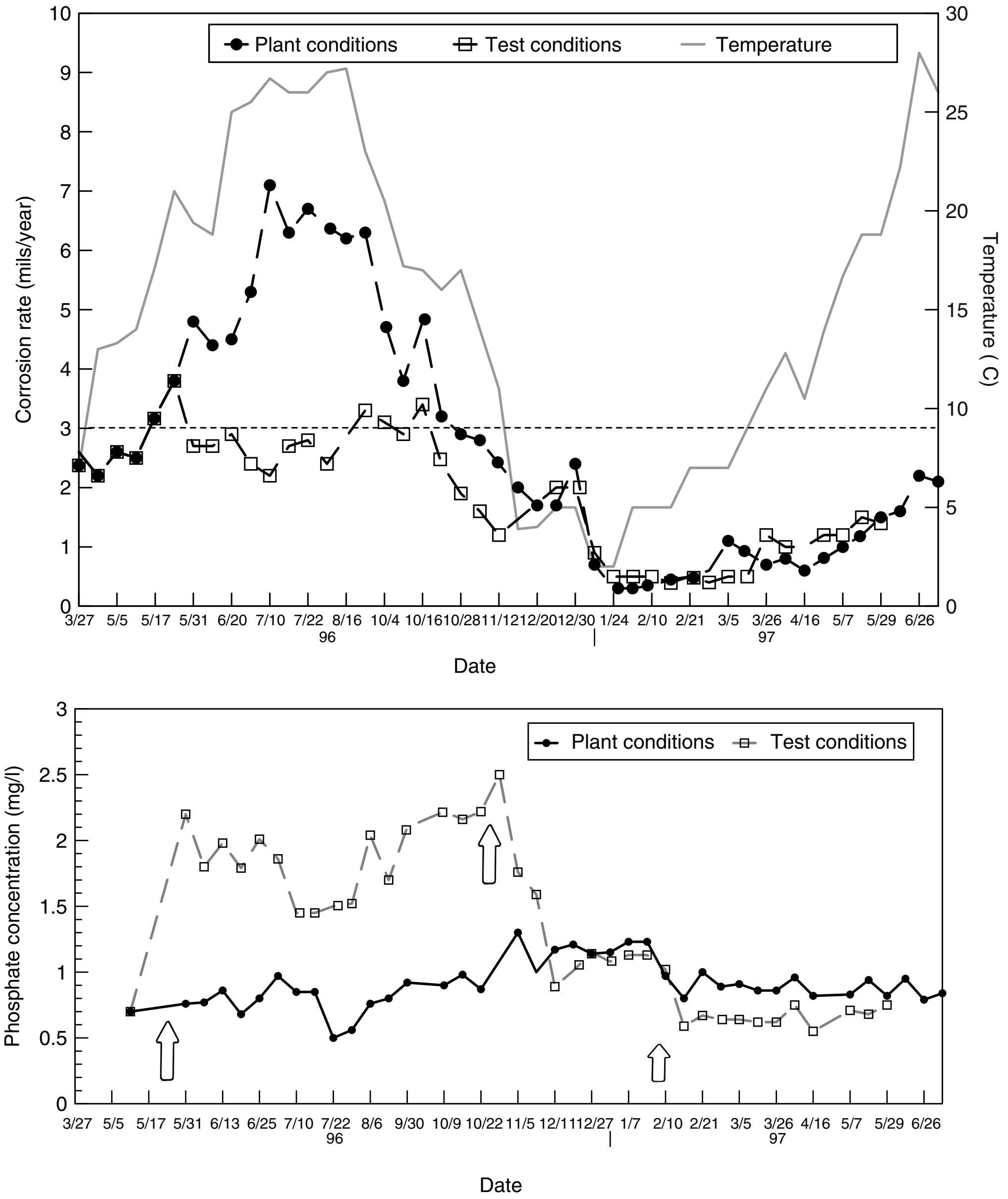

Figure 2. Corrosion rates as a function of corrosion inhibitor levels and temperature (the arrows show the changes in inhibitor levels to optimize corrosion control).

17. Ryder, R. and Wagner, I. (1985). Corrosion inhibitors. In: *Internal Corrosion of Distribution Systems*. AWWA Research Foundation, Denver, CO.
18. Schock, M.R. (1989). *J. Amer. Water Works Assoc.* **81**(7): 88–95.
19. Holin, T.R. and Shock, M.M. (1991). *J. Amer. Water Works Assoc.* **83**(7): 76–83.
20. Schock, M.R. and Buelow, R.W. (1981). *J. Amer. Water Works Assoc.* **73**: 636–751.
21. Sheiham, I. and Jackson, P.J. (1981). *J. Inst. Water Engrs. Scientists.* **35**(6): 491–496.
22. Rompre, A., Prevost, M., Brisebois, P., Lavois, J., and Lafrance, P. (1997). Comparison of corrosion control strategy efficiency and their impacts on biofilm growth. *Proc. AWWA Water Quality Tech. Conf.*, Denver, CO.
23. Volk, C., Dundore, E., Schiermann, J., and LeChevallier, M. (2000). *Water Res.* **34**: 1967–1974.

ECONOMICS OF RESIDENTIAL WATER DEMANDS

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This entry examines what is known regarding the economic characteristics of residential water use and how this type of information can be applied in managing water resources. Understanding the economic dimension of household water use is important for several reasons. First and most importantly, all households on the planet share the need for access to potable water supplies. On the other hand, households have very different degrees of access to safe water. For most of North America and Europe, access to clean water is almost taken for granted by many households. In contrast, a great number of households in low-income countries do not have access to reliable supplies of potable water. As the World Bank contends, "The challenge is enormous: one billion people still lack access to safe water, two billion lack safe sanitation. Slow progress is not acceptable, as more than three million children still die every year from avoidable water-related disease" (World Bank Water Supply and Sanitation web-site, September 1, 2001 http://www.worldbank.org/html/fpd/water/). Second, the agricultural sector dominates global water use, but residential and industrial demands have grown much more rapidly during the twentieth century. Third, empirical evidence indicates that the amount of water used by a household is a complex function of a number of influences, including the price of water (both in monetary terms and in time costs), household income, and household characteristics (for example, the number of residents and water-using appliances).

THE ECONOMIC PERSPECTIVE ON RESIDENTIAL WATER DEMANDS

Households use water for personal hygiene, waste removal, cooking, cleaning and a number of outdoor applications (lawn and garden watering, etc.) Table 1, Fig. 1. Except in some arid portions of the United States, the bulk of residential water use occurs indoors and is related to personal hygiene and waste removal (4). In North America, for example, these two applications account for 60% to 70% of the average household's daily indoor water use. Another important feature of residential water use is its cyclical character. On a daily basis, household water use typically displays two peak periods of use: early morning and early evening. On an annual basis, residential water use in summer months is usually substantially higher, than during the rest of the year due to the increase in outdoor water use. Hanemann (5), for example, indicates that for households in the Western states of the United States, total summer water use exceeds total winter water use by 50–60%. The multiplicity of water's uses and the cyclical nature of water use suggest that potentially a number of factors influence a household's water use decisions.

Economic theory provides a useful framework within which the nature of residential water use may be examined. Economists usually assume that a household's demand for any good such as potable water is, in the most general case, a function of all of the prices facing a household as well as its income and demographic characteristics. The household's estimated demand for water may be used to predict household consumption levels and to predict how households will respond to changes in the price of water. This degree of responsiveness is captured by a variable known as "elasticity." This variable is measured as the ratio of the percent change in the demand for a good to the percent change in a price or income. A household's demand is said to be 'inelastic' if the estimated elasticity is less than one. For example, if the price elasticity of demand equals −0.5, then a 10% increase in price, it is predicted, with to induce a 5% decrease in water use. The empirical water demand literature seeks to estimate households' price and income elasticities of water demand as well as those households' valuation of access to potable water supplies.

Table 1. Residential Water Use in 1995[a]

Country	Annual Residential Water Use (m^3/person)
Chad	4
Nigeria	9
China	21
India	25
Greece	45
Israel	45
South Africa	49
Argentina	67
Uruguay	73
France	94
Japan	137
Canada	157
U.S.A.	203

[a] Ref. 1.

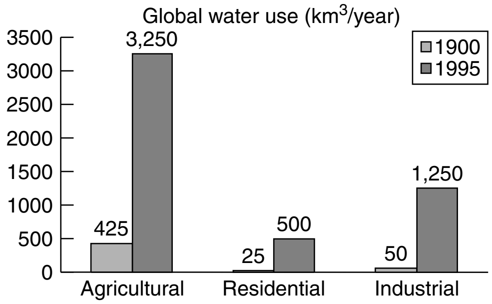

Figure 1. Global water use (1,2).

There are several ways in which the general model of household demand has been altered to reflect conditions that are important in the consumption of water. These include situations when households' choice of water use is constrained by their stock of water-using appliances and the size of the house and property (6), when households must choose not only the quantity of water to consume but also the source of its potable water (7), and when households face water prices that are complex functions of the quantity of water used. The last of these extensions is quite important because of the growing frequency of complex price schedules facing households and because of the implications of this type of price structure for the statistical estimation of residential water demands (5,8).

EMPIRICAL MODELS AND RESULTS

Residential water use has received a substantial amount of attention from economic researchers. There are a number of surveys that summarize the theoretical and empirical research (4,9–11). The main goal of statistical models of water demand is to estimate the relationship between the observed quantity of residential water use and the explanatory variables (such as the price of water) suggested by economic theory. During the evolution of the residential water demand literature, a number of issues have been at the forefront, including the appropriate definition of the price of water, the choice of statistical technique, and the role of other explanatory variables (such as climate and household characteristics).

The modern residential water demand literature begins with the work of Howe and Linaweaver (12). The authors estimate demand models for domestic (indoor) and sprinkling (outdoor) water demands. The demand models are further divided according to climatic zones. The authors assume that the quantity of water demanded by the average household is a function of water and sewage prices, age and value of property, the number of people in the household, and climate conditions. The estimation models indicate that indoor water use is responsive to the price of water to a limited degree (price elasticities ranging from −0.214 to −0.231) and outdoor water use is more responsive to prices (price elasticities ranging from −0.438 to −1.57). Income elasticities follow the same pattern: 0.314 to 0.378 for indoor water use and 0.447 to 1.45 for outdoor.

Since the work of Howe and Linaweaver, statistical models of residential water demand have become more sophisticated, and data on household water use and characteristics have become more detailed and comprehensive. A particularly important issue has been the manner in which the price of water is represented. When prices are set out as complex functions in which prices can increase or decrease with the amount purchased, researchers must take more care in measuring the influence of prices on water use (the variety of statistical methods used to do this is reviewed in Ref. 11).

A number of other factors, it has been found, are influential in determining household water demand. Researchers have found positive relationships between water use and family size, property value, and household income (4). In Hanemann's (5) comprehensive listing of estimated water demand elasticities, the average of the income elasticities reported is 0.52. Another important set of factors that, it has been found, influences residential water demand is related to climate. There is a consensus in the literature that increases in temperature or evaporation rates lead to higher residential water demand, whereas increases in precipitation have the opposite effect. However, indoor residential water use appears to be relatively insensitive to weather conditions, and most of the influence of climate on residential water use works through outdoor water uses.

LOW-INCOME COUNTRIES

Households in many low-income countries face a variety of challenges in their efforts to secure potable water. In large urban centers, water supply systems are often unreliable and fail to provide service to many of the city's poorest residents (13). Residents in rural areas frequently confront even greater risks from contaminated and distant water supplies (14). Households in low-income countries also differ from their high-income counterparts in that they spend a larger share of their income on water. They also may face a different set of circumstances regarding their supply of potable water. For example, it is common for households in low-income countries to have several possible sources of potable water. Mu, Whittington and Briscoe (14) report that the members of a small town in Kenya choose among private pipe, communal wells and pumps, kiosks, and water vendors for their potable water. These sources differ in their relative cost, convenience, reliability, and quality. It is important to note that the cost of each alternative is a combination of the time spent obtaining water, installation charges, continuing connection charges, and prices. Households face the challenge of deciding which supply source(s) to use as well as how much water to obtain from each source, and researchers face the challenge of understanding and modeling these decisions (15).

There have been a number of attempts to model, first, household decision-making regarding its choice of the source of its drinking water and, second, households' valuation of improved access to reliable water supplies in low-income countries. Researchers have conducted surveys that collect information on households' supply–source choices and characteristics. For example, Madanat and Humplick (16) examine the behavior of 900 households in Faisalabad, Pakistan. The authors conclude "the more expensive the in-house pipe connection relative to the other sources, the less likely the household is to connect" (p. 1337). In addition, the connection decision is strongly influenced by household expectations regarding the relative reliability and quality of alternative sources as well as their past experiences with alternative supply sources.

With respect to the value they assign to access to safe water, many households in low-income countries find themselves in what some researchers have termed a "low-level equilibrium trap" (17, p. 1931). By this, the authors mean that the existing water supply system has few connections, low prices, low revenues, low maintenance, poor reliability, and low usage by households. One of the ways to improve this situation is to demonstrate that the value of improved service to households (as expressed in their willingness to pay through higher prices) exceeds the costs of improving service.

The World Bank Water Research Team (15) is the most extensive effort to assess the preferences of households in low-income countries for connection to water supply systems. The authors find that household income is positively linked to the demand for improved services, but the link between the two is not strong. Households with higher levels of education are also willing to pay more for improved access. Gender is often an important factor in explaining willingness to pay, but "the direction of the influence depends on the specific cultural context" (p. 53). In Tanzania and Haiti, female respondents' willingness to pay exceeds that of males, but in Nigeria and India, the reverse is true. As expected, economic variables play an important role, and higher connection charges and monthly prices reduce demand. Finally, households are willing to pay more for private connections and for sources higher expected quality levels and reliability.

RESIDENTIAL WATER DEMAND MANAGEMENT

Historically, the challenge of managing water resources and providing potable water has concentrated on the engineering task of conveying and treating water so that it would be available for household use. However, as the construction and operation of water distribution and treatment systems becomes increasingly expensive (in monetary and environmental terms), attention has turned to the idea of balancing the costs of developing water supplies with the benefits derived from consumption. From this adoption of a more balanced perspective has come a renewed interest in using the information contained in estimated residential water demand to assist in planning and operating water delivery systems.

Estimated residential water demand equations provide information that can be used in a variety of ways to promote water conservation and in the development and operation of water supply systems. First, the structure of residential water demand can provide water utility operators with information regarding the relative efficacy of alternative policy instruments aimed at promoting water conservation. For example, Renwick and Archibald (18) examine the factors influencing Californian households' adoption of water conserving technologies such as low-flow toilets and showerheads. The results of the authors' empirical model suggest that both price and nonprice measures reduce household water use, although their impact varies across households.

Forecasting future water use is a second way in which demand information is used. Dziegielewski (19) provides a brief review of the history of urban water demand forecasting. In the "traditional" method of forecasting that has dominated historically, total future demand is predicted as the product of expected population growth and a fixed per capita water use coefficient. This method was not very accurate as it neglected other influences (such as prices) on water use. The development of the municipal and industrial needs (MAIN) model represents a major change in forecasting methods. The MAIN model disaggregates total water use into a large number (approximately 400) of categories and locations. The factors that influence water demand for each category are determined through statistical analysis. Changes in these explanatory variables (such as income, climate, and energy prices) translate into anticipated changes in water use and, in turn, form the basis for water demand forecasts. A third way in which water demand information is used in assessing the construction and operation of water delivery systems. For example, the costs of improving the reliability of a water supply system can be compared with households' valuation of that increase in reliability (20).

CONCLUSIONS

All households share the need for access to potable water, but actual consumption levels vary significantly due to differences in income, water prices, proximity to reliable water supplies, climate, and a variety of other factors. Economic models of household decision-making regarding water use indicate that households are influenced by these factors and that water prices, income levels, and climate play particularly influential roles. A different line of research highlights the challenges faced by households in low-income countries in their efforts to acquire potable water. One of the facets of this situation that has received attention recently concerns households' decision-making when confronted with more than one source of potable water. As predicted by economic theory, most households consider the relative quality, reliability, and cost of alternative sources when making their choices. The last topic considered here is the use of information regarding the economic features of residential water demand to encourage water conservation. Research indicates that both price and nonprice based conservation programs are effective in curtailing demands.

BIBLIOGRAPHY

1. Gleick, P. (2000). *The World's Water 2000–2001*, Washington, DC, Island Press.
2. Abramovitz, J. (1996). *Imperiled Waters, Impoverished Future: The Decline of Freshwater Ecosystems*, WorldWatch paper 128, Washington, DC, Worldwatch Institute.
3. Biswas, A.K. (1997). Water development and environment. In: *Water Resources: Environmental Planning, Management and Development*. A.K. Biswas (Ed.). McGraw-Hill, New York, pp. 1–37.
4. Baumann, D.J., Boland, and Hanemann, W.M. (1998). *Urban Water Demand Management and Planning*. McGraw-Hill, New York.
5. Hanemann, W.M. (1998). Determinants of urban water use. In: *Urban Water Demand Management and Planning*. D.J. Baumann, Boland, and W.M. Hanemann. McGraw-Hill, New York, pp. 31–75.
6. Lyman, R.A. (1992). Peak and off-peak residential water demand. *Water Resour. Res.* **28**(9): 2159–2167.
7. Asthana, A. (1997). Where the water is free but the buckets are empty: Demand analysis of drinking water in rural India. *Open Economies Review* **8**(2): 137–149.
8. Shin, J. (1985). Perception of price when information is costly: Evidence from residential electricity demand. *Rev. Econ. Stat.* **67**(4): 591–598.
9. Hanke, S. and de Maré, L. (1984). Municipal water demands. In: *Modeling Water Demands*. J. Kindler and C. Russell, (Eds.). Academic Press, London, pp. 149–170.
10. Gibbons, D.C. (1986). *The Economic Value of Water*, Resources for the Future, Washington, DC.
11. Renzetti, S. (2002). *The Economics of Water Demands*, Kluwer Academic, Norwell, MA.
12. Howe, C. and Linaweaver, F. (1967). The impact of price on residential water demand and its relation to system design and price structure. *Water Resour. Res.* **3**(1): 13–31.
13. Rivera, D. (1996). *Private Sector Participation in the Water Supply and Wastewater Sector: Lessons from Six Developing Countries*. The World Bank, Washington, DC.
14. Mu, X., Whittington, D., and Briscoe, J. (1990). Modeling village water demand behavior: a discrete choice approach. *Water Resour. Res.* **26**(4): 521–529.

15. World Bank Water Research Team. (1993). The demand for water in rural areas: Determinants and policy implications. *World Bank Res. Obs.* **8**(1): 47–70.
16. Madanat, S. and Humplick, F. (1993). A model of household choice of water supply systems in developing countries, *Water Resour. Res.* **29**(5): 1353–1358.
17. Singh, B., Ramasubban, R., Bhatia, R., Briscoe, J., Griffin, C., and Kim, C. (1993). Rural water supply in Kerala, India: How to emerge from a low-level equilibrium trap. *Water Resour. Res.* **29**(7): 1931–1942.
18. Renwick, M. and Archibald, S. (1998). Demand side management policies for residential water use: Who bears the conservation burden? *Land Econ.* **74**(3): 343–59.
19. Dziegielewski, B. (1996). Long-term forecasting of urban water demands. In: *Marginal Cost Rate Design and Wholesale Water Markets, Advances in the Economics of Environmental Resources*, Vol. 1, D. Hall (Ed.). JAI Press, Greenwich, CT, pp. 33–47.
20. Howe, C. and Griffin Smith, M. (1993). Incorporating public preferences in planning urban water supply reliability. *Water Resour. Res.* **29**(10): 3363–3369.

GRAY WATER REUSE IN HOUSEHOLDS

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Gray water is a loosely defined term representing discharges from wash basins, baths, showers, dishwashers and washing machines. This generally excludes wastewater from kitchen sinks and toilets, commonly known as black water. Gray water accounts for about 50% of the total household water consumption activities (Fig. 1).

The quality of gray water depends on factors, including the habits and affluence of the water users, the types of products used for clothes and personal washing, and the nature of the substances disposed of through sinks and other appliances. Substances found in gray water include detergents, shaving foam, toothpaste, soap, hair, body oils, and dried skin residues. Small amounts of fecal material arising from washing of baby diapers and traces of urine are also present in gray water. These pollutants exert oxygen demand and contain some disease causing microorganisms. Typical gray water pollutant concentrations from different sources are shown in Table 1. The average pollutant concentration measured in the effluent from different appliances housed in a residence hall (for example) is shown in Table 2.

Freshly produced gray water usually does not have any objectionable odor. Compared to black water, gray water has a relatively higher temperature and readily degradable pollutants. Therefore, it requires immediate treatment after collection. If stored untreated for long periods, oxygen deficient conditions will develop, and scum will be formed that can float or sink in the collection tank. Experiments have shown that bacterial population also increases with increased storage time (5).

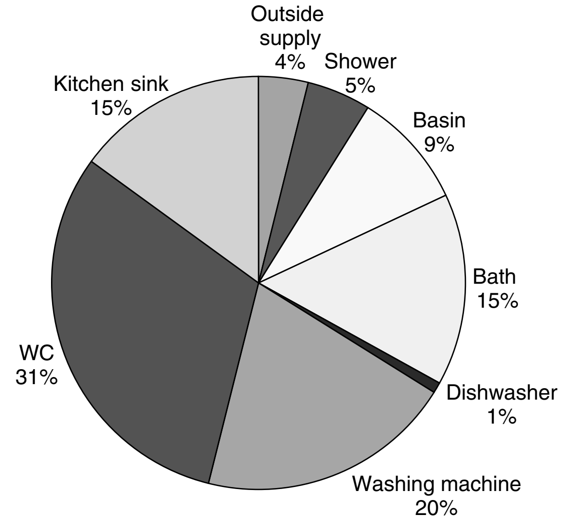

Figure 1. Components of domestic water use (2).

Table 1. Gray Water Quality from Various Sources[a]

	BOD (mg/l)	COD (mg/l)	Turbidity (NTU)	NH_3 (mg/l)	P (mg/l)	Total Coliforms
Single person	110	256	14	–	–	–
Single family	–	–	76.5	0.74	9.3	–
Block of flats	33	40	20	10	0.4	1×10^6
College	80	146	59	10	–	–
Large college	96	168	57	0.8	2.4	5.2×10^6

[a] Ref. 3.

Before gray water is reused, a certain level of treatment is required to minimize aesthetic concerns and the potential for health risk. Table 3 shows a summary of gray water quality criteria for toilet flushing followed in different countries. The level of treatment required depends on the scale and purpose of use. On a small scale (domestic level), a two-stage treatment consisting of filtration of coarse pollutants (hair and suspended impurities) followed by disinfection with chlorine, bromine, or UV is probably sufficient. On larger scales (hotels, commercial buildings), more complex and expensive methods of treatment could be employed.

Domestic gray water recycling systems, normally employed, produce water for toilet flushing. A recycling system (Fig. 2), typically, consists of an underground collection tank and an overhead distribution tank to supply toilet cisterns. The collection tank is designed to prevent groundwater contamination and ingress and is sized to accommodate water volumes intended for reuse. The optimal size of the collection tank has been modeled by Dixon (6), and systems storing 100–200 liters are considered sufficient for a family of five persons (7). Any excess gray water is diverted to the sanitary drain (i.e., the drain going out of the household). Devices are installed to prevent back-flow from the foul drain to the tank. Filtration is typically carried out at the tank inlet. The clogged filters are either replaced or cleaned using water jets. A submersible pump fitted with a float switch

Table 2. Average Pollutant Concentration in Gray Water Measured in a Residence Hall[a]

Parameter	Bath/ Shower	Washbasin	Washing Machine	Laundry and Dishwashing
BOD (mg/L)	216	252	472	110
COD (mg/L)	424	433	725	–
Ammonia as N (mg/L)	1.56	0.53	10.7	–
Phosphate as P (mg/L)	1.63	45.5	101	–
Total coliforms (cfu/100 mL)	6×10^6	5×10^4	7×10^5	5×10^6
Faecal coliforms (cfu/100 mL)	600	32	728	462
Turbidity (NTU)	92	102	108	148
Inorganic carbon (mg/L)	26	20	25	20
TOC (mg/L)	104	40	110	84
Total solids (mg/L)	631	558	658	538
Suspended solids (mg/L)	76	40	68	90
Dissolved solids (mg/L)	559	520	590	449
Volatile solids (mg/L)	318	240	330	277
pH	7.6	8.1	8.1	7.8
Copper (mg/L)	111	–	322	–
Lead (mg/L)	3	–	33	–
Zinc (mg/L)	59	–	308	–
Cadmium (mg/L)	0.54	–	0.63	–

[a] Ref. 4.

Table 3. International Water Quality Criteria for Toilet Flushing[a]

	Fecal coliforms (cfu/100 mL)	Total coliforms (cfu/100 mL)	BOD (mg/L)	Turbidity (NTU)	TSS	DO% (% saturation)	pH	Cl_2 residual (mg/L)
US EPA (g)	14 for any sample	–	10	2	–	–	6–9	1
	0 for 90% samples	–	–	–	–	–	–	–
Florida (m)	25 for any sample	–	20	–	5	–	–	1
	0 for 75% samples	–	–	–	–	–	–	–
Texas (m)	75 (m)	–	5	3	–	–	–	–
Germany (g)	100 (g)	500 (g)	20 (g)	1–2 (m)	30	80–120	6–9	–
Japan (m)	10 for any sample	10	10	5	–	–	6–9	–
South Africa (g)	0 (g)	–	–	–	–	–	–	–
WHO lawn irrigation	200 (g)	–	–	–	–	–	–	–
	1000 (m)	–	–	–	–	–	–	–
EC bathing water	100 (g)	500 (g)	2 (m)	–	–	80–120	6–9	–
	2000 (m)	10000 (m)	(g)	–	–	–	–	–
	–	–	1 (m)	–	–	–	–	–
	–	–	(m)	–	–	–	–	–
UK (BSRIA)	14 for any sample	–	–	–	–	–	–	–
Proposed (g)	0 for 90%	–	–	–	–	–	–	–

[a] Ref. 4.
g = guideline.
m = mandatory.

is normally used in the tank to transfer filtered water to the overhead tank. This then contains the disinfectant feeding arrangement and switches to control the water level. When the water volume in the overhead tank drops below a certain level, the pump turns on and stops when the water level in the tank reaches the design level. The overhead tank normally has an inlet to provide a top up supply of mains water when the treated gray water is not sufficient to meet the demand or the recycling system is inoperative. An air gap is typically provided between the inlet pipes of gray water and mains water. The pipework carrying gray water needs to be clearly marked or colored differently to avoid cross connections and contamination of potable water. The underground and overhead tanks will be designed to drain down fully to avoid problems of prolonged gray water storage. There are several packaged recycling systems available on the market. Each offers a different degree of treatment and safety controls. Experience has shown that they are not 'fit and forget' systems but require monitoring to ensure their smooth operation. Therefore, a clear warning mechanism that can show the failure of system components should be installed within the household, and clear maintenance instructions provided.

Gray water recycling is not a problem-free option, and particularly, issues related to health risk must

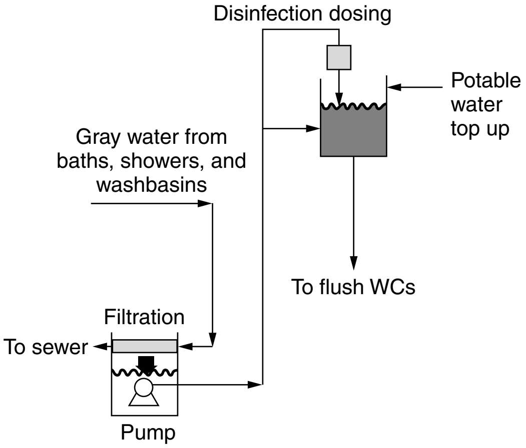

Figure 2. Water flows and components of a typical gray water recycling system.

be addressed. Although most waterborne pathogens are killed by conventional disinfectants, there are certain species (e.g., *Legionella* spp.) that are resistant to normal modes of treatment. *Legionella pneumophila*, a naturally occurring bacterium in domestic hot water supplies, showerheads, cooling waters, and other water services in buildings, has been linked to outbreaks of Legionnaires' disease. Surface fouling, biofilm formation, slow moving or stagnant waters, and increased temperatures are favorable conditions for *Legionella* growth. Therefore, recycling systems could provide an ideal environment for their growth. *Legionella* has an infection route through inhalation, and it is suspected that some bacteria may be inhaled through water vapors during toilet flushing (8). Fortunately, however, research shows that the *Legionella* count in gray water is typically low (3). To avoid in-pipe water stagnation for a prolonged period, the recycling system should be kept free from 'dead legs.' Past case studies on gray water recycling systems suggest that the relative health risk from gray water reuse is not high if it is properly treated and does not come in direct contact with users (8). For additional safety, the use of treated gray water should be discontinued when any of the users living in the household is ill. Spray irrigation with gray water is not advised because it will increase the bacterial exposure potential. There is also concern about the use of chlorine as a disinfectant. It has been found that chlorine can corrode metal switches and fittings in the overhead tank and toilet cistern. Excessive buildup of chlorine gas in the overhead tank (if located in a loft) may produce an unpleasant smell in the household and may be linked to asthma (9). Other disinfectants, such as ultraviolet radiation, are also available. UV lamps are expensive, and their germicidal efficiency reduces with time. They are most effective in waters of low turbidity. Therefore, fine filtration will be needed to achieve improved pathogen removal. The residual effect of UV as a disinfectant is not stable and microbial regrowth is possible, so UV treated waters should not be stored for long periods. Bromine is also used for pathogen removal from gray water. Some forms of bromine disinfectants such as hypobromous acid are considered harmful to plants, and the treated water would not be suitable for irrigation. The health risks from bromine use are yet to be quantified (7).

At present, gray water recycling systems on a single household scale are hardly financially viable. Although there are some savings from reduced consumption of mains water, the capital and operating expenditures incurred for these systems are relatively high, and the pay-back period is 20–25 years (10). The payback period reduces with increase in occupancy.

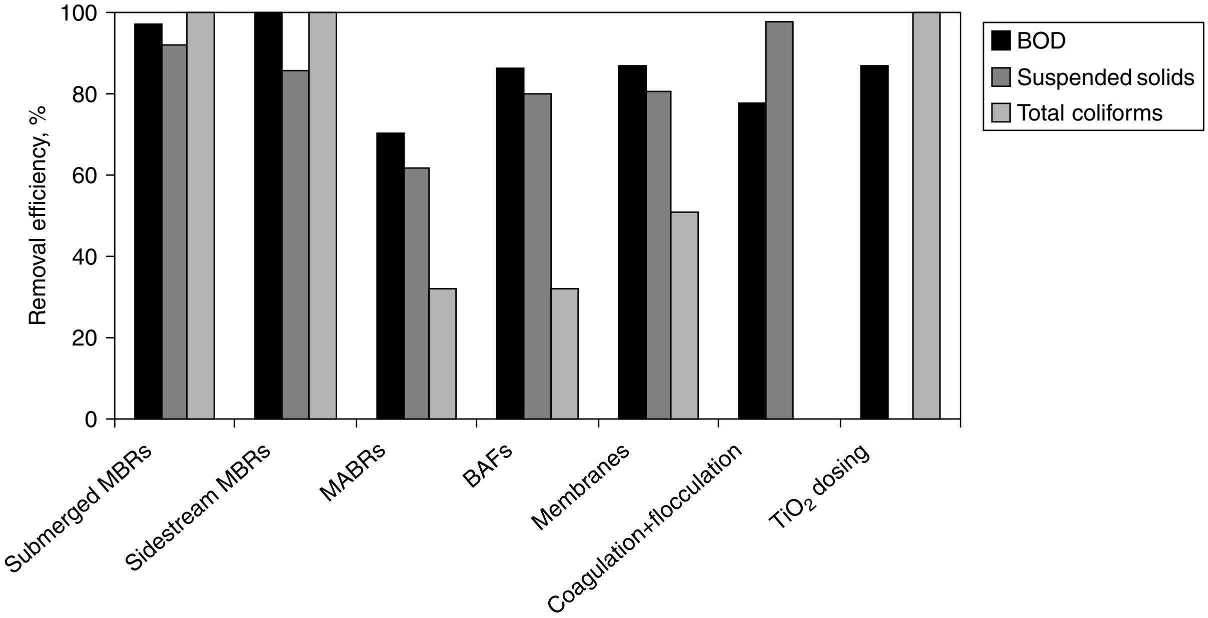

Figure 3. Technological performance in removing pollutants from gray water (3).

Gray water recycling on a medium to large scale (e.g., hotels, blocks of flats, commercial buildings,) may be more viable. A stepwise complex treatment sequence, instead of relying just on simple filtration and disinfection, produces water that has relatively low potential for health risk. A wide selection of gray water treatment technologies is currently available. These include biological aerated filters (BAFs), membranes, sidestream and submerged membrane bioreactors (MBRs), UV treatment, titanium dioxide (TiO_2) dosing, membrane aeration bioreactors (MABRs), and coagulation/flocculation with alum and ferric. Trials with these technologies have shown efficient and reliable removal of pollutants from gray water (3). The comparative efficiency of these technologies in removing BOD, suspended solids, and total coliforms is shown in Fig. 3. Large recycling units perform well, and their use in large buildings in the developed world and particularly in Japan is well established.

The main barrier to wider uptake of gray water recycling systems is lack of adequate consolidated legislation, high capital and maintenance costs, and potential health risks due to technology failure. Studies carried out to gauge public perception have shown that individuals have a positive attitude toward using treated gray water produced within their own households for toilet flushing, as long as safety is guaranteed and it is cost-effective (3).

BIBLIOGRAPHY

1. Butler, D. and Dixon, A. (1998). Assessing the viability of the household grey water and rainwater re-use. *21AD: Water, Architectural Digest for the 21st Century*. Oxford Brookes University, Oxford, pp. 20–23.
2. POST. (2000) *Water Efficiency in the Home*. Parliamentary Office of Science and Technology Note 135, London.
3. Jeffrey, P. and Jefferson, B. (2001). Water recycling: How feasible is it? *Filtration + Separation* **38**(4): 26–29.
4. Surendran, S. and Wheatley, A.D. (1998). Gray water reclamation for non-potable reuse. *J. Chartered Inst. Water Environ. Manage.* **12**(6): 406–413.
5. Dixon, A., Butler, D., Fewkes, A., and Robinson, M. (2000). Measurement and modelling of quality changes in stored untreated gray water. *Urban Water* **1**(4): 293–306.
6. Dixon, A. (2000). *Simulation of Domestic Water Reuse Systems: Gray Water and Rainwater in Combination*. PhD Thesis, Imperial College, London.
7. CIRIA. (2000). *Rainwater and Gray Water Use in Buildings: Best Practice Guidance*. Construction Industry Research Information Association Report, London.
8. Dixon, A., Butler, D., and Fewkes, A. (1999). Guidelines for gray water reuse—health issues. *J. Chartered Inst. Water Environ. Manage.* **13**(5): 322–326.
9. HAZOP. (2000). *HAZOP-Single house gray water recycling system*. Report No. WROCS HAZOP1, The School of Water Science, Cranfield University. http://www.cranfield.ac.uk/sims/water/gray waterhazopstudy.pdf.
10. WROCS. (2000). *Water Recycling Opportunities For City Sustainability*. Final Report prepared by Cranfield University, Imperial College and Nottingham Trent University in collaboration with industrial partners. http://www.cranfield.ac.uk/sims/water/finalreport-wrocs.pdf.

WATER AND HUMAN HEALTH

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INTRODUCTION

Water in the literal sense is the source of life on the earth. Research has shown that the human body is 70% water. Generally, human beings begin to feel thirst after a loss of only 1% of body fluids and risk death if fluid loss exceeds 10%. It has been proved that human beings can survive for only a few days without fresh water. Although it is true that life depends on water, society does not usually act as though water has value equal to life itself. The reason is that the supply of water in many parts of the world far exceeds what is required to sustain life. Estimates revealed that about 9000 cubic meters (9.0×10^6 liters) of water is available for use per person per year. Based on projected population growth, this amount will drop to 5100 cubic meters per person by the year 2025 because another 2 billion people are expected to join the world's population by the year 2025. Despite this sharp drop (by nearly 50% in 35 years), the amount of water available would be sufficient to meet human needs if it were distributed equally among the world's population and less polluted by human activities.

Present estimates give a false picture of freshwater available for human use because the distribution of the world's available freshwater is uneven throughout the seasons and from year to year. According to Falkenmark (1), water is not always where we want it. Sometimes, it is not available in sufficient quantities where we want it or at another time too much water is in the wrong place. Yet, in many parts of the world, people are withdrawing water from surface and ground sources at a rate faster than they can be recharged.

In the last century, world population has tripled, but water withdrawals have increased by more than six times (2,3). For example, since 1940, annual global water withdrawals have increased by an average of 2.5% to 3% a year compared with annual population growth of 1.5% to 2% (4,5). In the past decade, however, water withdrawal has increased from 4% to 8% a year, especially in developing countries (6). If the present consumption patterns continue, by year 2025, about two billion people will be living in areas where it will be difficult or impossible to meet all their needs for fresh water. Half of them will face severe shortages (3,7,8).

Apart from the pressure of population growth on water resources, the supply of freshwater available to humanity is shrinking, in effect, because of increasing pollution. Population growth, urbanization, and industrialization with little regard for the environment are polluting and decreasing the quantity of freshwater available for human consumption (or use). Farming is said to be responsible for a great deal of water pollution in the United States (9). Similarly, in India (where there is heavy dependence on irrigation farming for food supplies), more than 4 million hectares of high-quality land have been abandoned as a result of salinization and waterlogging caused by excessive irrigation (10,11). More than 90% of the rivers in Europe have high nitrate concentrations, mostly from agrochemicals, and 5% of these rivers have concentrations at least 200 times higher than nitrate levels naturally occurring in unpolluted rivers (12–14). Moreover, in the Czech Republic, 70% of all surface waters are heavily polluted mostly with municipal and industrial wastes (15). Havas-Szilagyl (16) reported that 600 out of the 1600 well fields tapping groundwater in Hungary are already contaminated, mostly by agrochemicals.

In developing countries, an average of 90% of all domestic sewage and 75% of industrial wastes are discharged into surface waters without any kind of treatment (17,18). Generally, oil and salts are washed off city streets, and heavy metals are leached from municipal and industrial dump sites. There is also the possibility that pollutants, such as sulfur dioxide and oxygen or nitrogen, combine in the atmosphere to form acid rain which has devastating effects on both surface water and land ecosystems (19) and accompanying health implications (3).

On the whole, both water scarcity and water pollution pose serious health problems. Unclean water is by far the largest environmental killer around the world; it claims millions of lives every year. According to the World Health Organization (WHO), a large percentage of urban population in developing countries do not have access to proper sanitation facilities, and about half lacks a regular supply of potable water (12). In the year 2000, an estimated 1.1 billion people remained without access to improved drinking water (7), and the number of persons drinking water contaminated by human sewage was much higher (21). Obviously, scarce and unclean water supplies are critical public health problems in many parts of the world and are likely to be one of the major factors that will limit economic development in the near future (10,11,13,14).

WATER SCARCITY AND STRESS: IMPLICATIONS FOR HUMAN HEALTH

The world's population of nearly 6 billion is growing by about 80 million people each year (3). This rapid population growth coupled with increasing demands for water for irrigation agriculture, domestic (municipal), and industrial uses puts tremendous pressure on the world's freshwater resources. As population grows, water use per person rises and freshwater withdrawal becomes faster than it can be recharged, resulting in water mining (7,22). If this continues and water needs consistently outpace available supplies, a level will be reached when depletion of surface and groundwater resources results in chronic water shortages (23), as illustrated in Fig. 1.

Investigations have revealed that up to 31 countries, which represent nearly 8% of the world population, face chronic water shortages (3). It has also been estimated that by the year 2025, the number of countries facing water shortages is expected to be near 48, affecting more than 2.8 billion people—35% of the world's projected population (24–27). Figure 2 shows the population in water-scarce and water-stressed countries. It is obvious from this figure that, as population grows, many more countries will face water shortages. Accordingly, a more optimistic outlook predicts that 2.8 billion people in 48 countries will be struggling with water scarcity by the year 2025, whereas worst case scenarios for water shortages

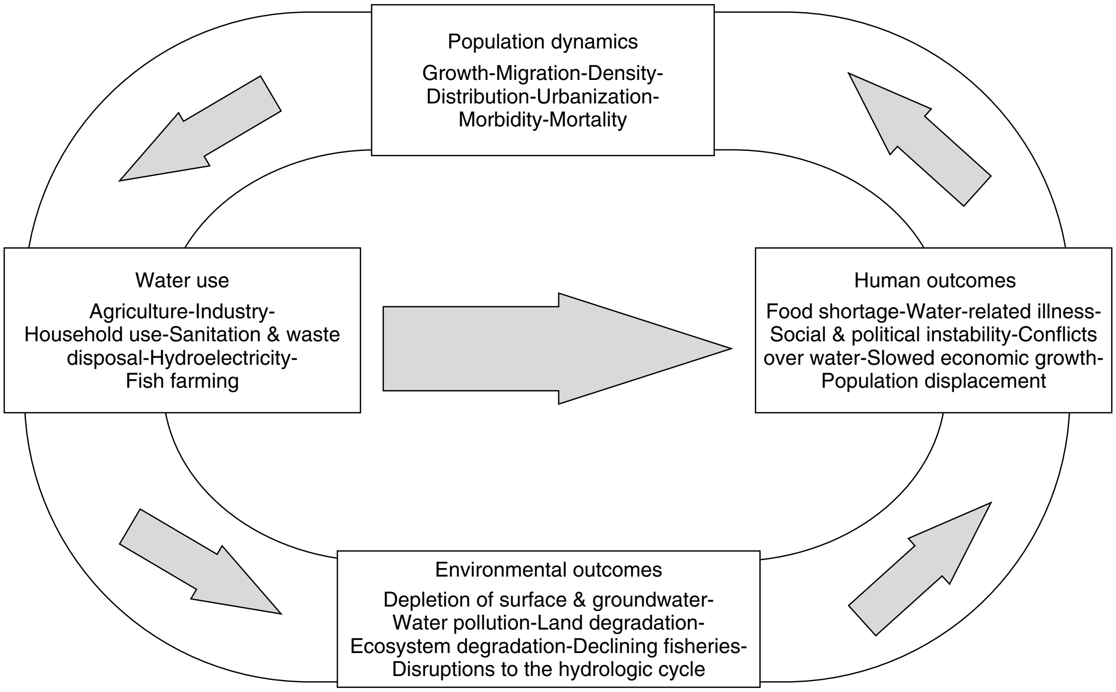

Figure 1. Links between world population and freshwater (3).

foresee 4 billion people in 54 countries facing water shortages in 2050. This critical trend is supported by the water scarcity and population projections of the United Nations (28–30).

From the growing consensus among hydrologists, a country is said to experience water stress when its annual water supply is between 1000 and 1700 cubic meters per person. Such a country can expect to experience temporary or limited water shortages. But when the annual supply of renewable freshwater drops below 1000 cubic meters per person, the country faces water scarcity (1,20,25).

In such cases, chronic and widespread shortages of water that hinder development result, and this could lead to severe health problems. Among countries likely to run short of water in the next 25 years are Ethiopia, Kenya, Nigeria, India, and Peru, whereas most parts of China and Pakistan are already approaching water stress. The list of water-stressed countries and those already suffering from water scarcity has been tabulated in Gardner-Outlaw and Engleman (25) and PR (3) based on the 1995 world population and water per capita and a projection for the year 2025. Gardner-Outlaw and Engelman (25) based their calculations on United Nations Population Division population estimates and growth rate and total fertility rate (TFR) data from the Population Reference Bureau (24), World Population Data Sheet. According to the estimates, it is obvious that in this century, water crises in more and more countries will present obstacles to better living standards and better health and may even bring risks of outright conflict over access to scarce freshwater supplies.

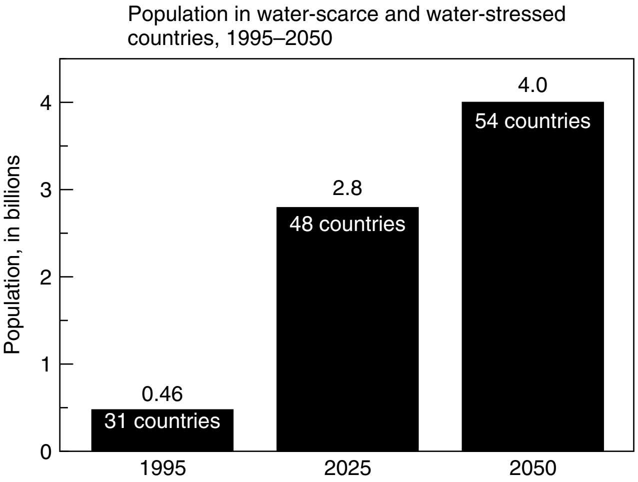

Figure 2. The rising trend in water scarcity and stress, 1995—2025 (3).

Available statistics show that more than half of the world's population suffers from water services that are inferior to those of the ancient Greeks and Romans (8). According to Gleick, this has long been recognized as a serious global water problem that even generated attention at the World Water Conference organized by the United Nations at Mar del Plata in 1977, where strong commitments and resolution were made to finding lasting solutions. Since this initial attempt, considerable efforts have been geared toward providing access to safe drinking water and adequate sanitation services. The United Nations in its Millennium Developmental Goal (during the World Summit on Sustainable Development held in Johannesburg in September 2002) planned to reduce by half, by the year 2015, the proportion of people without sustainable access to safe drinking water and basic sanitation services. Yet, a high percentage of the world's population is still without access to adequate water supply and sanitation (see Fig. 3a, b).

The 1990 world population without access to clean drinking water was estimated at 1300 million, and close to 2600 million people have no access to basic sanitation

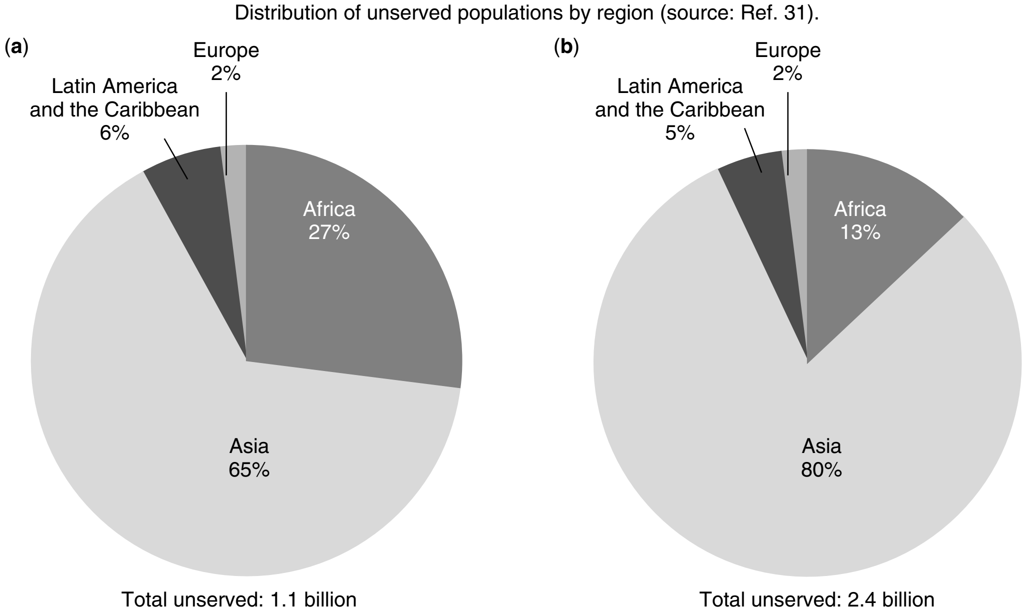

Figure 3. Distribution of unserved populations by region.

services (32). In Africa alone, 54% of the 1994 total estimated population of 707 million have no access to clean drinking water (33). Table 1 shows access to safe drinking water in developing countries by region; the percentage of population that has access to sanitation services is tabulated in Table 2. Illustrative world maps showing estimates of population without access to clean drinking water and adequate sanitation services are included in Gleick (8).

It is important to point out that the failure to provide basic clean water and sanitation services takes a serious toll on human health and results in economic loss in many countries of the world. Reports have shown that water, shortages, polluted water, and unsanitary living conditions claim millions of lives annually (7,20,34). The World Health Organisation reports that 80% of diseases are overtly or covertly waterborne (35) and/or consequent to freshwater shortages. Moreover, in much of the world, polluted water, improper waste disposal, and poor water management cause serious public health problems. For example, diarrheal diseases leave millions of children underweight, mentally as well as physically handicapped, and vulnerable to other diseases.

BASIC WATER, REQUIREMENTS FOR HUMAN HEALTH

Generally, in developing and using water resources, priority has to be given to the satisfaction of basic human needs (35). Therefore, providing water sufficient to meet basic human needs should be an obligation of governments and nongovernmental organizations. The postconference reports on the *International Symposium and Technology Expo* on small drinking water and wastewater systems held at the Hyatt Regency in Phoenix, Arizona (from January 12–15, 2000), demonstrated that the provision of safe drinking water and effective wastewater system managements are key elements that ensure safe and healthful living linked to social and economic development.

The basic water requirements for humans depend on the purpose for which water is used in the different sectors of our society. Among these are drinking (and other domestic use), removing and diluting waste (including disposing of human waste), growing food, producing manufactured goods, producing and using energy, and so on. The water requirement for each of these activities varies with domestic conditions, lifestyle, culture, tradition, diet, technology, and wealth (36).

It has been argued that water requirements for humans should also include any water necessary for disposing of human wastes (33). For example, in regions where absolute water quantity is a major problem, waste disposal options that require no water are available, in most developing nations, preference is given to alternatives that use at least some water (8). However, there are societies that use enormous amounts of fresh water to dispose of wastes. Based on the research carried out so far, a recommendation for a basic water requirement has been made. In 1996, Gleick proposed the overall minimum water required per person per day as 50 liters. This covers

Table 1. Population that has Access to Safe Drinking Water in Developing Countries, by Region, 1980 and 1994[a]

Region and Country	1980 Population, Millions	Percent With Access	Number Unserved, Millions	1994 Population, Millions	Percent with Access	Number Unserved, Millions
			Africa			
Urban	120	83	20	239	64	86
Rural	333	33	223	468	37	295
Total	453	46	243	707	46	381
			Latin America & the Caribbean			
Urban	237	82	43	348	88	42
Rural	125	47	66	125	56	55
Total	362	70	109	473	80	97
			Asia & the Pacific			
Urban	549	73	148	955	84	150
Rural	1823	28	1,313	2167	78	477
Total	2373	38	1,461	3122	80	627
			Western Asia			
Urban	28	95	1	52	98	1
Rural	22	51	11	29	69	9
Total	49	75	12	81	88	10
			Total			
Urban	**933**	**77**	**215**	**1594**	**82**	**279**
Rural	**2303**	**30**	**1612**	**2789**	**70**	**836**
Grand total	**3236**	**44**	**1827**	**4383**	**74**	**1115**

[a] Reference 8.

Table 2. Population that has Access to Basic Sanitation Services in Developing Countries, by Region, 1980 and 1994[a]

Region and Country	1980 Population, Millions	Percent with Access	Number Unserved, Millions	1994 Population, Millions	Percent with Access	Number Unserved, Millions
			Africa			
Urban	120	65	42	239	55	108
Rural	333	18	273	468	24	356
Total	453	30	315	707	34	464
			Latin American & the Caribbean			
Urban	237	78	52	148	73	94
Rural	125	22	97	125	34	83
Total	362	59	150	473	63	176
			Asia & the Pacific			
Urban	549	65	192	955	61	371
Rural	1823	42	1058	2167	15	1835
Total	2373	47	1250	3,122	29	2206
			Western Asia			
Urban	28	79	6	52	69	16
Rural	22	34	14	29	66	10
Total	49	59	20	81	68	26
			Total			
Urban	**933**	**69**	**289**	**1594**	**63**	**589**
Rural	**2303**	**37**	**1451**	**2789**	**18**	**2284**
Grand total	**3236**	**46**	**1740**	**4383**	**34**	**2873**

[a] Reference 8.

the minimum standards for drinking, sanitation, domestic (bathing and washing), and cooking. Out of this overall water requirement, 25 liters/person/day is required for basic hygiene (washing, showering, and bathing) and for cooking (33). A minimum of 20 liters/person/day offers the maximum benefits of combining waste disposal and related hygiene, thereby meeting cultural and societal preferences for water-based disposal (8). In other words, the minimum amount of water needed for drinking, cooking, bathing, and sanitation is 50 liters. The average person needs a minimum of 5 liters of water per day to survive in a moderate climate at an average activity level. However, average people in the United States uses between 250 to 300 liters of water per day for drinking, cooking, bathing, and watering their yards, whereas the average person in the Netherlands uses only 104 liters per day for the same tasks (33,37). This amount is slightly above the minimum target of 20–40 liters/person/day set by the United States Agency for International Development, the World Bank, and the World Health Organisation. Many people in the poorest nations survive on far less than the recommended amount. For example, the average person in Somalia uses only 8.9 liters of water per person per day (7,37).

Although different sources use different figures for total water consumption and for water use by sector of the economy (1,25,33,34,37–39), yet from drinking water and sanitation needs, it became obvious that a basic requirement of 25 liters/person/day of clean water must be provided for drinking and sanitation by water agencies, governments, or community organisations. An estimate made in 1990 revealed that about 55 countries whose population was nearly 1 billion people did not meet this standard (33). Yet, it is a desirable goal from a health perspective and from a broader objective of meeting a minimum quality of life. Further information on basic water requirements can be obtained in *The World's Water 1998–1999, The World's Water 2000–2001*, and The World's Water 2002–2003, which are available from Island Press, Washington (http://www.islandpress.com/).

WATER-RELATED, DISEASES

Water-related diseases that affect human health are relatively widespread and abundant, especially in rural communities of developing nations, although there is evidence that they have been reduced to a greater extent as a serious health problem in industrialized countries. The incidence of these diseases depends on local climate, geography, culture, sanitary habits and facilities, and on the quantity and quality of the local water supply as well as the methods of waste disposal (3). Changes in water supply do affect different groups of diseases in different ways. Some may depend on changes in water quality, others on water availability, and yet others on the indirect effects of standing water.

A World Health Organisation (40) estimate of the number of people suffering from water-related diseases is staggering (see Table 3). Generally, in many developing countries, waterborne diseases such as cholera, dysentery,

Table 3. Estimates of Global Morbidity and Mortality from Water-Related Diseases (Early 1990s) Culled from Reference 8[a]

Disease	Morbidity, Episodes/Year or People Infected	Mortality, Deaths/Year
Diarrheal diseases	1,000,000,000	3,300,000
Intestinal helminths	1,500,000,000 (people infected)	100,000
Schistosomiasis	200,000,000 (people infected)	200,000
Dracunculiasis	150,000 (in 1996)	—
Trachoma	150,000,000 (active cases)	—
Malaria	400,000,000	1,500,000
Dengue fever	1,750,000	20,000
Poliomyelitis	114,000	—
Trypanosomiasis	275,000	130,000
Bancroftian filariasis	72,800,000 (people infected)	—
Onchocerciasis	17,700,000 (people infected; 270,000 blind)	40,000 (mortality caused by blindness)

[a] Original *Source*: Reference 33.

typhoid, malaria, and schistosomiasis are increasing and harm or kill millions of people every year. The Pacific Institute's recent research indicates that lack of clean drinking water leads to nearly 250 million cases of water-related disease each year and roughly five to ten million result in deaths (7). Earlier estimates have shown much higher numbers of people in the world suffering from diseases that are linked with water (5,41) and resultant death (8,15). The true extent of these water-related diseases is unknown, and even the WHO data (40) suggest there may be many more cases of the diseases and resultant death.

However, about 60% of all infant mortality is linked to infectious and parasitic diseases; most are water-related (42), and a large percentage of these diseases is attributable to inadequate water supply and sanitation.

Research has shown that, at any one time, there are probably millions of people who have trachoma, elephantiasis, bilharzias (snail fever), malaria, diarrhea, dracunculiasis (guinea worm disease), and onchocerciasis (river blindness). For example, according to Edungbola (43), at least 15 million Africans suffered from guinea-worm infection; of these, nearly 75,000 people are permanently disabled every year, and about 3 million individuals were irreversibly crippled in Africa. His estimates have further shown that subsistence farmers in Africa lost at least 80 million man-days each year to guinea worm disease.

Water-related diseases are generally classed into four categories: waterborne, water-washed, water-based and water-related insect vectors (8,44,45). Waterborne diseases include those caused by both fecal—oral organisms and those caused by toxic substances; water-washed (also referred to as water-scarce) consists of diseases that develop where clean fresh water is scarce (44). Aquatic organisms that spend part of their life cycles in water and other part as parasites of animals cause water-based diseases. Insects that transmit infections, such as mosquitoes and tsetse flies, cause water-related vector diseases. A full description of each class of water-related disease together with their causative agents and routes of transmission as well as the geographical extent and number of reported cases has been compiled in Population Reports (3).

According to Population Reports, diarrheal disease (which belongs to the class of waterborne disease) is prevalent in many countries where sewage treatment is inadequate or where human wastes are disposed of in open latrines, ditches, canals, and watercourses or are spread indiscriminately on farmland. In the mid-1990s, a large number of people drank water contaminated with human sewage (28), and the World Health Organisation reported that drinking contaminated water contributes directly to diarrhea-related deaths (46). An estimated 4 billion cases of diarrheal diseases are reported annually that cause 3–4 million deaths, mainly among children (34,47–49). In Nigeria alone, more than 300,000 children less than 5 years of age die annually from diarrheal diseases (50). For example, in 1996, a large outbreak of severe diarrhea (which was later confirmed as cholera from tests conducted at the Institut Pasteur, Paris, France) struck the commercial city of Kano in northern Nigeria. According to Hutin et al. (51), a total of 5600 cases and 340 deaths (attack rate $= 86.3$ per $100,000$ inhabitants) were reported to the Kano State Ministry of Health within 5 months of the incident. This incidence was highest among children less than 5-years-old and was linked to drinking street-vended water and failure to wash hands with soap before meals (51).

Earlier, the consumption of street-vended water was reportedly associated with a cholera outbreak in Latin America (52–54). A similar cause of a cholera outbreak was also reported in India (55,56) and in Peru (57). Recent research has also shown that childhood mortality from diarrhea in Latin America remains high (58).

Gleick (8), using available data on the prevalence of different water-related diseases, presented and discussed two of these diseases extensively—dracunculiasis (guinea worm) and cholera—as case studies. He traced the history and reported the total global cases of these diseases by region and the recurrent deaths as a result of the epidemic from 1990 to 1997 with an update on the complete eradication programs. Reported guinea worm cases, globally, have fallen from an estimated 3.5 million in 1986 to 150, 000 in 1996 (59,60). This is approximately a 97% reduction, and there are hopes that it may have been completely eradicated in accordance with the "New Millennium Plan."

On the other hand, little has been achieved in the effort to control the transmission of other parasitic infections such as schistosomiasis, intestinal helminthiasis, and malaria which are related to water supply and sanitation, especially in the developing world and particularly in Africa. For further information and statistics on other water-related diseases, readers are referred to (5,12,14,24,34,47–49,59–68).

The issue of water quality or maximum permissible limits of certain elements that can constitute health risks in drinking water should be included here as another source of waterborne disease. For example, increased nitrate concentrations in drinking water add to the variety of water-related health risks. Health problems from nitrate in water sources are generating serious concern in almost all countries of the world, particularly in urban and rural communities where agricultural practises are intensive (69–73). There is increasing evidence that nitrate levels in many aquifers are rising and that the problem of increased exposure of the world population to high nitrate inputs will become more pressing, as speculated earlier by the WHO (74).

Agricultural activities such as fertilizer and pesticides applications are frequent sources of contamination in surface and groundwaters. An estimate from Population Reports has shown that in more than 150 countries, nitrate from the application of fertilizers has seeped into water wells and polluted drinking water (75). Increased concentrations of nitrate often cause blood disorders (76). High levels of nitrate and phosphates in drinking water also encourage the growth of blue-green algae, resulting in deoxygenation (eutrophication) and subsequent reduction in metabolic activities of the organisms that purify fecal-polluted water in the human system. Details of nitrate health hazards are discussed in Adelna (in this volume).

Other sources of water pollution include animal wastes, excess nutrients, salinity, pathogens, and sediments that often render water unusable for drinking, unless it is purified (77–81). Even when any of these substances or chemicals occurs in low concentrations, they can accumulate in humans over time to cause serious health problems such as cancer if the water is used for drinking. For maximum permissible and acceptable levels of ions/elements in water, refer to the standards of the World Health Organisation (62) and of most national authorities, which are consistent with standards for the composition of drinking water (82).

The average contribution of drinking water to the daily intake of mineral nutrients is important in health considerations. Of note here are those for fluoride (F^-) and arsenic (As). Generally, excessive concentrations of these elements often limit the use of groundwater for drinking. Too high an intake of fluoride is often the general cause of painful skeleton deformations called fluorosis, which is a common disease in East Africa, especially in Kenya and Ethiopia. The occurrence of fluoride in groundwater for human consumption has also been reported in Argentina (83). High concentrations of arsenic in groundwater used for drinking are reported in many countries such as India, Bangladesh, China, Thailand, Vietnam, Taiwan, Hungary, Mexico, and Finland (84–88). Nearly 50 million people are at risk of cancer and other arsenic-related diseases due to consumption of high arsenic groundwater in India and Bangladesh (64,89). About 44% of the population of West Bengal (India) is suffering from arsenic-related diseases such as conjunctivitis, melanosis, hyperkeratosis, and hyperpigmentation (90). In certain areas, gangrene in the limb, malignant neoplasm, and even skin cancer have also been observed. High arsenic concentrations lead to black-foot disease. This is sometimes visible in a blackening of the fingers and toe tops and induces general lethargy in the patient. Arsenic toxicity affects almost all organs of the human body. Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes but may be delayed when taken with food (90). High arsenic concentrations have also been reported in Southeast Asia (91), the United States (92), Argentina, and Chile (93–97); all have consequent health implications.

THE IMPACT OF IMPROVED WATER SUPPLY AND SANITATION

The direct consequence of water scarcity and failure to meet basic water requirements is the prevalence of most water-related diseases. In the past, this has caused serious economic and social loss to both governments and communities. Estimates in the late 1970s have shown that water-related diseases cost more than $125 billion per year, excluding social costs, the loss of education and other opportunities, lost economic productivity of sick workers, and other hidden costs (8,98). For example, in sub-Saharan Africa, malaria costs an estimated $1.7 billion US annually in treatment and lost productivity (48). A study in Pakistan (within its capital city, Karachi) has shown that people living in areas without proper sanitation or hygiene education spent six times more on medical care than residents in areas with access to sanitation and basic hygiene (63). In Peru, an economic loss of more than $1 billion dollars in seafood exports and tourist revenues has been reported due to a cholera epidemic (99).

However, the huge investments by governments in Asia, Africa, and Latin America in basic water and sanitation services (5,100) have reduced the prevalence of these diseases in the last decade. The World Bank estimates spending for water and sanitation in developing countries at nearly $26 billion per year (101). Not until clean drinking water and improved sanitation services are universally available will millions of people stop dying from preventable water-related illnesses (8). Rogers (101) estimated that completely meeting basic water supply needs up to the year 2020 would require total capital costs of about $24 billion per year. If the additional costs of meeting a higher level of services, such as advanced wastewater treatments, were included, the cost would be up to $50 billion a year.

Several studies have reported the high reduction in water-related morbidity and mortality as a result of improvements in water services and sanitation consequent to these huge financial investments. According to Population Reports, a review in 1991 of more than 100 studies of the effects of clean water and sanitation on human health revealed a medium reduction in deaths from water-related diseases (up to 69%) among residents, who have access to clean drinking water and improved sanitation services, because effective disposal of human wastes controls the spread of infectious agents and interrupts the transmission of water-related diseases. Table 4 shows the impact of improved water infrastructure on reducing water-related diseases.

Another approach that has shown improved water quality and reduced the incidence of waterborne disease (for example, diarrhea) is the Center for Disease Control (CDC) safe water system. This system combines locally produced sodium hypochlorite solution (chlorine bleach), a CDC water storage vessel, and a public health campaign to change the behavior of rural dwellers to basic hygiene (102,103). This system has improved water quality and reduced the incidence of diarrhea by 68% in Uzbekistan (104), by 44% in Bolivia (105), and by 48% in Zambia (106). It further serves as an alternative method of disinfecting drinking water in rural Guatemala and prevents excessive morbidity and mortality from waterborne diseases (103).

Moreover, according to Population Reports (3), some water development schemes have started disease control programs along with construction of water and sanitation facilities. As a result of such a program in the Philippines, for example, the prevalence of water-related diseases fell from 24% in 1979 to 9% in 1985 (67). There are indications of good progress made so far, and, at this point, some water-related diseases are on the verge of complete eradication. A good example is guinea worm (dracunculiasis) eradication. Pakistan, reportedly the first country to have completely eradicated guinea worm during the new global eradication program, recorded zero cases every month since October 1993 (8). In India, guinea worm was completely eliminated from the Tamil Nadu area in 1984, the Gujarat area in 1989, and Maharashtra in 1991; only nine cases were reported for the entire country in 1996 (60). In the Kwara State of Nigeria (where guinea worm once had devastating effects on the rural populace), any reported case of guinea worm now attracts a monetary prize (107).

Globally, only five of the countries that had guinea worm recorded slightly above 100 cases in 1996. The number of cases has generally dropped by nearly 97% during the past decade (8). Although the eradication program has shown impressive progress, guinea worm is still prevalent in nearly 17 developing nations, mostly in Africa as of the end of 1996 (8). In the final analysis, guinea worm has been eradicated most effectively by providing protected clean drinking water in all countries where the disease was prevalent. Successful eradication programs for guinea worm and other water-related diseases are documented in the series of articles in Population Reports, Series M (3), as well as in (5,59,60,100,108–110). Therefore, an improved water supply and sanitation system will consequently generate tremendous improvements in the health, social welfare, and economic development of any nation, especially a developing one. For details of this and several other studies related to reduction in waterborne morbidity and mortality as a result of improvements in sanitation and water supplies, refer to Esrey et al. (111), Alam (112), Aung and Thein (113), Baltazar (114), Cairncross and Cliff (115), Young and Briscoe (110), Esrey and Habicht (116), Henry (117), Rahman (118), Haines and Avery (119), Khan (120), Torun (121), Ankar and Knowles (122), Koopman (123), Misra (124), and White et al. (36).

SUMMARY

Water is essential for life and health and has cultural and religious significance. Water plays a vital role in transmitting infectious diseases, and 80% of diseases reported are directly or indirectly water-related. Scarce and unclean water supplies are critical public health problems in many parts of the world and are likely to be one of the major factors that will limit economic development in the near future. It has been reported that

Table 4. Impact of Improved Water Infrastructure on Reducing Water-Related Diseases[a]

Place	Type of Facilities or Improvement	Type of Study	Diseases	Difference in Incidence After Improvement
Teknaf, Bangladesh	Hand pumps and health education	Case-control	Diarrheal diseases	17% difference between groups
Northeast Brazil	Latrines, communal taps, laundry facilities, showers, and hand pumps	Case-control	Schistosomiasis	77% difference between groups
Khuzestan, Iran	Courtyard latrine and public standpipes	Case-control	Ascariasis	16% difference between groups
Uttar Pradesh, India	Piped water	Before and after	Dysentery	76% reduction
Peninsular Malaysia	Toilets and running water	Case-control	Diarrheal diseases	82% difference in infant mortality between groups
Kwara State, Nigeria	Boreholes, hand pumps, and health education	Before and after	Dracunculosis	81% reduction
Cebu, Philippines	Private, sanitary latrines	Before and after	Diarrheal diseases	42% reduction
St. Lucia	Household water and latrines	Case-control	Ascariasis	31% difference between groups
Lusaka, Zambia	Extension of piped water supply	Before and after	Typhoid	37% reduction

[a] *Source*: Selected studies compiled in Reference 3.

water shortages, polluted water, and unsanitary living conditions claim millions of lives annually via various water-related diseases.

Research has shown that, at any one time, there are probably millions of people who have trachoma, elephantiasis, bilharzias (snail fever), malaria, diarrhea, dracunculiasis (guinea worm disease), and onchocerciasis (river blindness). The incidence of these diseases, it has been shown, depends on local climate, geography, culture, sanitary habits and facilities, and on the quantity and quality of the local water supply as well as methods of waste disposal. Effective disposal of human wastes controls the spread of infectious agents and interrupts the transmission of water-related diseases. The role of good quality drinking water and access to adequate sanitation facilities in reducing water-related diseases has been reviewed in this article. The universal provision of treated pipe-borne water is not currently feasible due to economic and political constraints, and this consequently leaves millions of people without access to safe drinking water. Generally, the failure to provide clean drinking water and adequate sanitation services has serious implications for human health and is consequent to severe economic loss in many countries.

Furthermore, the water requirements for each of the basic human activities vary with domestic conditions, lifestyle, culture, tradition, diet, technology, and wealth. In any case, the minimum amount of water needed for drinking, cooking, bathing, and sanitation is set at 50 liters. The average person needs a basic minimum of 5 liters of water per day to survive in a moderate climate at an average activity level. This is the absolute minimum amount of water required to maintain adequate human health, independent of lifestyle and culture.

About 60% of all infant mortality is linked to infectious and parasitic diseases; most are water-related, and a large percentage of these diseases is attributable to inadequate water supply and sanitation. Diarrheal diseases, for example, leave millions of children underweight, mentally as well as physically handicapped, and vulnerable to other diseases. However, the huge financial investments by governments in Asia, Africa, and Latin America (as well as by nongovernmental organizations) in basic water and sanitation services have reduced the prevalence of these diseases in the last decade.

BIBLIOGRAPHY

1. Falkenmark, M. (1994). Landscape as life support provider: Water-related limitations. In: F. Graham-Smith (Ed.), *Population—The Complex Reality*. North American Press, Golden, CO, pp. 103–116.
2. Juma, C. (1998). *The CBD and the Biological Diversity of Inland Waters*. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–4.
3. Population Reports. (1998). *Solutions for a Water-Short World*. Series M, No. 14, September 1998.
4. Dowdeswell, E. (1996). Editorial. *Our Planet*, Oct. pp. 1–2.
5. United Nations Children's Fund. (1997). Facts and figures. Online: http://www.unicef.org/factx/facright.htm.
6. Marcoux, A. (1994). *Population and Water Resources*. United Nations Food and Agriculture Organization, Rome, pp. 4–33.
7. The Pacific Institute for Studies in Development, Environment and Security. (2003). Threats to the World's Freshwater Resources. Online: http://pacinst.org/reports/freshwater_threats.htm.
8. Gleick, P.H. (1998). *World Water 1998–1999: The Biennial Guide to Freshwater*. Island Press, Washington, DC.
9. New York Times. (1998). Farms are polluters of nations waterways. *New York Times*, May 14, A19.
10. Serageldin, I. (1995). *Toward Sustainable Management of Water Resources*. World Bank, Washington, DC, pp. 1–33.
11. Serageldin, I. (1995). Water resources management: New policies for a sustainable future. *Water Front*, Jun. 1, Stockholm 2–3.
12. World Health Organization. (1997). *Health and Environment in Sustainable Development Five Years after the Earth Summit*. WHO, Geneva, pp. 19–133.
13. World Health Organization. (1992). *Our Planet, our Health—Report of the WHO Commission on Health and Environment*. WHO, Geneva, pp. 106–144.
14. World Health Organisation. (1992). *The International Drinking Water Supply and Sanitation Decade: End of Decade Review*. Geneva.
15. Nash, L. (1993). Water quality and health. In: *Water in Crisis*. P. Gleick (Ed.). Oxford University Press, New York, pp. 25–39.
16. Havas-Szilagyi, E. (1998). *National Groundwater Protection Programs in Hungary*. Presented *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–5.
17. Allaoui, K. (1998). *Long-Term Finance for Water Projects: The IDB's Approach*. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–7.
18. Carty, W. (1991). Towards an urban world. *Earthwatch* **43**: 2–4.
19. Hinrichsen, D. (1988). Acid rain and forest decline. In: *The Earth Report: Monitoring the Battle for Our Environment*. E. Goldsmith and N. Hildyard (Eds.). Mitchell Beazley, London, pp. 66–78.
20. Davidson, J., Myers, D., and Chakraborty, M. (1992). *No Time to Waste—Poverty and the Global Environment*. Oxfam, Oxford.
21. United Nations. (1996). *Human Development Report 1996. United Nations Development Program*. Oxford University Press, New York.
22. Abramovitz, J. (1996). *Imperilled Waters, Impoverished Future: The Decline of Freshwater Ecosystems*. Worldwatch Institute, Washington, DC, pp. 5–66.
23. Merla, A.A. (1998). *Commitment to the Global Environment: The role of GEF and International Waters*. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–3.
24. Population Reference Bureau. (1998). *World Population Data Sheet [wallchart]*. Washington, DC.
25. Gardner-Outlaw, T. and Engleman, R. (1997). *Sustaining Water, Easing Scarcity: A Second Update*. Population Action International, Washington, DC, pp. 2–19.
26. United Nations Population Fund. (1997). *Population and Sustainable Development—Five Years after Rio*. UNPF, New York, pp. 1–36.
27. Falkenmark, M. (1993). Water scarcity: Time for realism. *Populi* **20**(6): 11–12.

28. United Nations. (1997). *Comprehensive Assessment of the Freshwater Resources of the World*. Report of the Secretary-General, UN, Commission on Sustainable Development, New York.
29. United Nations. (1997). *Critical Trends—Global Change and Sustainable Development*. Department for Policy Coordination and Sustainable Development, UN, New York, pp. 43–56.
30. United Nations Educational Scientific and Cultural Organization. (2003). *Water for People, Water for Life*. (UNESCO Release, March 5, 2003).
31. World Health Organisation. (WHO/UNICEF). (2002). *Executive Summary of the World Water Day Report*. WHO/UNICEF Joint Monitoring Programme, updated in September 2002.
32. World Health Organization. (1996). *The World Health Reports: Fighting Disease, Fostering development*. WHO, Geneva, Switzerland.
33. Gleick, P.H. (1996). Basic water requirements for human activities: Meeting basic needs. *Water Int.* **21**: 83–92.
34. United States Agency for International Development. (1990). *Strategies for Linking Water and Sanitation Programs to Child Survival*. USAID, Washington, DC, pp. 1–62.
35. United Nations. (1992). *Protection of the Quality and Supply of Freshwater Resources: Application of Integrated Approaches to the Development, Management and Use of Water Resources of Agenda 21*. United Nations Publications, New York, chap. 18.
36. White, G.F., Bradley, D.J., and White, A.U. (1972). *Drawers of Water: Domestic Water Use in East Africa*. University of Chicago Press, Chicago.
37. Gleick, P. (2000). Amount of water per capita in year 2000 on global basis. Global Environment Program of the Pacific Institute. http://pacinst.org/reports.
38. Food and Agriculture Organization of the United Nations. (1995). *Dimensions of Need: An Atlas of Food and Agriculture*. FAO, Rome.
39. Falkenmark, M. and Widstrand, C. (1992). Population and water resources: A delicate balance. *Population Bull.* **47**(3): 1–36.
40. World Health Organization. (1995). *Community Water Supply and Sanitation: Needs, Challenges and Health Objectives*. *48th World Health Assembly*, A48/INF.DOC./2, April 28, 1995, Geneva, Switzerland.
41. Kristof, N. (1997). For third world, water is still a deadly drink. *New York Times*, Jan. 9, A1, A8.
42. Rowley, J. (1990). Linking population to conservation—special report on Pakistan. *Earthwatch* **40**: 3–5.
43. Edungbola, L.D. (1988). The impact of a UNICEF-assisted rural water project on the prevalence of guinea worm disease in Asa, Kwara State, Nigeria. *Am. J. Trop. Med. Hyg.* **39**: 79–85.
44. Kjellén, M. and Mcgranahan, G. (1997). *Urban Water—Towards Health and Sustainability*. Stockholm Environmental Institute, Stockholm, pp. 1–54.
45. Bradley, D. (1994). Health, environment, and tropical development. In: *Health and the Environment: The Linacre Lectures 1992–3*. B. Cartledge (Ed.). Oxford University Press, Oxford, pp. 126–149.
46. World Health Organisation. (1999). *The World Health Report 1999*. Geneva, Switzerland.
47. Warner, D. (1998). *Drinking Water Supply and Environmental Sanitation for Health*. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–10.
48. Olshansky, S.J., Carnes, B., Rogers, R., and Smith, L. (1997). Infectious diseases—New and ancient threats to world health. *Population Bull.* **52**(2): 2–43.
49. World Bank. (1993). *Water Resources Management: A World Bank policy Paper*. World Bank, Washington, DC.
50. Idika, N. (2001). Water Purification: Strategy for reducing waterborne diseases in Nigeria. *Waterfront—Nig. Water Sanit. Assoc.* **1**: 4–6.
51. Hutin, Y., Luby, S., and Paquet, C. (2003). A large cholera outbreak in Kano City, Nigeria: The importance of hand washing with soap and the danger of street-vended water. *J. Water Health* **1**(1): 45–52.
52. Tauxe, R.V., Mintz, E.D., and Quick, R.E. (1995). Epidemic cholera in a new world: Translating field epidemiology into new prevention strategies. *Emerging Infect. Dis.* **1**: 141–146.
53. Weber, J.T. et al. (1994). Epidemic cholera in equador: Multidrug-resistance and transmission by water and sea food. *Epidemiol. Infect.* **112**: 1–11.
54. Ries, A.A. et al. (1992). Cholera in Piura, Peru: A modern epidemic. *J. Infect. Dis.* **166**: 1429–1433.
55. Deb, B.C. et al. (1986). Studies on interventions to prevent El Tor cholera transmission in urban slums. *Bull. WHO* **64**: 127–131.
56. Deb, B.C. et al. (1982). Intra-familial transmission of *Vibro cholerae* biotype El Tor in Calcutta slums. *Indian J. Med. Res.* **76**: 814–819.
57. Swerdlow, D.L. et al. (1992). Waterborne transmission of epidemic cholera in Trujilo, Peru: Lessons for a continent at risk. *Lancet* **340**: 28–33.
58. Pan American Health Organisation. (2002). *Health in the Americas*. Pan American Health Organisation, Washington, DC.
59. World Health Organisation. (1997). *Dracunculiasis: Disease Sheet*. Division of Control of Tropical Diseases, Geneva, Switzerland.
60. World Health Organisation. (1997). Dracunculiasis: Global surveillance summaries. *Wkly. Epidemiol. Rec.* **57, 60, 61, 66, 68–70, 72**: Geneva, Switzerland
61. World Health Organization. (1998). Division of Control of Tropical Disease homepage. Online: http://www.who.ch/ctd/. Feb. 25.
62. World Health Organisation. (1998). *Guidelines for Drinking-Water Quality, Health Criteria and other information*, 2nd Edn. Geneva, Switzerland, pp. 281–283.
63. Khan, A.H. (1997). The sanitation gap: Development's deadly menace. In: *The Progress of Nations*. UNICEF, New York, pp. 5–13.
64. Chatterjee, A. et al. (1995). Arsenic in groundwater in six districts of West Bengal, India: The biggest arsenic calamity in the world. Part 1: Arsenic species in drinking water and urine of the affected people. *Analyst* **120**: 643–650.
65. Garrett, L. (1994). *The Coming Plague: Newly Emerging Diseases in a World Out of Balance*. Farrar, Straus and Giroux, New York.
66. Muller, R. and Morera, P. (1994). Helminthoses. In: *Health and Disease in Developing Countries*. K.S. Lankinen, S. Berström, P.H. Mäkelä, and M. Peltomaa (Eds.). Macmillan, London, pp. 195–209.
67. Hunter, J.M., Rey, L., Chu, K.Y., Adekolu-John, E.O., and Mott, K.E. (1993). *Parasitic Diseases in Water Resources*

Development: The Need for Intersectoral Negotiation. World Health Organization, Geneva.

68. Basch, P.F. (1990). *Textbook of International Health*. Oxford University Press, New York.
69. Adelana, S.M.A. and Olasehinde, P.I. (2003). High nitrates in rural water supply in Nigeria: Implications for human health. *Water Res.* **14**(1): 1–11.
70. Tredoux, G., Tama, A.S., and Engelbrecht, J.F.P. (2000). *The Increasing Nitrate Hazard in Groundwater in the Rural Areas*. Paper presented at *Water Inst. S. Afr. Conf.*, May, Sun City.
71. Colvin, C. (1999). *Increased Risk of Methaemoglobinaemia as a Result of Bottle-Feeding by HIV Positive Mothers in South Africa*. Paper presented at *IAH Cong.*, 1999, Bratislava, Slovakia.
72. Marais, S. (1999). *Dependency of Communities on Groundwater for Water Supply and Associated Fluoride and Nitrate Problems*. Paper presented at Workshop on Fluorides and Nitrates in Rural Water Supplies, Mafikeng, March 9–10, 1999.
73. Fan, A.M. and Steinberg, V.E. (1996). Health implications of nitrate and nitrite in drinking water: An update on methaemoglobinaemia occurrence and reproductive and developmental toxicology. *Regul. Toxicol. Pharmacol.* **23**, Academic Press Inc.
74. World Health Organisation. (1985). *Health Hazards from Nitrates in Drinking Water*. Copenhagen.
75. Maywald, A., Zeschmar-Lahl, B., and Lahl, U. (1988). Water fit to drink? In: *The Earth Report: Monitoring the Battle for Our Environment*. E. Goldsmith and N. Hildyard (Eds.). Mitchell Beazley, London, pp. 79–88.
76. Bowman, J. (1994). 'Water is best': Would pindar still think so? In: *Health and the Environment: The Linacre Lectures 1992–3*. B. Cartledge (Ed.). Oxford University Press, Oxford, pp. 85–125.
77. Maurice-Bourgoin, L., QuirogA, I., Guyot, J.L., and Maim, O. (1999). Mercury pollution in the Upper Beni River, Amazonian Basin: Bolivia. *Ambio* **28**(4): 302–306.
78. Silva-Forsberg, M.C., Forsberg, B.R., and Zeidemann, V.K. (1999). Mercury contamination in humans linked to river chemistry in the Amazon Basin. *Ambio* **28**(6): 519–521.
79. Klohn, W. and Wolter, W. (1998). *Perspectives on Food and Water*. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–6.
80. Satterthwaite, D. (1993). The impact on health of urban environments. *Environ. Urbanization* **5**(2): 87–111.
81. Witt, V.M. and Reiff, F. (1991). Environmental health conditions and cholera vulnerability in Latin America and the Caribbean. *J. Public Health Policy* **12**(4): 450–463.
82. Safe Drinking Water Communication (SDWC) (1980). *Drinking Water and Health*, Vol. 3, National Academy Press, Washington, DC, p. 415.
83. Schultz, C.J., Castro, E., Marino, E., and Dalmaso, G. (2001). Occurrence of fluoride in groundwater for human consumption in the province of La Pampa, Republica Argentina. In: *New Approaches Characterizing Groundwater Flow*. K.P. Seiler and S. Wohnlich (Eds.). A.A. Balkema, Lisse, pp. 637–639.
84. Arsenic Crisis Information Center. (2001). West Bengal and Bangladesh Arsenic Crisis Information Center. http://bicn.com/acic/.
85. Kurttio, P. et al. (1998). Urinary excretion of arsenic species after exposure to arsenic present in drinking water. *Arch. Environ. Contamination Toxicol.* **34**: 297–305.
86. Chen, S.L., Dzeng, S.R., Yang, M.H. (1994). Arsenic species in groundwaters of the black-foot disease area, Taiwan. *Environ. Sci. Technol.* **28**: 877–881.
87. Varsa'nyi, I., Fodre, Z., and Bartha, A. (1991). Arsenic in linking water and mortality in the southern Great Plain, Hungary. *Environ. Geochem. Health* **13**: 14–22.
88. Del Razo, L.M., Arellano, M.A., and Cebrián, M.E. (1990). The oxidation states of arsenic in well water from a chronic arsenicism area of northern Mexico. *Environ. Pollut.* **64**(2): 143–153.
89. Bhattacharya, P., Frisbie, S.H., Smith, E., Naidu, R., Jacks, G., and Sarkar, B. (2001). Arsenic in the environment: A global perspective. In: *Handbook of Heavy Metals in the Environment*. B. Sarkar (Ed.). Marcel Dekker, New York.
90. Chandrasekharam, D. (2002). Geogenic arsenic pollution in groundwater. In: *Groundwater and Human Development*. E. Bocanegra, D. Martínez, and H. Massone (Eds.). Mar del Plata, pp. 1990–1994.
91. Bhattacharya, P. (2002). Arsenic contaminated groundwater from the sedimentary aquifers of Southeast Asia. In: *Groundwater and Human Development*. E. Bocanegra, D. Martínez, and H. Massone (Eds.). Mar del Plata, pp. 1973–1979.
92. Welch, A.H., Lico, M.S., and Hughes, J.L. (1988). Arsenic in groundwater of western United States. *Groundwater* **26**(3): 333–347.
93. Herrera, H., Farias, B., Martin, R., Cortés, J., Ferreyra, G., Thir, J., and Storniolo, A. (2000). El arsenico en la zona rural del dpto. Robles, Santiago del Estero, Argentina. *Proc. Cong.* Agua, Junio 2000, Santiago del Estero, Argentina.
94. Sancha, A.M. and Frenz, P. (2000). *Estimate of Current Exposure of the Urban Population of Northern Chile to Arsenic*. Interdisciplinary Perspectives on Drinking Water Risk Assessment and Management. *Proc. Santiago* (Chile) *Symp.*, IAHS Publ. 260, pp. 3–8.
95. Fiorentino, C., Sequeira, M., Paoloni, D., and Echeverría, N. (1998). *Detección y distribución de arsénico, fluor y boro en aguas subterráneas regionales*. Mapas de Riesgo. *Cong. Nacional Agua, Actas*: 71–79. Santa Fe, Argentina.
96. Smedley, P.L., Nicolli, H., Barros, J., and Tullio, O. (1998). *Origin and Mobility of Arsenic in Groundwater from the Pampean Plain, Argentina*. *9th Int. Symp. Water-Rock Interactions*, Taupo, New Zealand.
97. Nicolli, H. et al. (1989). Groundwater contamination with arsenic and other elements in an área of the Pampa, province of Córdoba, Argentina. *Environ. Geol. Water Sci.* **14**: 1–15.
98. Pearce, D.W. and Warford, J.J. (1993). *World Without End: Economics, Environment, and Sustainable Development*. Oxford University Press, New York.
99. Epstein, P.R. and Nutter, F. (1997). Climate change: Assessing the economic damages. *Newsl. Center Health Global Environ.*, Harvard Medical School. Online: http://www.med.harvard.edu/chge/.
100. United Nations Children's Fund. (1997). Water and sanitation progress and disparity. Online: http://www.unicef.org/pon97/p12b.htm.
101. Rogers, P. (1993). Integrated urban water resources management. *Nat. Res. Forum*, pp. 33–42.
102. Mintz, E., Reiff, F., and Tauxe, R. (1995). Safe water treatment and storage in the home: A practical new strategy to prevent waterborne disease. *J. Am. Med. Assoc.* **273**(12): 948–953.

103. Rangel, J.M. et al. (2003). A novel technology to improve drinking water quality: A microbiological evaluation of in-home flocculation and chlorination in rural Guatemala. *J. Water Health* **1**(1): 15–22.
104. Semenza, J. et al. (1998). Water distribution system and diarrheal disease transmission: a case study in Uzbekistan. *Am. J. Trop. Med. Hyg.* **59**(6): 941–946.
105. Quick, R. et al. (1999). Diarrhea prevention in Bolivia through point-of-use water treatment and safe storage: A promising new strategy. *Epidemiol. Infect.* **122**(1): 83–90.
106. Quick, R. et al. (2002). Diarrhea prevention through household-level water disinfection and safe storage in Zambia. *Am. J. Trop. Med. Hyg.* **66**(5): 584–589.
107. Adebisi, S.A. (2003). Medical Consultant & Director, Community-Based Health Program, Chemical Pathology & Immunology Department. University of Ilorin, Ilorin, personal communication, June 14, 2003.
108. Carter Center. Former President Jimmy Carter travels to Africa for guinea worm eradication. News release, Mar. 17, 1995. Online: http://www.cc.emory.edu/Carter_Center/RLS95/GWtrip.htm.
109. Carter Center. USAID joins Carter Center for final assault on guinea worm. Carter Center News, Fall 1994. Online: http://www.cc.emory.edu/Carter_Center/CCN-F94/gw.htm.
110. Young, B. and Briscoe, J. (1987). A case-control study of the effect of environmental sanitation on diarrhea morbidity in Malawi. *J. Epidemiol. Community Health* **42**: 83–88.
111. Esrey, S.A., Potash, J.B., Roberts, L., and Shiff, C. (1991). Effects of improved water supply and sanitation on ascariasis, diarrhea, dracunculiasis, hookworm infection, schistosomiasis, and trachoma. *Bull. World Health Organ.* **69**(5): 609–621.
112. Alam, N. (1989). Mother's personal and domestic hygiene and diarrhea incidences in young children in rural Bangladesh. *Int. J. Epidemiol.* **18**: 242–247.
113. Aung, M.H. and Thein, H. (1989). Prevention of diarrhea and dysentery by hand washing. *Trans. R. Soc. Trop. Med. Hyg.* **83**: 128–131.
114. Baltazar, J. (1988). Can the case-control method be used to assess the impact of water supply and sanitation on diarrhea? A study in the Philippines. *Bull. World Health Organ.* **66**: 627–635.
115. Cairncross, S. and Cliff, J.L. (1987). Water use and health in Mueda, Mozambique. *Trans. R. Soc. Trop. Med. Hyg.* **81**: 51–54.
116. Esrey, S.A. and Habicht, J.P. (1986). Epidemiologic evidence for health benefits from improved water and sanitation in developing countries. *Epidemiol. Rev.* **8**: 117–128.
117. Henry, F.J. (1981). Environmental sanitation infection and nutritional status of infants in rural St. Lucia, West Indies. *Trans. R. Soc. Trop. Med. Hyg.* **75**: 507–513.
118. Rahman, M. (1985). Impact of environmental sanitation and crowding on infant mortality in rural Bangladesh. *Lancet* **8445**(2): 28–31.
119. Haines, M.R. and Avery, R.C. (1982). Differential infant and child mortality in Costa Rica: 1968–1973. *Population Stud.* **36**: 31–43.
120. Khan, M.U. (1982). Interruption of shigellosis by handwashing. *Trans. R. Soc. Trop. Med. Hyg.* **76**: 164–168.
121. Torun, B. (1982). Environmental and educational interventions against diarrhea in Guatemala. In: *Diarrhea and Malnutrition: Interactions, Mechanisms, and Interventions*. L.C. Chen and N.S. Scrimshaw (Eds.). Plenum Press, New York, pp. 235–266.
122. Anker, R. and Knowles, J.C. (1980). An empirical analysis of morbidity differentials in Kenya at the macro- and micro-levels. *Econ. Dev. Cul. Change* **29**: 165–185.
123. Koopman, J.S. (1978). Diarrhea and school toilet hygiene in Cali, Colombia. *Am. J. Epidemiol.* **107**: 412–420.
124. Misra, K.K. (1975). Safe water in rural areas. *Int. J. Health Educ.* **18**: 53–59.

READING LIST

Agardy, T. (1997). *Marine Protected Areas and Ocean Conservation*. Academic Press, Austin.

Falkenmark, M. and Lindh, G. (1993). Water and economic development. In: *Water in Crisis*. P. Gleick (Ed.). Oxford University Press, New York, pp. 80–91.

Safe Drinking Water Communication. (1980). *Drinking Water and Health*, Vol. 3. National Academy Press, Washington, DC, p. 415.

NITRATE HEALTH EFFECTS

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INTRODUCTION

Nitrate is a stable nitrogen (N) species under certain natural conditions and forms highly soluble compounds. These are peculiar features that allow nitrate ion to be transported in some groundwater systems to environments where it can be converted into other nitrogen species that either promote surface water eutrophication or are hazardous to humans, livestock, and the environment. Nitrate test results are usually expressed in milligrams per liter as either nitrogen (NO_3-N, sometimes written as plain N) or as nitrate (NO_3).

The following conversion factors can be useful for nitrate reporting:

1 milligram (mg) of compound expressed as nitrogen (N) is equivalent to 4.43 mg when expressed as nitrate (NO_3^-).

1 milliequivalent (meq) of compound expressed as N is equivalent to 62 mg when expressed as NO_3^-.

Therefore the nitrate reporting expressions (mg NO_3-N/L, mg NO_3/L) are used interchangeably throughout this article without any special preference for one or the other.

Problems of nitrate pollution, particularly in groundwater, are widespread in many countries of the world. In the United States, several illustrations of nitrate pollution in groundwater are available in the literature. For example, more than 30 references dealing with nitrate groundwater pollution studies in 15 of the 50 states in America have been reviewed. Information from all these references have been tabulated and presented in detail in Canter (1). Survey results from a study of 25 pesticides and nitrate in 201 rural wells in eight agricultural areas in Missouri revealed that 22% of the wells exceeded the drinking water standard for nitrate (2). A summary of the nature and geographical extent of nitrate pollution of groundwater in Nebraska is given in Exner and Spalding (3).

A total of 27 references dealing with case studies of nitrate groundwater pollution (outside the United States) have been reviewed. Of these references, 22 addressed groundwater nitrate pollution studies in Europe. One of these references (4) is a conference proceeding with 52 papers addressing nitrogen as a surface and groundwater pollutant; Tessendorff (5) and Kraus (6) provided a general discussion of groundwater nitrate problems in the European community countries (EEC). The countries noted with adequate references on groundwater nitrate problems include Czechoslovakia, Germany, The Netherlands, United Kingdom, Denmark, Israel, and Chile.

Overgaard (7), in a nationwide investigation of nitrate concentrations in groundwater in Denmark, based on analyses of samples from about 11,000 wells and drinking water from 2800 groundwater works, revealed that the overall mean level of nitrate in groundwater had trebled within the last 20–30 years and is increasing at a rate of about 3.3 mg NO_3/L per year. Consequently, the result showed that 8% of the water produced in Danish Waterworks now has a nitrate concentration above the EEC guide limit of 50 mg NO_3/L (6). It has been estimated that 800,000 people in France, 850,000 in the United Kingdom, and 2.5 million in Germany are drinking water whose nitrate concentrations are above the permissible limit of the European Community (1).

A survey conducted in France revealed that 81% of the population had nitrate levels less than 25 mg NO_3/L and 96 to 98% had levels less than 50 mg NO_3/L in their drinking water supplies (8). Out of the 53 million people accounted for in the survey, 280,000 at most had a water supply exceeding 100 mg NO_3/L at least once during a 3-year period. Of 20,000 distribution units surveyed, nearly 1000 had nitrate above 50 mg NO_3/L; however, only 61 units were above 100 mg NO_3/L. Most of the high nitrate levels were found in groundwater supplies.

Custodio (9) reported that agricultural nitrate pollution is a widespread problem in irrigated areas in Spain, where nitrate in groundwater often exceeds 50 mg NO_3/L and sometimes reaches 500 mg NO_3/L. A regional survey of nitrate in the Anglian area of the United Kingdom in 1975 indicated that 50 public supply boreholes, wells, and springs had recorded nitrate levels in excess of 11.3 mg/L (as nitrogen), 50 mg NO_3/L (10). Due to increasing agricultural activity after the 1960s, both shallow and deep-water resources in the Czech Republic, including karstic systems, have been contaminated by infiltrating nitrate. The nitrate content of one of the largest springs (yielding up to 19 L/s during minimum discharge) in the Republic now varies from 50 to 60 mg NO_3/L (11). Others reported nitrate pollution studies in Canada (12,13), India (14,15), Israel (16), Chile (17), Portugal (18), Southern Africa (19,20), Nigeria (21–25), Ghana (26), Burkina Faso (27), and Senegal (28).

Note the pollution of groundwater from industry and waste dumps is a serious problem, particularly in the more developed countries in the European community. This is also the case in the United States, Canada, and Australia. High concentrations of nitrates are the other main cause of groundwater pollution. Concentrations of nitrate that approach or exceed 10 mg/L as N, equivalent to 44.3 mg/L as NO_3, present health hazards. Thus, the international drinking water quality standard is set at 10 mg/L for NO_3-N (or plain nitrogen), and it is approximately 45 mg/L as NO_3 (29). Therefore, it is important to consider the health implications of this common pollutant of groundwater with respect to humans, livestock, and the environment, which is the main focus of this paper.

OCCURRENCE AND EXTENT OF NITRATE IN WATER AND FOODS

The occurrence of nitrate concentrations has been reported in many parts of the world such as Europe, the United States, Australia, Chile, Ghana, South Africa, Nigeria, and Cote d'Ivoire. The World Health Organization (WHO) studied the occurrence of nitrate in water and came to the conclusion that nitrate concentrations in surface waters have increased substantially over the last 30–40 years (29). Many countries, mostly in Western Europe and the United Kingdom, showed a more marked increase in the levels of nitrates in groundwater, especially between 1970 and 1980 (30). The reason for these increases in groundwater nitrate is not unconnected with the vast increase in fertilizer application and other forms of animal manure.

In the United States, the occurrence of high nitrate concentrations in groundwater is widespread, particularly as a result of agricultural usage of fertilizers or land disposal of domestic wastewaters. Much research has been conducted to determine the amounts of nitrates in drinking water wells. "USGS data show that the 20 states with the largest agricultural marketing in 1989 had a notably higher percentage of wells with nitrate concentrations above 10 mg NO_3-N/L than the remaining 30 states, 7.1% compared to 3.0%, respectively" (31). Research conducted by private firms also links high nitrogen content in wells with agricultural activity. A survey of 1430 randomly selected and sampled drinking water wells in agricultural areas of 26 states, conducted in 1988 and 1989 by the Monsanto Agricultural Products Company, found nitrate above 10 mg NO_3-N/L in 4.9% of the wells. For wells on farmsteads only, however, the proportion was 10% (31). Monsanto, however, concluded that the frequency of wells with nitrate exceeding 10 mg NO_3-N/L doubled for wells located on farm property.

Several case histories have indicated the geographical extent and seriousness of high nitrate in groundwater in the United States. For example, the Metropolitan Water District of Southern California has indicated that annually it loses 4% of its drinking water supply primarily to nitrate pollution, compared to less than 1/2% from toxic organic chemicals (1). About 12% of the wells sampled in the service area exceeded the state maximum contaminant level for nitrate.

It was estimated that by the year 2000, the groundwater in most of the water table aquifers in Salinas Valley

Table 1. Summary of Nitrate Data in the United States[a]

State	Counties Tested	Number of Samples	Average Nitrate Concentration, mg/L	Percent Over 10 mg/L
Illinois	8	286	5.76	19.9
Indiana	33	5,685	0.92	3.5
Kentucky	90	4,559	2.50	4.6
Louisiana	23	997	1.19	0.8
New Jersey	5	1,108	2.60	6.8
Ohio	80	18,202	1.32	3.0
Virginia	24	1,054	2.92	7.1
West Virginia	13	1,288	0.83	0.8

[a] Reference 33.

would have exceeded the state's drinking water standard of 45 mg/L for nitrate (32). It is expected that the rising trend in groundwater nitrate will continue for many more years, even if nitrate leaching from soils is reduced by changes in agricultural practices. A summary of nitrate data by state is presented in Table 1. This was the result of the multistate groundwater quality testing undertaken for several years at Heidelberg College in Tiffin, Ohio and reported by Swanson (33). The data indicate higher nitrate occurrence in the sampled groundwater from Illinois, Virginia, New Jersey, and Kentucky.

The extent of nitrate and nitrite as (both anthropogenic and natural) water pollutants has been widely reported and published in the hydrogeologic and biochemical/pharmacological literature, especially, in developed nations (1,13,34–43). Such information is scanty in developing countries until recently (19–27,39,44–48). It has been reported that nitrate health hazards are also posed greatly by solid foods from agricultural and diary products and preservatives (24,44,49), yet the greatest threats come from polluted water; fluids and foods cooked and washed are contaminated directly or indirectly with such waters. The occurrence of nitrate is known in foods, especially in African foods. Okonkwo et al. (49) researched and reported high concentrations (in parts per million) for various African foods (Table 2).

Most of these foods are heavily consumed in West Africa and are now largely exported to Europe, America, Canada, and Australia. If the rate and volume at which these foods are consumed continues, nitrate could become potentially hazardous. A high percentage of the world population, as projected by the WHO (29), would ingest increased nitrates in the near future. Nitrates are easily converted to nitrite (the more poisonous form of nitrogen) by various mechanisms. It has been observed that drying tends to change the nitrite content of food items (Table 3). Drying is a common method of food preservation in the tropics, particularly in developing countries. Drying reduces the ascorbate level in food thereby inhibiting its antagonism to the carcinogenic action of nitrites (50). Thus, dried foods especially vegetables, have high nitrite concentrations and consequently increase the hazard. Ezeonu (51) reported high nitrate concentration in some Nigerian beers with frightening statistics. All ten brands of beer selected for study whose production locations are in different parts of the country showed high nitrate content. Yet large volumes of beer are consumed daily in Nigeria. Most breweries in Nigeria do not treat their water sources (i.e., boreholes) for nitrate, yet anthropogenic nitrate is widespread in the country (21).

Table 2. Nitrate Levels in Typical African Foods[a]

Beverages	Range, ppm	Mean, ppm
Palm Wine	0.1–1.4	1.2
Tap water (pooled urban supply)	0.1–0.3	0.2
Cereals		
Guinea Corn & Rice	2.0–4.9	3.0
Proteins (Animal Source)		
Crayfish	18.2–30.8	28.7
Fish	7.9–10.4	8.6
Meat	0.4–1.7	0.7
Proteins (Plant Source)		
Beans (black)	3.2–6.6	4.9
Bean (white)	3.1–6.5	4.9
Ground nuts	4.4–9.7	6.1
Melon	9.0–11.6	10.3
Pigeon pea	1.9–2.7	2.4
Vegetables and Fruits		
Bitter leaf	8.0–9.8	8.9
Flutted pumpkin leaf	0.8–1.2	1.1
Garden egg leaf	0.7–1.2	1.0
Green amaranth leaf	0.5–0.8	0.7
Okra	2.0–2.2	2.1
Pumpkin lead	5.6–15.0	11.3
Nitrate Not Detected in these Foods		
Beer (premier brand)	Corn	Sida
Native Gin	Cassava (Gari)	Yams

[a] After Reference 49.

WATER QUALITY CONCERNS RELATED TO NITRATE LEVELS

The issue of water quality related to nitrate concentrations, especially in drinking water, is of concern worldwide in view of the various health implications of ingesting high doses of nitrates. Usually, drinking water contributes <30% of the total dietary nitrate intake (52), but when the drinking water nitrate level exceeds 10 mg/L (as N), the

Table 3. Changes in Nitrite Content of Food Items After Drying[a]

Food Item	Number of Samples Analyzed	Change on Drying, ppm Mean Values
Meat	17	0.7–2.0
Bitter leaf	17	9.4–14.2
Flutted pumpkin leaf	17	1.1–2.8
Garden egg leaf	17	1.0–10.5
Green amaranth leaf	17	2.1–14.7
Pumpkin leaf	17	11.5–21.7

[a] After reference 49.

contribution may become considerably higher and result in health problems. This is why the World Health Organization (WHO) originally set the standard at 10 mg NO_3-N/L for nitrate in drinking water (29), although the first limit was set by the United States Public Health Service in 1962 (53). Therefore, most governmental authorities consider approximately 10 mg/L (as NO_3-N) or 45 mg/L (as NO_3) an acceptable limit for nitrate in drinking water for their countries (Table 4). The United States Environmental Protection Agency (USEPA) standard for nitrate in drinking water is set at 10 mg/L NO_3-N to protect babies under about 3 months of age, the most nitrate sensitive segment of the U.S. population. This level of 10 mg/L NO_3-N has been determined as the No Observable Adverse Effect Level (NOAEL) and is therefore considered the safe drinking water limit for nitrate. This was based on the epidemiological studies carried out mainly in the United States (e.g., References 54,55).

However, on the basis of their epidemiological studies, both Super et al. (56) and Hesseling et al. (57), argued that up to 20 mg NO_3-N/L of nitrate would still be an acceptable limit as it presented a low risk to infants. Nevertheless, the maximum permissible nitrate level (in drinking water) still remains 45 mg/L (as NO_3) and 10 mg/L (as NO_3-N), as set by the World Health Organization (29).

The concentration of nitrates in groundwater is of primary concern due to potential human impacts from its usage. Depending on the use of the groundwater, animals, crops, and industrial processes could also be affected (1). The United States Environmental Protection Agency (58,59) conducted a 5-year National Survey of Nitrates in drinking water wells, the main aim was developing national estimates of the frequency and concentration of nitrates in drinking water wells in the United States in two phases. The drinking water wells include both community water system (CWS) wells and rural domestic wells (RDW). Based on the results from phase I, 52.1% (49,300) of all the CWS wells (94,600), it was estimated, contain detectable nitrate, of which 45% of the pollution was due only to nitrate (1). Out of the 827 RDW wells sampled, it was estimated that 57% had detectable nitrate (60). A total of 1.2% of the CWS wells and 2.4% of the RDW wells, it was projected, have nitrate-nitrogen concentrations above the health-based level of 10 mg/L (60).

The phase I survey report further identified some of the chemical characteristic factors related to detection and concentration of nitrates, and that from the phase II survey included estimates of national population exposure and the resultant health risks due to nitrate for RDW and CWS wells (59). Estimates were provided of the populations corresponding to quartiles of general interest (e.g., 95th and 99th percentiles) and of the number of individuals exposed above health-based levels (1). The information related to CWS wells is summarized in Tables 5 and 6.

SOURCES OF NITRATES IN GROUNDWATER AND FOODS

Agriculture is the primary source of elevated nitrate levels, although in some rare cases certain geologic units can

Table 4. Limits and Standard Guideline Value for Nitrate in Drinking Water[a]

			Concentration, mg/L[b]	
Organization	Year	Limit of Specification	As NO_3	As N
WHO (European standard)	1970	Recommended	50	(11.3)
		Acceptable	11.3–22.6	
WHO (International)	1971		45	10.2
WHO	1984	Guide value	(44.3)	10
US EPA[c]	1977		(44.3)	10
European Communities	1980	Maximum admissible	50	(11.3)
	1980	Guide level	25	(5.6)
Health & Welfare, Canada	1978		(44.3)	10
Mexican Standard[e]	1988	Maximum permissible	22	5
SABS[f]	1984	Recommended[d]	(26.6)	6
		Maximum allowable[d]	44.3	10
NFEPA[g]	1991	Recommended	45	10

[a] Modified from References 1 and 52.
[b] Brackets indicate derived units.
[c] U.S. Environmental Protection Agency.
[d] Nitrate plus nitrite.
[e] From Reference 98.
[f] South African Bureau of Standards.
[g] Nigerian Federal Environmental Protection Agency.

Table 5. Estimates of Population Exposed to Nitrate in Community Water System Wells by Distribution Percentile[a]

			95% Confidence Interval	
Percentile	People Exposed	Concentration, mg/L	Lower Bound, mg/L	Upper Bound, mg/L
Median	68,000,000	0.63	0.45	0.95
95	6,800,000	6.52	5.34	7.60
99	1,360,000	14.2	10.6	17.7

[a] Reference 59.

Table 6. Estimates of Population Exposed to Nitrate by Concentration in Community Water System Wells[a]

		95% Confidence Interval	
Concentration, mg/L	Population Exposed	Lower Bound, mg/L	Upper Bound, mg/L
All concentrations >0	85,300,000	78,100,000	98,900,000
≥10	2,980,000	1,600,000	4,260,000

[a] Reference 59.

be the origin of the nitrate. Nitrate sources other than applied fertilizers such as wastes from livestock, dairy, or poultry and accidents or careless precautionary handling of fertilizers near well sites may be involved (31). In the United States, for example, there are locations with high agricultural production in at least 14 states where nitrate contamination has been associated with the application of nitrogen fertilizers (1). In certain categories, organic and inorganic compounds of nitrogen, phosphorus, and potassium that originate from many commercial fertilizers may be released into groundwater. In some cases, it has been demonstrated that the leaching of nitrate is accelerated by irrigation (1,31,61).

Septic tank systems also represent a significant fraction of the nitrogen load to groundwater in the United States (62). About 25% of the population in America is served by individual home sewage disposal systems. Research revealed that effluent from a typical septic tank system has a total nitrogen content of 25 to 60 mg/L (62). In the Netherlands, the reason for the rising nitrate level can be due to the application of nitrogen fertilizer (63,64). Jacks and Sharma (15) reported nitrate levels in excess of 300 mg/L (as N) in wells in Southern India owing to anthropogenic and agricultural influences. In Australia, biological fixation in the soil is considered the principal origin, although point sources such as sewage effluent, animal and industrial waste could be significant locally (65). However, in Nigeria and most parts of West Africa, high nitrate levels in groundwater result mostly from indiscriminate waste disposal (21–25,27) and agricultural activities (26,46,47). Table 7 is a summary of nitrate sources in groundwater.

HEALTH EFFECTS OF NITRATE

Nitrate and the nitrite form of nitrogen constitute a general public health concern, related especially to infant methemoglobinemia (infantile cyanosis) and carcinogenesis (66). The concentrations of nitrate and nitrite in foods that include vegetables, crayfish, meat, etc. and drinking water may indicate serious potentials for pollution and also could result in severe health problems. For example, the nitrate levels in Nigerian foods that include drinking water (from surface and subsurface sources) and beverages are reportedly high and generally perceived to be associated with adverse health effects in humans (24,49,51,67). These have resulted in reported cases of water-related diseases such as diarrhea in children or cancerous diseases that claimed lives yearly (24,68,69). According to Population Reports (70), diarrheal disease is a class of waterborne disease, which is prevalent in many countries where sewage treatment is inadequate or where human wastes are disposed of in open latrines, ditches, canals, and watercourses or is spread indiscriminately on farmland. These practices are frequent in developing nations and favor the accumulation of anthropogenic nitrate.

Certain vegetables (e.g., lettuce, spinach, beetroot, and celery) contain relatively high levels of nitrate [>3000 mg/kg for lettuce (Ref. 71)] but the nitrite levels are usually very low. Nitrates and nitrites are also added as preservatives in some foods, such as cured meats, consequently exposing consumers to higher health risks. The World Health Organization (29) estimated daily dietary intake of nitrate and nitrite in different countries.

In most European countries, the mean nitrate intake is about 10–30 mg/day. Vegetarians usually have a two to fourfold higher intake of nitrates than nonvegetarians. In India, it has been estimated that 20–50% of the wells in areas of high population density produce water whose nitrate level is above 50 mg/L, thus causing severe health hazards (72,73). Terblanche (74) reviewed the health hazards of nitrate in drinking water in many developed countries, including South Africa. Of an estimated 219 million people using public drinking water

Table 7. Examples of the Various Sources of Nitrate in Groundwater[a]

Natural Sources
Geologic nitrogen which can be mobilized and leached to groundwater via irrigation practices
Unmanaged (natural) climax forests that are normally nitrogen conserving; however, nitrogen losses to groundwater can occur from human-initiated clear cutting and other forest disturbances
Waste Materials
Animal manures, which may be concentrated in large commercial poultry, dairy, hog, and beef operations
Land application of municipal or industrial sludge or liquid effluent on croplands, forests, parks, golf courses, etc.
Disposal of household wastes or small business wastes into septic tank systems (septic tank plus soil absorption field)
Leachates from sanitary or industrial landfills or upland dredged material disposal sites
Row Crop Agriculture[b]
Nitrogen losses to the subsurface environment can occur as a result of excessive fertilizer application, inefficient uptake of nitrogen by crops, and mineralization of soil nitrogen
Nitrogen losses to the subsurface environment can occur as a function of fertilizer application rates, seasonal rainfall and temperature patterns, and tillage practices
Irrigated Agriculture
Enhanced leaching of nitrogen from excessive fertilizer application rates and inefficient irrigation rates
Associated leaching of nitrogen from soils periodically subjected to leaching to remove salts so that the soils do not become saline and unproductive

[a] Culled from Reference 1.
[b] Refers to annual crops.

supplies in the United States, approximately 1.7 million are exposed to nitrate levels above 10 mg/L. About two-thirds of those exposed, 1.1 million, are served by public water systems using groundwater supply sources. Almost 27,000 infants a year are exposed to tap water with nitrate levels exceeding 10 mg/L (31). The resulting health hazards and associated statistics in the United States are documented in the Federal Register (75). The following section describes the details of the various health effects of nitrate.

Methemoglobinemia

High nitrate levels in water can cause infant methemoglobinemia. Methemoglobinemia is a disease primarily affecting babies and is often described by the lay term "blue baby syndrome." Infants are the primary concern because they are the most vulnerable. The USEPA standard for nitrate in drinking water is set at 10 mg/L to protect babies under about 3 months of age. Such infants are much more sensitive to nitrate toxicity than the rest of the population for many reasons. For example, bacteria that live in the digestive tracts of such infants convert nitrate into toxic nitrite.

Nitrite transforms hemoglobin to methemoglobin, preventing transport of oxygen and producing symptoms of asphyxiation (another term for blue baby syndrome). This methemoglobin is considerably more stable than the oxygen hemoglobin complex that fulfils the oxygen transport function of the blood. Once the concentration of methemoglobin in the blood exceeds 5% the first symptoms of 'cyanosis' are generally noticeable; anoxia (death) results at levels of 50% and higher (74) or if the condition is left untreated (66). After babies reach the age of 3 to 6 months, acid in their stomachs increases, thereby creating an unfavorable environment for the bacteria causing the problem (31). It must be borne in mind that nitrate itself has low primary toxicity, but acute toxicity occurs as nitrate is reduced to nitrite (NO_2), a process that can occur under specific conditions in the stomach and saliva (66). Consequently, the nitrite ion formed becomes an oxidizing agent, transforming hemoglobin in the blood to methemoglobin (29), thereby preventing transport of oxygen and resulting in methemoglobinemia. Most reported cases of infantile methemoglobinemia have been associated with the use of water containing more than 10 mg/L NO_3-N.

The occurrence of infant methemoglobinemia from consumption of water with high nitrate concentrations was first recognized clinically by Comly (72). The infants were both less than 1 month old and had received rural well water containing 90 and 140 mg/L, respectively. Earlier, Comly (72) suggested a recommended limit of 10 mg/L NO_3-N in drinking water and a maximum of 20 mg/L.

Later on, Shuval and Gruener (76) studied 1702 infants living in the Israel coastal plain in areas with medium to high nitrate (11.3 to 20.3 mg NO_3-N/L) and compared them with a control group of 759 infants in Jerusalem where only 1.1 mg/L of nitrate is in the water supply. There were no significant differences found between the methemoglobin levels in the 1702 infants in the study areas compared to the 758 infants in the control area. In most countries, methemoglobinemia is not a notifiable disease, making its true incidence unknown. From 1945 until 1970, some 2000 cases of methemoglobinemia have been reported in the world literature (76) with a case fatality of about 8%. The WHO (29) cites literature indicating that 10 cases of methemoglobinemia have been reported in the United Kingdom since 1950 when the first cases of methemoglobinemia were reported in East Anglia. Only one death was reported during this period. In 1986, a 2-month-old infant in South Dakota

(USA) died of methemoglobinemia (77). The exact nitrate concentration is unknown. In another nonfatal case in Iowa, the water apparently contained 285 mg/L nitrate (as N) but the 5-week-old infant survived (42). Hungary is one of the countries, with exceptions, that possibly has the best statistics on the occurrence of infantile methemoglobinemia. Table 8 shows the occurrence of methemoglobinemia in Hungary between 1976 and 1990 (78).

Methemoglobinemia became a notifiable disease in Hungary in 1968 (29), and in the first 5 years after 1968, 883 cases were reported. Of the recorded cases, 92% had a nitrate level in the drinking water exceeding 22.6 mg/L as N; in the remaining 8%, it was between 9 and 22.6 mg/L. The highest number of cases was reported in 1977, and the measures taken to supply the population with drinking water low in nitrate have resulted in a definite decrease in the number of cases each year. For detailed statistics on infant methemoglobinemia, readers are referred to WHO (29) and Csanady (78).

In a later publication, Shuval and Gruener (79) confirm a direct relationship between the occurrence of methemoglobinemia in infants and high concentrations ($>$10 mgNO_3-N/L) of nitrate in water. According to Ross and Desforges (80), other factors important in the pathogenesis of the disease are age, the presence of bacteria in sufficient numbers in the gastrointestinal tract, gastric acidity (a pH $>$4), gastrointestinal disturbances, the types of powdered milk product used as baby food, high fluid intake, and the effect of nutrition because foods rich in nitrate can increase the severity of illness.

The first epidemiological survey in South Africa to assess the effect of well water nitrates on infant health was published (57) after the review of health hazards by Terblanche (74). The survey was undertaken due to the risk of methemoglobinemia in infants in the Rietfontein area as a result of the large number of boreholes where nitrate-nitrogen exceeded 10 mg/L. Unfortunately, no correlation was found between the nitrate content of the groundwater used and the methemoglobin levels in the blood. A clinical health risk assessment was attempted in South Africa due to high ingestion of nitrate water (81). There was an increased risk of methemoglobinemia as a result of increased in bottle-feeding by HIV positive mothers. In South Africa, it has been shown that breast-feeding increases the risk by 12–43% that HIV-positive mothers transmit the virus to their children (82). For this reason, the South African Department of Health advises HIV-positive mothers to bottle-feed infants to reduce the risk of mother to child transmission of the HIV virus via breast milk (81). This assessment attempts to quantify the potential additional total exposed population (PATEP) facing increased risk from nitrates. Table 9 shows the potential additional total exposed population at significant risk of methemoglobinemia as a result of bottle-feeding infants by HIV-positive mothers. The number of infants has been calculated as proportional to the area of the province in which groundwater contains $>$10 mg/L NO_3-N (81).

Table 8. The Occurrence of Methemoglobinemia in Hungary[a]

Year	Number of Cases	Number of Fatalities
1976	207	4
1977	293	7
1978	239	3
1979	180	2
1980	172	3
1981	166	1
1982	91	1
1983	67	—
1984	33	—
1985	46	1
1986	41	—
1987	30	—
1988	31	2
1989	35	2
1990	22	—
TOTAL	**1653**	**26**

[a] Reference 78.

According to Colvin (81), Gauteng has 10% of the PATEP for $>$10 mg/L NO_3-N groundwater, due mainly to the high infant population density (7.5 per km^2). This province includes over half of the total area underlain by groundwater with $>$50 mg/L NO_3-N and has 88% of the potential additional population exposed to very high risk (in South Africa), shown in Table 10.

The qualitative banding of degrees of risk following the matrix model developed by Carpenter and Maragos (83) and simplified by Genthe (84) is shown in Fig. 1.

Severity is defined according to the potential for exposure to nitrate in groundwater sources. For example, a risk that combines high severity with frequent probability is rated “high,” whereas a risk that combines low severity with occasional or the remote probability of occurrence is rated “acceptable.” The highest risk is for infants $<$3 months old who are bottle-fed using groundwater with $>$50 mg/L NO_3-N, and confounding factors (such as lack of vitamin C and gastrointestinal infections) are evident (81).

In another epidemiological study on a comparable population group in Namibia (56), a correlation was found between the nitrate level in the groundwater and blood methemoglobin levels. The main difference between the two studies was that the level of nitrate in groundwater in the Namibian study was much higher, up to 56 mg/L of nitrate-nitrogen (52). However, the ingestion of nitrate has no apparent short-term effects on adults such as methemoglobinemia. Research has shown that adults on a farm near Otjiwarongo, Namibia, continued drinking water with 268 mg/L of nitrate with no apparent ill effects, even after stock losses occurred on that farm (85).

Gastric Cancer

Infants are not the only ones at risk; it is possible that high nitrate concentrations can cause cancer in adults. “Nitrate itself is not directly carcinogenic. However, there is recognition of the fact that nitrate could be converted to nitrite in the human body that can react with secondary and tertiary amines to form nitrosamines—which have been identified as potent carcinogens” (31). Several studies have shown that simultaneous ingestion of nitrite (or nitrate with amines) results in cancers of many organ

Table 9. Potential Additional Total Population Exposed to Significant Risk of Methemoglobinemia as a Result of Bottle-Feeding by HIV-Positive Mothers[a]

Province	>10 mg/L NO_3-N, km^2	%Area of Province	Total Infants <1 yr/Province, 1996	%HIV+, Oct/Nov 1998	Estimated% Groundwater Dependency	PATEP[b]
Free State	45,739	35	48,418	23	30	1167
Gauteng	1,760	10	136,373	23	30	896
Mpumalanga	6,153	8	61,678	30	6	88
North-West	80,958	70	75,097	21	80	8831
Northern Cape	210,603	58	17,711	10	35	357
Northern Province	74,434	60	119,644	12	75	6460
Eastern Cape	0	0	137,552	16	35	0
Kwazulu-Natal	0	0	182,858	33	30	0
Western Cape	765	1	76,908	5	20	5
Total South Africa	**420,411**	**34**	**856,239**	**23**	**40**	**17,804**

[a] Reference 81.

[b] PATEP: Potential additional total exposed population.

Table 10. Potential Additional Total Population Exposed to Very High Risk of Methemoglobinemia as a Result of Bottle-Feeding by HIV-Positive Mothers[a]

Province	>50 mg/L NO_3-N Area (km^2)	%Area of Province	Total Infants <1 yr per Province, 1996	%HIV+ (Oct–Nov 1998)	Estimated% Groundwater Dependency	PATEP[b]
Gauteng	985	5.45	136,373	23	30	513
Mpumalanga	160	0.21	61,678	30	6	2
North-West	416	0.36	75,097	21	80	45
Northern Province	262	0.21	119,644	12	75	22
Total South Africa	**1823**	**0.001**	**856,239**	**23**	**30**	**582**

[a] Reference 81.

[b] PATEP: Potential additional total exposed population.

systems (1). The N-nitroso compounds are presumed to be the ultimate carcinogenic substances (86). The role of nitrite as a precursor to carcinogenic nitrosamines and other N-nitroso compounds has been established (1). Nitrite reacts with amines or amides under several conditions resulting in N-nitroso derivatives, the majority of which are carcinogenic to animals. The expectation that these N-nitroso derivatives are also human carcinogens suggests a mechanism whereby exposure to nitrite might result in carcinogenesis (86).

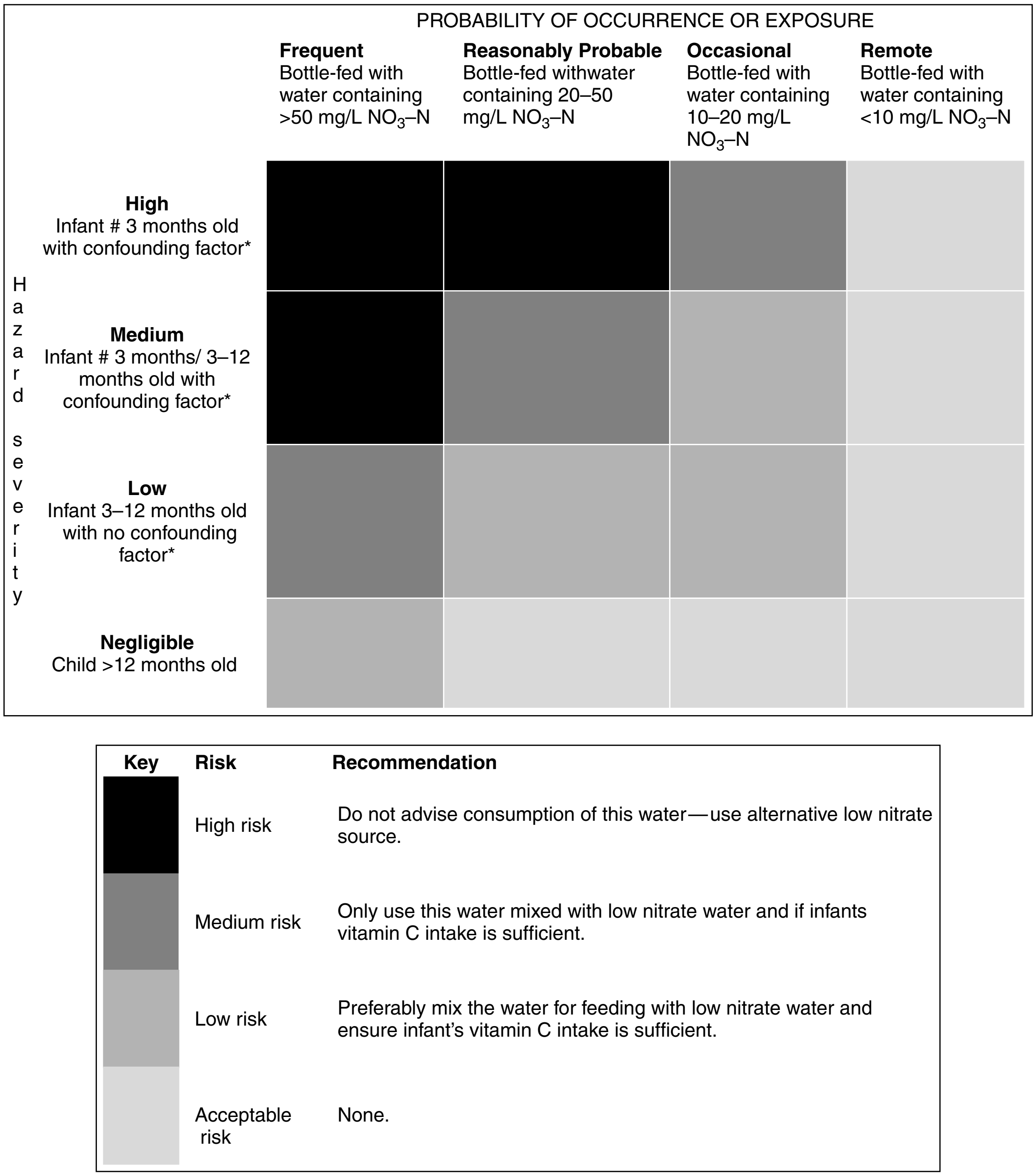
In earlier publications, Wolff and Wasserman (87) reviewed 60 articles on the potential hazard of nitrate, nitrite, and nitrosamines in the environment. Furthermore, Shuval and Gruener (79) refer to the possible carcinogenic, teratogenic, and mutagenic properties of nitrosamines, which can theoretically develop in food or in the human digestive tract if nitrates and nitrites are exposed to secondary and tertiary amines under certain conditions. In both cases, no conclusions were drawn as to the real nature of the potential risks involved. From all available data, the WHO (29) came to the conclusion that no convincing evidence of a relationship between gastric cancer and consumption of drinking-water containing nitrate levels up to 10 mg/L has emerged, yet a link cannot be ruled out; perhaps the inadequacy of the data available would explain this.

However, Hartman (88) in his publication showed a graphical relationship between gastric cancer mortality rates and nitrate ingestion in twelve countries (Fig. 2). Hartman's (88) data on gastric cancer mortality rates are for the years 1974–1975. This graph refers to total nitrate ingestion and does not specifically refer to ingestion via drinking water. Tredoux (52), however, questioned whether the seemingly good correlation is actually related only to nitrate ingestion or possibly also to other dietary factors relating to the various population groups.

Several epidemiological studies have indicated further significant positive correlations between exposure to nitrate and cancer risk. For instance, nitrate in drinking water has been correlated with gastric cancer risk in Colombia and England, and exposure to nitrate-containing fertilizers appeared to be linked to gastric cancer mortality in Chile (1). It should be noted that high risk for gastric cancer correlates with nitrate, and also with several other dietary or environmental factors. These associations, however, cannot be fully traced to the causation of gastric cancer (86,89).

Other Health Effects

The ingestion of nitrate in excess of 10 mg NO_3-N/L is also the possible cause of a number of other adverse effects such as birth defects (congenital malformations), which were studied in South Australia and also in eastern England. Detailed investigation has provided no evidence that these were associated with nitrate levels in water supplies (29). It has also been suggested that



Hazard severity	PROBABILITY OF OCCURRENCE OR EXPOSURE			
	Frequent Bottle-fed with water containing >50 mg/L NO_3–N	**Reasonably Probable** Bottle-fed withwater containing 20–50 mg/L NO_3–N	**Occasional** Bottle-fed with water containing 10–20 mg/L NO_3–N	**Remote** Bottle-fed with water containing <10 mg/L NO_3–N
High Infant # 3 months old with confounding factor*	■	■	▩	□
Medium Infant # 3 months/ 3–12 months old with confounding factor*	■	▩	▨	□
Low Infant 3–12 months old with no confounding factor*	▩	▨	▨	□
Negligible Child >12 months old	▨	□	□	□

Key	Risk	Recommendation
■	High risk	Do not advise consumption of this water—use alternative low nitrate source.
▩	Medium risk	Only use this water mixed with low nitrate water and if infants vitamin C intake is sufficient.
▨	Low risk	Preferably mix the water for feeding with low nitrate water and ensure infant's vitamin C intake is sufficient.
□	Acceptable risk	None.

Figure 1. Risk characterization of methemoglobinemia (after References 83 and 84).

chronic exposure to high levels of nitrate in drinking water may have adverse effects on the cardiovascular system. The WHO (29), however, reported that an inverse relationship between cardiovascular mortality and nitrate concentration in water supplies had been demonstrated.

Moreover, excessive nitrates in drinking water have also resulted in problems with ruminants (cud-chewing animals with divided stomachs). Sheep and cattle, in particular, can be seriously affected by nitrates from birth through adulthood (1). Infants of monogastric (single-stomach) animals like horses, pigs, and chickens are also susceptible to problems from nitrate ingestion. However, as chickens and pigs mature, they are much less susceptible to the health effects of nitrate, but horses can be affected through adulthood (90).

Other possible effects of nitrates relate to the thyroid function in animals. Some animal studies indicate that chronic exposure to high levels of nitrates can reduce the intrathyroid iodine pool and thus render the gland more sensitive to goitrogens (29). However, whether or not exposure to nitrate is an etiological factor in human goiter remains unclear (52).

Symptoms of nitrate-nitrite poisoning in livestock include cyanosis in or about the non pigmented areas (mouth and eyes), shortness of breath, rapid heartbeat, staggered gait, frequent urination, and collapse. In severe cases, convulsions, coma, and death may result within a

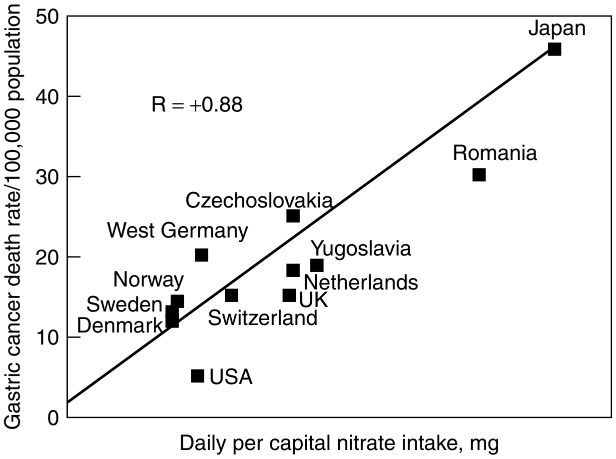


Figure 2. Relationship between gastric cancer mortality rates and nitrate ingestion in 12 countries (after Reference 88).

few hours (1). Loss of milk production in cows and aborted calves are also indicative of nitrate poisoning (90). Stock losses due to nitrate poisoning have been reported in Namibia (91), in the dolomitic area of South Africa (92), and in Bophuthatswana (52).

Exposure to high doses of nitrate is also associated with adverse effects such as the 'hot-dog headache' (52). The 'hot-dog headache' has been described in the literature as related to nitrites used in curing meat to give it a uniform color (93). Nitrites are also vasodilators, so that some people find that soon after eating these meat products, they develop flushing of the face and headache. The 'hot-dog' is the classical example, but other meat products, including bacon, ham, and salami, can also cause these symptoms (52). A farmer in the Springbok Flats regularly complained about hot-dog headaches. The problem was solved when he started using nitrate-free water (94).

Finally, detailed information on the health effects of nitrate and nitrite in humans and animals, the mechanism and quantification of toxicological effects of nitrate and nitrite, as well as other health-related information on nitrates are available in literature (29,43,56,74,76,79, 95–97). Obviously, pollution and contamination problems from NO_3-NO_2 compounds must be causing environmental public health havoc yet to be fully determined and documented. Therefore, nitrate-nitrite pollution control programs must be established to reduce the health effects of these common and widespread contaminants. Excessive chemical fertilizer and animal manure applications must be controlled and curtailed. Exceptionally high NO_3 borehole waters must be abandoned, and unpolluted groundwater exploited. These and possible biodenitrification water treatment (for affected waters before use) could contribute solutions.

SUMMARY

The occurrence of high nitrate concentrations in groundwater is widespread, particularly from agricultural usage of fertilizers and animal manure or land disposal of domestic waste and wastewaters. Much research has been conducted to determine the amounts of nitrates in drinking water wells as well as in foods. Exposure to high doses of nitrate is generally perceived to be associated with adverse health effects in humans and other species. These range from infant methemoglobinemia, cancers, the 'hot dog headache,' and hypertension, to other adverse effects such as birth defects (congenital malformations) and spontaneous abortions. Most reported cases of infantile methemoglobinemia have been associated with the use of water containing more than 10 mg/L NO_3-N.

Pollution and contamination problems from NO_3-NO_2 compounds may be causing environmental public health havoc yet to be fully determined and documented. The evidence as outlined in this article is overwhelming. Therefore, nitrate-nitrite pollution control programs must be established to reduce the health effects of these common and widespread contaminants. Excessive chemical fertilizer and animal manure applications must be controlled and curtailed. Exceptionally high NO_3 borehole waters must be abandoned, and unpolluted groundwater exploited. These and possible biodenitrification water treatment could contribute solutions.

BIBLIOGRAPHY

1. Canter, L.W. (1996). *Nitrates in Groundwater*. Lewis, New York.
2. Sievers, D.M. and Fulhage, C.D. (1992). Survey of rural wells in Missouri for pesticides and nitrates. *Groundwater Monitoring Rev.* **12**(4): 142–150.
3. Exner, M.E. and Spalding, R.F. (1990). *Occurrence of Pesticides and Nitrate in Nebraska's Ground Water*. Report WC1, Water Center, Institute of Agriculture and Natural Resources, University of Nebraska, Lincoln, Nebraska, pp. 3–30.
4. Anonymous. (1975). *Proc. Conf. Nitrogen Water Pollutant, Int. Assoc. Water Pollut. Res.*, August, Copenhagen, Denmark.
5. Tessendorff, H. (1985). Nitrates in groundwater: A European problem of growing concern. *Aqua* **4**: 192–193.
6. Kraus, H.H. (1993). *The European Parliament and the EC Environment Policy*. Working Paper W-2, April, European Parliament, Luxembourg, p. 12.
7. Overgaard, K. (1984). Trends in nitrate pollution of groundwater in Denmark. *Nordic Hydrol.* **15**(4–5): 174–184.
8. Anonymous. (1983). Nitrate in water for human consumption: The situation in France (1979–1981). *Aqua* **2**: 74–78.
9. Custodio, E. (1982). Nitrate build-up in Catalonia coastal aquifers. *Memoires, Int. Assoc. Hydrogeol.* **16**(1): 171–181.
10. Greene, L.A. (1978). Nitrates in water supply abstractions in the Anglian region: Current trends and remedies under investigation. *Water Pollut. Control* **77**(4): 478–491.
11. Buzek, F., Kadlecová, R., and Zák, K. (1998). *Nitrate pollution of a karstic groundwater system*. In: *Isotope Techniques in the Study of Environmental Change*. IAEA, Vienna, pp. 453–464.
12. Hill, A.R. (1982). Nitrate distribution in the ground water of the Alliston region of Ontario, Canada. *Ground Water* **20**(6): 696–702.
13. Egboka, B.C.E. (1984). Nitrate contamination of shallow groundwater in Ontario, Canada. *Sci. Total Environ.* **35**: 53–70.
14. Handa, B.K. (1983). Effect of Fertilizer use on Groundwater Quality in India. *Proc. Symp. Ground Water Water Resour. Plann.*, Vol. II, IAHS Publication, No. 142, pp. 1105–1119.

15. Jacks, G. and Sharma, V.P. (1983). Nitrogen circulation and nitrate in ground water in an agricultural catchment in southern India. *Environ. Geol.* **5**(2): 61–64.
16. Ronen, D. and Margaritz, M. (1985). High concentration of solutes at the upper part of the unsaturated zone (water table) of a deep aquifer under sewage-irrigated land. *J. Hydrol.* **80**(3/4): 311–323.
17. Schalscha, E.B. (1979). Nitrate movement in a Chilean agricultural area irrigated with untreated sewage water. *J. Environ. Qual.* **8**(1): 27–30.
18. Duque, J. and Almeida, C. (2001). Nitrate contamination in a shallow gabbro hard rock aquifer, Beja—South Portugal. In: *New Approaches Characterizing Groundwater Flow*, K.P. Seiler and S. Wohnlich (Eds.). Swets & Zeitlinger Lisse, Lisse, pp. 1169–1173.
19. Tredoux, G., Engelbrecht, J.F.P., and Tama, A.S. (2001). Nitrate in groundwater in Southern Africa. In: *New Approaches Characterizing Groundwater Flow*. K.P. Seiler and S. Wohnlich (Eds.). Swets & Zeitlinger Lisse, Lisse, pp. 663–666.
20. Tredoux, G. and Kirchner, J. (1985). *The occurrence of nitrate in groundwater in South West Africa/Namibia*. Paper presented at *Conf. Nitrates in Water*, Paris.
21. Adelana S.M.A. and Olasehinde P.I. (2003). High nitrate in water supply in Nigeria: Implications for human health. *Water Resour.* **14**(1): 1–11.
22. Edet, A.E. (2000). Water Pollution by Nitrate Near Some Waste Disposal Sites in Calabar (Nigeria). *Groundwater 2000, Proc. Int. Conf. Groundwater Res.*, Copenhagen, June 6–8, pp. 239–240.
23. Uma, K.O. (1993). Nitrates in shallow (regolith) aquifers around Sokoto Town, Nigeria. *Environ. Geol.* **21**: 70–76.
24. Egboka, B.C.E. and Ezeonu, F.C. (1990). Nitrate and nitrite pollution and contamination in parts of SE Nigeria. *Water Resour.* **2**(2): 101–110.
25. Langenegger, D. (1981). High nitrate concentrations in shallow aquifers in a rural area of central Nigeria caused by random deposits of domestic refuse and excrement. In: *Studies in Environmental Science*. W. van Duijvenbooden, P. Glasbergen, and H. van Lelyveld (Eds.). Elsevier, Amsterdam, Vol. 17, pp. 147–153.
26. Akiti, T.T. (1982). *Nitrate levels in some granitic aquifers from Ghana*. *Proc. Int. Symp. Impact Agric. Activities Groundwater*, IAH Mem. XVI, Part 1, pp. 87–98.
27. Groen, J., Schuchnann, J.B., and Geinaert, W. (1988). The occurrence of high nitrate concentration in groundwater in villages in northwestern Burkina Faso. *J. African Earth Sci.* **7**(7/8): 999–1009.
28. Tandia, A.A., Gaye, C.B., and Faye, A. (1998). Origin, process and migration of nitrate compounds in the aquifers of Dakar region, Senegal. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*. IAEA, Vienna, pp. 67–80.
29. World Health Organization. (1985). *Health Hazards from Nitrates in Drinking Water*. Copenhagen.
30. Schroder, H., Harremoes, P., and Simonsen, J.F. (1985). *Water Pollution Caused by Nitrogen from Urban Wastewater and from Agriculture*. Paper presented at *Conf. Nitrates Water*, Paris.
31. Fedkiw, J. (1991). *Nitrate Occurrence in Waters*. USDA, Washington, DC.
32. Anton, E.C., Barnickol, J.L., and Schnaible, D.R. (1988). *Nitrate in Drinking—Report to the Legislature*, Report No.88-11 WQ, October, Division of Water Quality, State Water Resources Control Board, State of California, Sacramento, California, pp. 35–38.
33. Swanson, G.J. (1992). Well testing program is cooperative effort. *Water Well J.* **46**(8): 39–41.
34. George, W.W. and Hustings, W.W. (1951). Nitrate in groundwater of Texas. *Trans. Am. Geophys. Union* **32**(3): 316–342.
35. Ferlmutter, N.M. and Koch, E. (1972). *Preliminary Hydrogeologic Appraisal of Nitrate in Groundwater and Streams, Southern Nassau County, Long Island, New York*. U.S. Geol. Surv. Prol. Paper, No. 800-B, pp. B225–B235.
36. Schmidt, K.D. (1972). Nitrate in groundwater of Fresno–Clovis Metropolitan area, California. *Ground Water* **10**(1): 60–64.
37. Behnke, J.J. and Haskell, E.E. (1968). Groundwater nitrate distribution beneath Fresno, California. *J. Am. Water Works Assoc.* **4**: 477–480.
38. Devitt, D., Leley, J.J., Lund, L.J., and Blair, J.W. (1976). Nitrate nitrogen movement through soil as affected by soil profile characteristic. *J. Environ. Qual.* **5**(3): 283–288.
39. Marais, S. (1999). *Dependency of Communities on Groundwater for Water Supply and Associated Fluoride and Nitrate Problems*. Paper presented at Workshop on Fluorides and Nitrates in Rural Water Supplies, Mafikeng, March 9–10.
40. Trudell, M.R., Gillham, R.W., and Cherry, J.A. (1986). An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *J. Hydrol.* **83**: 251–268.
41. Miller, L.W. (1971). Methemogolobinaemia associated with well water. *J. Am. Med. Assoc.* **216**: 1642–1643.
42. Rajagopal, R. and Tobin G. (1989). Expert opinion and groundwater quality protection: The case of nitrate in drinking water. *Ground Water* **27**(6): 835–847.
43. Fan, A.M. and Steinberg, V.E. (1996). Health implications of nitrate and nitrite in drinking water: An update on methemoglobinemia occurrence and reproductive and developmental toxicology. In: *Regulatory Toxicology and Pharmacology*. 23, Academic Press, London.
44. Bassir, O. and Maduagwu, E.N. (1978). Occurrence of nitrate, nitrite, dimethylamine and dimethylnitrosamine in some fermented Nigerian beverages. *J. Agric. Food Chem.* **26**(1): 200–203.
45. Faillat, J.P. (1986). *Aquiferes Fissures en Zone Tropicale Humide : Structure, Hydrodynamique et Hydrochimie. (Afrique de l'Ouest)*. These Doc. D'Etat. U.S.T.L. Montpellier.
46. Faillat, J.P. (1990). Origin desnitrates dans les nappes de fissures de la zone tropicale humide. Exemple de la Cote d'Ivoire. *J. Hydrol.* **113**: 231–264.
47. Faillat, J.P. and Rambaud, A. (1988). La teneur en nitrates des nappes de fissures de la zone tropicale humide en relation avec les problems de deforestation. *C.R. Acad. Sci. Paris* **306**(II): 1115–1120.
48. Edmunds, W.M. and Gaye, C.B. (1997). High nitrate baseline concentrations in groundwaters from the Sahel. *J. Environ. Qual.* **26**: 1231–1239.
49. Okonkwo, P.O., Nwokolo, C., and Onwuamaeze, I.C. (1981). Dietary nitrite and carcinogenesis in the Nigeria environment. *J. Nutr. Sci.* **2**: 9–13.
50. Mirvish, S.S., Wallcare, I., Eagen, M., and Shubik, P. (1972). Ascorbate-nitrite. Reactions; possible means of blocking the transformation of carcinogenic N-nitroso compounds. *Science* **177**: 65–68.
51. Ezeonu, F.C. (1989). The Role of Rat Liver Microsomal Enzyme in the *in vitro* Metabolism of Nitrate and Formation of Nitrosamine. Paper presented at the *14th Annual Biochem. Soc. Nigeria Conf.*, Imo State University, Okigwe, Nigeria.

52. Tredoux, G. (1993). *Preliminary Investigation of Nitrate Content of Groundwater and Limitation of the Nitrate Input*. WRC Report No. 368/1/93, Pretoria.
53. Packham, R.F. (1991). Public health and regulatory aspects of inorganic nitrogen compounds in drinking water. *Int. Workshop, Inorg. Nitrogen Comp. Water Supply*, Hamburg, November 1991.
54. Bosch, H.M. et al. (1950). Methemoglobinemia and Minnesota well supplies. *J. Am. Water Works Assoc.* **42**: 91–95.
55. Walton, G. (1951). Suvey of literature relating to infant methemoglobinemia due to nitrate contaminated water. *Am. J. Public Health* **41**: 1141–1152.
56. Super, M. et al. (1981). An epidemiological study of well water nitrates in a group of Namibian infants. *Water Res.* **15**: 1265–1270.
57. Hesseling, P.B., Toens, P.D., and Visser, H. (1991). An epidemiological survey to assess the effects of well water nitrates on infants' health at Rietfontein in the northern Cape Province, South Africa. *South Afr. J. Sci.* **87**: 300–304.
58. United States Environmental Protection Agency. (1990). *National Survey of Pesticides in Drinking Water Wells—Phase I Report*, EPA 570/09-90-015, Office of Water, Washington, DC.
59. United States Environmental Protection Agency. (1992). *Another Look: National Survey of Pesticides in Drinking Water Wells—Phase II Report*, EPA 579/09-91-020, January, Office of Water, Washington, DC.
60. Cohen, S., (1992). Results of the National Drinking Water Survey: Pesticides and well characterized. *Water Well J.* **46**(8): 35–38.
61. Keeney, D. (1989). Sources of nitrate to ground water. In: *Nitrogen Management and Groundwater Protection*. R.F. Follett (Eds.). Elsevier Science, Amsterdam, The Netherlands, Chap. 2, pp. 23–34.
62. United States Environmental Protection Agency. (1994). *Nitrogen Control*. Technomic, Lancaster, PA, pp. 1–22.
63. Van Duyvenboden, W.V. and Loch, J.P.G. (1983). Nitrate in the Netherlands—A serious threat to groundwater. *Aqua* **2**: 59–60.
64. Van Beek, C.G.E.M. (1985) Nitrate situation. Paper presented at *Conf. Nitrates Water*, Paris.
65. Lawrence, C.R. (1983). Occurrence and genesis of nitrate-rich groundwaters of Australia. *Int. Conf. Groundwater Man, Sydney* **2**: 237–247.
66. United States Environmental Protection Agency. (1993). *Nitrogen Control*. EPA 625/R-93-010, September 1993, Office of Water, Washington, DC.
67. Bassir, O. and Maduagwu, E.N. (1978). Occurrence of nitrate, nitrite, dimethylamine and dimethylnitrosamine in some fermented Nigerian beverages. *J. Agric. Food Chem.* **26**(1): 200–203.
68. United States Agency for International Development. (1990). *Strategies for Linking Water and Sanitation Programs to Child Survival*. USAID, Washington, DC, pp. 1–62.
69. Warner, D. (1998). Drinking water supply and environmental sanitation for health. Presented at the *Int. Conf. Water Sustainable Dev.*, Paris, March 19–21, pp. 1–10.
70. Population Reports. (1998). *Solutions for a Water-short World*, Series M, **14**, September.
71. Parsons, M.L (1977). Current research suggests the nitrate standard in drinking water is too low. *J. Environ. Health* **40**: 140–142.
72. Comly, H.H. (1945). Cyanosis in infants caused by nitrates in well water. *J. Am. Med. Assoc.* **129**: 112–116.
73. Pande, S.P., Hassan, M.Z., and Saxena, K.L. (1986). Nitrates and nitrites in the environment. *J.I.W.W.A.* **XVIII**(3): 145.
74. Terblanche, A.P.S. (1991). Health hazards of nitrate in drinking water. *Water SA* **17**(1): 77–82.
75. Federal Register. (1985). *National Primary Drinking Water Standards*. **219**: November 13, 46,880–47,022.
76. Shuval, H.I. and Gruener, N. (1972). Epidomiological and toxicological aspects of nitrates and nitrites in the environment. *Am. J. Public Health* **62**: 1045–1052.
77. Groundwater Newsletter. (1986). Blue-baby death from contaminated well in South Dakota stirs investigation. *Groundwater Newsl.* **15**(18): 1.
78. Csanady, M. (1991). Nitrite formation and bacteriological deterioration of water quality in distribution networks. Paper presented at *Int. Workshop: Inorg. Nitrogen Comp. Water Supply*, Hamburg, IWSA, Pre-Prints, 45–49.
79. Shuval, H.I. and Gruener, N. (1977). Infant methaemoglobinemia and other health effects of nitrates in drinking water. *Prog. Water Technol.* **8**: 183–193.
80. Ross, J.D. and Desforges, J.F. (1959). Reduction of methemoglobin by erythrocytes from cord blood. *Pediatrics* **23**: 718–721.
81. Colvin, C. (1999). Increased risk of methemoglobinemia as a result of bottle-feeding by HIV positive mothers in South Africa. Paper presented at *IAH Congr. 1999*, Bratislava, Slovakia.
82. McIntyre, J. (1997). *Affordable option for the prevention of mother to child transmission of HIV 1 from research to clinical care*. *National AIDs Programme Perinatal HIV Res. Unit Conf.*, November 1997, Johannesburg, South Africa.
83. Carpenter, R.A. and Maragos, J.E. (1989). How to assess environmental impact on tropical islands and coastal areas. In: *Training Manual for South Pacific Regional Environment Programme*, South Pacific Regional Environment Programme (SPREP), Apia, pp. 119–122.
84. Genthe, B. (1998). *Specialist Study on the Potential Health Impacts of the Proposed Wastewater Treatment Facility on the West Bank of East London*. CSIR report ENV/S—198003.
85. Tredoux, G. (1974). *'n Intensiewe opname van waterbronne in die omgewing van Otjiwarongo*, Project Report No. 12 (unpublished), NIWR-CSIR, Windhoek, Namibia.
86. Tannenbaum, S.R. and Green L.C. (1985). *Selected Abstracts on the Role of Dietary Nitrate and Nitrite in Human Carcinogenesis*. International Cancer Research Data Bank Program, National Cancer Institute, Washington, DC.
87. Wolff, I.A. and Wasserman, A.E. (1972). Nitrates, nitrites and nitrosamines. *Science* **177**: 15–19.
88. Hartman, P.E. (1983). Review: Putative mutagens and carcinogens in foods. *Environ. Mutagenesis* **5**: 111–121.
89. Kleinjans, J.C.S. et al. (1991). Nitrate contamination of drinking water evaluation of genotoxic risk in human populations. *Environ. Health Perspect.* **94**: 189–193.
90. Chandler, J. (1989). Nitrates in water. *Water Well J.* **3**(5): 45–47.
91. Anonymous. (1974). Nitrate vergif water in noorde: Beeste en skape vrek. *Die Suidwester*, Windhoek, Namibia, June 26.
92. Marais, S. (1991). *Written communication*. Department of Water Affairs, Mmabatho, Bophuthatswana.
93. Johnson, G.T. and Goldfinger, S.E. (1982). *The Harvard Medical School Health Letter Book*. Warner Books, New York.
94. Talma, A.S. (1991). *Written Communication*, CSIR, Pretoria.
95. Life Systems, Inc. (1987). *Drinking Water Criteria Document for Nitrate/Nitrite*, TR-832-77. Cleveland, Ohio.

96. Dahab, M.F. and Bogardi, I. (1990). *Risk Management for Nitrate-Contaminated Groundwater Supplies*. University of Nebraska, Lincoln, NE, pp. 9–16.
97. Kross, B.C., Ayebo, A.D., and Fourtes, L.J. (1992). Methemoglobinemia: nitrate toxicity in rural America. *Am. Family Physician*, July.
98. *Secretaria de Salud. (1988). Reglamento de la Ley General de Salud en Materia de Control Sanitario de Actividades, Establesimientos, Productos y Servicios* (General law for sanitary control of activities, products and services): Official News of the Mexican Government, January 8, Mexico, p. 27.

DOMESTIC WATER SUPPLY—PUBLIC–PRIVATE PARTNERSHIP

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INTRODUCTION

> "Food and water are basic rights. But we pay for food. Why should we not pay for water?"
>
> Ismail Serageldin

> "Water should not be privatised, commodified, traded or exported in bulk for commercial purposes."
>
> Maude Barlow

The above two quotes typify the two extremes of the arguments surrounding public–private partnerships (PPPs). Although this ideological debate is intellectually exciting, the more challenging problem can be summarized as follows (1):

- How do you provide access to safe water to around I billion people?
- How do you provide sanitation services to around 2.6 billion people?

Time is ticking by, and the global community must meet the above targets soon. Policymakers and water and sanitation practitioners alike should be prepared to include PPPs as a tool in achieving the above. Before going into detail, a brief summary of the context follows.

Water is essential for life. This is not only in terms of its biological utility, for water also has social, economic, health, technical, financial, and political dimensions. Historically, the availability of a domestic water supply has been a significant factor in the development and sustenance of civilizations.

Water is one of Earth's most important natural resources. If naturally occurring freshwater is polluted as a result animal (including human), plant, or other activities, processes are required to convert the then raw water to a quality fit for a particular use, such as drinking. In most cases, because of high levels of pollution by humans, water must be treated before and after its use.

Various water sources exist, for example, rainwater, groundwater, spring water, surface water, rivers, lakes, ponds, fog, and even glaciers. Water can be supplied from such sources in many different ways, but these can then be divided into either piped or nonpiped options.

The behavior of humans in terms of their consumption of water also has historical, geographical, and cultural dimensions. For example, in some parts of Bolivia people only consume 5 or 6 L per capita each day as compared with the 30 to 250 L consumed each day by a person in developed economies.

Water has various uses, including agricultural, recreational, industrial, and domestic. In terms of its domestic use, water is used for sanitation facilities as well as for drinking. Indeed, a high level of consumption—up to 80%—is caused by piped sanitation wherever such facilities are available. Think about how much water a person flushes as compared with how much he or she drinks! With a limited amount of useable water, there is competition, sometimes tension, among various water users. Both market-oriented and hierarchy-based rules are used to distribute water among its various consumers.

In the supply chain of water—its production, distribution, management, and consumption—private sector organisations are key players. Before moving on to the main discussion of this paper, it is useful to summarize some of the more important concepts.

CONCEPTS

Public and Private Goods

Private goods are those for which consumption (or use) by one person prevents consumption (or use) by another. Public goods are those that can be used by one person without diminishing the opportunity for use by others. There is a seemingly unending debate over whether water should be treated as a public or private good, or both.

Commodification

Commodification is the process of converting a good or service formerly subject to non-market social rules into one that is subject to market rules. Treating water as an economic good implies that the resource will be allocated across competing uses in a way that maximizes its economic value across society. However, it also implies that safety nets will be needed for people who cannot afford to pay. Meanwhile, for some people, considering water to be a commodity at all is sacrilegious!

Governance

Governance refers to the relationship that can be manifested in various types of partnerships and networks. Water governance is the wider context within which water services procurement plays a key role and under which PPP is a niche tool.

What is Partnering?

At the very least, partnering should be viewed as the absence of adversarial behavior.

WHAT ARE PPPS?

The involvement of the private sector in partnership with government has long been advocated as a means of improving the development of sustainable water and sanitation systems. The author uses PPPs in this document as a general term to cover a wide range of agreements or partnerships between private sector (nongovernment) concerns or organizations, public sector utilities, government departments, and consumer groups in relation to the delivery of water and sanitation services. The community has a direct role to play in such arrangements as a beneficiary and in expressing the price people would be willing to pay for an acceptable level of service. It also has an indirect role to play in shaping policy for the urban environment. In a small PPP, the community could take the role of the private partner.

One of the difficulties in determining the scope of discussion concerning private sector involvement in water and sanitation is the sheer diversity of possible partnership arrangements and potential actors. The three main roles are those of the private sector, users (consumers), and the government (often referred to a the client or sponsor; it also may act as regulator). The possible arrangements include complex concession arrangements operated by multinational corporations lasting perhaps 30 years; shorter duration, simpler forms of management or service contract undertaken by medium-sized private enterprises; and service delivery by small-scale independent providers (local entrepreneurs). An outline of formal contracting arrangements is produced in Appendix A.

WHY PPPS FOR DOMESTIC WATER SUPPLY?

The role of the private sector in domestic water supply is not new. Many water supply-related activities in many municipalities in the world have started out as small private water firms or informal organizations of people.

Considering the potential demand for water sanitation, it is obvious that already budget-constrained governments cannot improve services alone. Some estimates indicate huge capital outlays are needed to meet water and sanitation targets; Camdessus and Winpenny (2), for example, estimate US$90 billion per year is needed globally to meet such targets. On the other hand, there is an argument that unless national governments make environmental sustainability a priority, the shortage of water and sanitation services will remain as they are. Other people believe that improved water management and better use of current assets is what is crucial and will reduce the need for more capital infrastructure significantly.

In any case, private finance is only one of the benefits of PPPs. Others include the managerial capacity of the private sector in managing assets for water and sanitation services. The private sector is also more likely to be innovative than the public sector, which leads to more effective and efficient services provision.

Governments are turning to PPP arrangements for the provision of services for a variety of reasons; therefore, these may include the following:

- Lack of capacity of government institutions to deliver a reasonable level of service or to improve service quality.
- Financial weakness of public utilities.
- The inability of public institutions to respond to an increasing growth in demand for services because of, for example, rapid urbanization.
- Problems related to the large numbers of employees in public sector providers.
- The requirement that international financing institutions (IFIs) place on certain indebted countries to reduce domestic spending as part of structural adjustment programmes. Such institutions promote the idea that the private sector is more efficient and effective and delivers a better quality service.

HOW PUBLIC-PRIVATE PARTNERSHIPS GET STARTED

There are various ways in which a partnership can be initiated. In some cases, the initiative comes from the likely partners and in some cases the demand comes from an third party. Public-private partnerships may not always seem to be a desirable solution at first. Most organizations prefer to stay on paths they know well, sharing goals and work practices with other groups that think and act like them—governments working with governments, businesses with businesses, and nonprofit groups with nonprofit groups.

Governments and private firms have long worked together under simple arrangements, such as government purchase of products produced by the private sector. However, both parties often hesitate to enter into more complex relationships. Governments are frequently concerned that private businesses will take advantage of them, whereas businesses often consider government approaches to be burdensome and a waste of time. Therefore, it is useful to allow some time for trust to be established among the key partners.

Three main conditions favor the formation of a partnership: urgency, the involvement of a champion, and some kind of catalyst.

Urgency

Generally, it takes a widely acknowledged urgency—for instance, the lack of particular services or the waste of resources—before key stakeholders start looking for partnerships and partners are open to cooperate to resolve the problem. Although it is hoped that progress can be made in the absence of a crisis, in practice, the inertia that keeps many people on familiar paths is usually broken only by a pressing need for change.

Entrepreneurs/Champion

Sometimes, even in the absence of a urgency, an individual, group, or organization may realize that separate, uncoordinated actions are creating redundancies, missed opportunities, and less-than-optimal use of scarce resources. In reality, even if the crisis is clear and the interest is there, partnership arrangements will not succeed without the drive and commitment of a few individuals. Such “champions” (leaders or pioneers) can be government officials, NGOs, business people, or citizens who—through their personal motivation—make partnerships happen. In other cases, champions are service providers who stand to profit from the partnership.

Catalyst

Frequently, there is a need for some kind of catalyst to bring the partners together. Such a catalyst could be the actions of an external actor, such as one or more international finance institutions or other bodies that are respected and trusted by all partners.

WHAT ARE THE KEY FEATURES OF SUCCESSFUL PARTNERSHIPS?[1]

Characteristics of Successful Partnerships

Compatible Goals. Government , businesses, and community leaders must understand and respect one another’s goals. For instance:

- Government may initially have difficulty accepting the profit motive of private businesses.
- Private companies may be tempted to walk away from the more bureaucratic decision-making processes used in the public sector.
- Local communities may not have the patience needed to address issues affecting other areas of the city.

To resolve these differences, all parties must focus on the broader, complementary goals that are to be achieved. It is important for them to realize that public and private goals do not necessarily need to be the same for partnerships to work—they must be merely compatible.

Enabling Environments. An enabling regulatory, legal, and political environment is the cornerstone of sustainable private sector participation.

Legal Framework. Early on, the public sector must establish an appropriate legal framework for contract procurement and private sector investment. It is important that mechanisms be put into place to minimize the likelihood or appearance of corruption in any procurement processes. Unpredictable and unfair procurement processes reduce both political acceptability and the interest of many private investors.

Regulatory Framework. The government must also establish a clear regulatory framework, and it must implement appropriate tariff regimes and subsidy mechanisms. The creation of a regulatory framework alone, however, does not necessarily guarantee effective regulation. As all local governments are different, the public and private sectors will face a steep learning curve as they try to define and regulate their relationship with one another and their roles in providing services. In particular, the public sector needs to define a clear allocation of responsibilities between the national and municipal governments and a clear statement of its role as a provider and a regulator.

In general, private sector companies prefer that the contract serve as the major regulatory mechanism, and that governments have limited regulatory discretion once the contract is in place. Highly specific contract terms that establish duties, performance targets, rules for changing prices, and dispute resolution procedures allow the private sector to better predict the profitability of the venture and decide whether and what to bid for the contract. Given these preferences, governments will have to make important decisions about the degree of regulatory discretion they are willing to give up, particularly for long-term contracts.

Political Environment. In addition to the regulatory climate, a bad political climate caused by the pressure of election cycles, the potential instability of new democracies, the personal agendas of government officials, and the special status of some services (particularly in terms of access to water, for example) can create barriers to starting or maintaining public–private collaborations. Governments must provide assurances whenever possible to private sector partners that such political factors will not disrupt the contractual partnership.

Acceptance. The government and business leaders cannot build partnerships alone; political and social acceptance of private sector involvement is essential. The population must see private sector participation as beneficial if the partnership is to last over time. Public support of private involvement over the long term will depend on primarily the delivery of promised services and benefits at reasonable costs. Therefore, it is of the utmost importance that mechanisms be developed to ensure that the organization providing the service, whether it is a public or a private sector organization, be accountable to its customers.

Public support will also depend on the ability of the partnership to meet the needs of all stakeholders. For example, public sector workers can be a source of tremendous opposition to increased private involvement in the provision of services. Contracts should ensure the employment or placement of public employees and local residents to the greatest degree possible.

Credibility and Transparency. Effective cooperation between local government, businesses, and the community is always difficult to achieve because of the wide range of participants involved, the low level of trust that often exists between potential partners, and the lack of predictability in the process. The credibility of champions and other leaders involved, as well as transparency in the process, are critical determinants of long-term success. Experience suggests that genuine partnerships must include the principles of equity, transparency of operations, and mutual benefit. Trust and confidence in any project is necessary for successful partnerships.

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[1] The following section is based on Sohail and Olena (3).

Factors Contributing to the Durable Partnerships

Governments clearly want to establish PPPs that are sustainable over time. Essential ingredients of durable PPPs include those listed below.

Commitment of Resources. All partners to the arrangement should be obliged to commit resources (financial, human, capital) to increase their interest in seeing the partnership succeed, which implies shared risks and rewards.

Capacity Development. Projects requiring substantial institutional change or large capital investments will require capacity development within all groups of stakeholders. For example, development of:

- Consumers, in terms of their knowledge of the service they are to receive and the costs associated with its provision
- Service providers, particularly local organizations, in terms of entrepreneurial skills
- Governments, in terms of their capacity to adopt the frameworks necessary for, and oversee the provision of, the service

Roles and Responsibilities. The delineation of appropriate roles and responsibilities is another element necessary in the development of effective, durable partnerships. It is essential that partnerships be organized in a concerted fashion to make the most effective use of the resources committed by both parties.

Individual responsibilities should be clearly outlined from the beginning so that there is no ambiguity in the tasks that each party is expected to perform. Furthermore, these responsibilities need to be defined realistically with a clear understanding of the strengths and weaknesses of each partner.

Flexibility. All partnerships are context-based and different locally. Partnerships should draw on other experiences but at the same time should be opportunistic about exploiting the comparative advantage of local resources. Over the long term, changes in investment plans, technology choices, and priority actions will be necessary in response to unforeseen circumstances. Including clear procedures for making such changes over the life of the project will reduce the chance that they will have a negative impact on the partnership.

Time. Partnerships take time. The process of understanding the problems to be addressed and the impacts on potential partners, as well as those partners' needs and aspirations, all takes time. Progress can certainly be made along the way, but the process of achieving and maintaining acceptance among users, providers, and regulators is a continuing one; a cooperative dialogue to address shared needs must be maintained throughout the project.

Patience. Projects requiring substantial institutional change or large capital investments require a lot of patience. Careful attention must be paid to the balance between responding rapidly to the most pressing crises and developing integrated solutions that will last. Political cycles and the desire for immediate improvement in a crisis situation often lead to the development of time frames that are too short. Such short-term agendas and limited horizons lead to unrealistic expectations and unsustainable solutions. It is not realistic to expect that private sector involvement will overcome public institutional and operational inefficiencies quickly, nor that it will compensate immediately for a history of insufficient public sector resources and funding.

Social Responsibility. Public services provide public goods—in other words, goods that should be available to everyone. Improving provision of such services is about making people's lives better, especially those of the urban poor. Governments should always make sure that the changes they make promote increased access to, and better quality of, services. An emphasis on social responsibility will also increase political gain, as better services will lead to greater political acceptance by the general population.

What are the Major Obstacles to Forming a Successful Partnership?

A range of possible obstacles or deficiencies in the capacity of both public and private actors could hinder the formation of a successful partnership. Major obstacles in this respect include:

- Reciprocal mistrust and lack of understanding of one another's interests and needs across the public and private sectors
- Absence of locally available information on, and experience with, arranging sustainable partnerships
- Underlying legal, political, and institutional obstacles to forming effective public–private relationships

These obstacles often lead to lengthy negotiations, increased transaction costs, and make smaller projects much less attractive to potential investors. To minimize the harm from such obstacles, PPP arrangements should provide certain safeguards for the public and private sectors and for the community.

The public sector usually expects the private sector to contribute in one or all of the following ways:

- To provide agreed services
- To make agreed investments
- To meet agreed standards/targets
- To not exploit any monopoly situation that might exist

The private sector expects the public sector to contribute in one or all of the following ways:

- To create an enabling environment suitable for the PPP
- To pay agreed fees promptly and in full
- To implement tariff increases as agreed

- To prevent unexpected competition from others during operation (exclusivity)

The community expects the PPP to:

- Provide appropriate levels of services
- Be affordable to the community, either through direct charges or indirectly through general taxation

THE CURRENT SITUATION

Quantitative information in this section is based mainly on the World Bank Private Participation in Infrastructure (PPI) database (4).

- At least 203 water and sanitation projects are taking place in 43 developing countries, with a corresponding commitment of some US $40 billion.
- A few large projects in, for example, Argentina, Chile, and Manila, Philippines can explain peaks in water and sanitation investment during 1991–2000.
- Latin America and the Caribbean are the most active regions in terms of global investment (52%), followed by East Asia and the Pacific (38%) and only then Europe and Central Asia (8%).
- Concession contracts provide the largest proportion of such investment (69%) through the largest number of projects (90).
- Private investment reached a peak in 1999.
- The top five countries by cumulative investment in water and sewerage projects with private participation were Argentina, the Philippines, Malaysia, Chile, and Brazil during 1991–2000.

The above figures relate only to formal PPPs and do not take into account many informal private sector and community-based operations; such operations could be serving many users well.

CHALLENGES[2]

Political Acceptance

Infrastructure services such as water and sanitation are intrinsically political and that fact, along with the politicians' individual agendas, should be acknowledged in policy discussions. For example, PPPs are still seen to be a political risk by many politicians, whose principle objectives include acquiring or retaining power. Quick fixes may be favored to attain popularity rather than making hard decisions for the long-term sustainability of water and sanitation services. Nonetheless, socially sensitive PPPs are more likely to be politically acceptable.

Social Acceptance in Developing Countries

Policy Issue: The Poor are Seldom Mentioned. In many developing countries, private sector involvement in services provision is expected to also fulfill the social role of the public sector. However, where this is the case, it must be negotiated as part of the PPP right from the beginning of the procurement process.

Knowledge and Understanding of Advisers. Terms of Reference mostly appear to be drafted by advisers, who tend to be distant from the sponsor/client's organization. Their expertise will be determined by the requirements specified by the sponsor/client and normally focus on technology and finance. A lack of understanding on the part of those responsible for developing and negotiating the contracts can lead to the omission of important existing informal arrangements among public utility staff, water vendors, and low-income customers. Hence the inclusion of expert staff members that have PPP experience and a workable knowledge of how to improve water and sanitation facilities for low-income (poor) areas and communities is important if PPPs are to become socially sensitive.

The time scale for the sponsor/client's advisers to prepare the necessary bidding information is relatively short, and this inevitably results in workloads being prioritized. Consequently, the complex and little understood issues involved in service provision for the poor are unlikely to receive serious consideration at this stage. The "time factor" may therefore have contributed to the historic underrepresentation of services to low-income communities in many PPP contract documents.

Governance and Relationships with Consumers. Public sector utilities and private companies are experienced in service provision to regular settlements and housing developments occupied by middle and high-income consumers with individual service connections. However, public sector utilities rarely have much experience in dealing with service delivery to the poor, whereas operators from the formal private sector appear to have even less. A key feature of extending coverage to the urban poor therefore involves working out new relationships between a diverse range of actors who have little if any experience of one another.

Direct Links: Partnership does not have to Involve Formal Private Sector. In cases where small local entrepreneurs or civil society groups take on the role of private sector operator, they generally act as an intermediary between the public sector sponsor/client and the consumer. This may, for instance, involve acting as a retailer of water services. In such circumstances, there tends to be more negotiation to address problems and issues at the local level, with local entrepreneurs communicating directly with consumers or their representative groups. Although there is less recourse to legally binding agreements, the key issue remains the same, namely, whether the mechanism works for poor consumers.

User Perceptions

In recent years, consumers have been asked to voice their opinions on the overall process of PPP development involving the formal private sector. Concerns that have

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[2] This section is based on Sohail (5).

emerged include lack of consultation; concern over lack of public control or safeguards; fear of corruption; high tariffs; unemployment; and the assumption that there will be increased burdens on the "common people," who in turn have no clear idea of the benefits.

Involvement in the processes leading up to change is critical. Although this does not guarantee success, case studies have found that projects in which stakeholder participation was absent or minimal were the least successful in terms of feedback from people on low incomes. In such cases, consumers tended to raise objections to the involvement of private companies in their water supply, especially foreign companies. Commonly, such involvement is precipitated by increases in tariffs, which are perceived to be making profits for private companies at the consumer's expense.

Financial Issues and Tariffs

Payment Problems. Some of the problems faced by households include high arrears, high repayment levels, disconnection of the water supply, and inability to pay reconnection charges. The introduction of higher charges through both metering and increased standing charges creates additional pressure on the household budget. Low-income people are clearly under most pressure to economize, and this results in reduced water consumption and less cash being available for other needs.

Technology

Scope for Innovation. Simple yet innovative technology changes may form part of the implementation of PPP arrangements. Such changes are the result of various factors, including:

- Analysis of settlements and their needs
- Taking community needs and preferences into account
- Knowledge of alternative options, relevant technologies, and proven models—for example, simplified, lower cost designs
- Willingness to experiment to find innovative alternatives to standard technological approaches

Levels of Service and Service Differentiation. There are several cases where PPP has led to the introduction of more appropriate and flexible levels of service. This has involved lowering the conventionally accepted, high levels of service that predominate in wealthier areas.

Information

The Need to Communicate Effectively. The introduction of PPPs normally changes existing roles and responsibilities, and these have to be communicated to consumers. If one of the partners (usually the operator) has no working knowledge of the area, then it is crucial for that partner to find out about consumer needs.

Regulation, Monitoring and Complaints

Formal Regulatory Systems. These should be developed during the preoperational phases of PPP contracts, and they are notably absent during the preparation for many PPPs. No provisions are made to check the operation of a monopoly supplier or to impose penalties for substandard performance. In addition, there may be no defined procedures for routine external monitoring of performance. In particular, lack of capacity for monitoring and reporting is a problem for the relatively small municipalities involved in many PPPs.

Effectiveness of Regulation. International PPP experience has shown there to be situations where regulation does not necessarily safeguard the different interests of the various parties to the arrangement. For instance, poor consumers are often dissatisfied with services and tariffs in formally regulated environments; billing and bill collection by the public partner may be inefficient; and the private operator may perceive lack of control over customer management to be a significant risk.

CREATING TRUST

Communication and information alone are not enough. In many PPPs, consumers are unsure of what to expect from privatization because they have not been involved in the development process. If user groups and other stakeholders had been integrated into the process from the start, then there might not be such widespread opposition.

In conclusion, then:

- There is a pressing need to develop a base of information about low-income groups; this can then be used directly in the development of PPP arrangements. Such action requires a clearer understanding of information needs on the part of both the designers of PPPs and the local institutions and organizations.
- There is also a clear need to provide information for consumers, particularly about proposed roles and responsibilities. Lack of understanding and consensus leads to operational problems and is ultimately disempowering.
- Communication is a vital component of PPPs, and investment in this will pay dividends in operational terms. Lack of information could result in low-income communities refusing to accept or comply with the partnership, and this in turn could lead to the risk of nonpayment.

BIBLIOGRAPHY

1. World Health Organization and UNICEF (2004). *Meeting the MDG Drinking Water and Sanitation Target: A Mid-Term Assessment of Progress*. WHO, Geneva.
2. Camdessus, M. and Winpenny, J. (2003). Report of the World Panel on Financing Water Infrastructure: Financing Water For All. World Water Council, 3rd World Water Forum, Global Water Partnership. Ahmed, N. and Sohail, M. (2003). Alternate water supply arrangements in peri-urban localities: Awami (People's) tanks in Organgi Township, Karachi. *Environ. Urbanisation* **15**(2): 33–42.
3. Sohail and Olena (2003).

4. World Bank (2003). *Private Participation in Infrastructure: Trends in Developing Countries in 1990–2001*. World Bank, Washington, DC.
5. Sohail, M. (2003). *Making Partnering Work for All—A Guideline*. Margraf Publishers, Frankfurt, Germany.
6. Blokland, M., Braadbaart, O., and Schwartz, K. (Eds.). (1999). *Private Business, Public Owners: Government Shareholdings in Water Enterprises*. Netherlands Ministry of Housing, Spatial Planning and the Environment and WSCC, the Netherlands.
7. Calaguas (1999).
8. Kempe, A.H. and Schreiber, P. (1997). Rural water services benefit from PPP. *Water Supply* **15**(3): 99–111.
9. Johnstone, N. and Wood, L. (1999). *The Regulation of Private Sector Participation in Urban Water and Sanitation: Realising Social and Environmental Objectives in Developing Countries*. IIED, London.
10. Lewis, M.A. and Miller, T.R. (1987). Public-private partnerships in water supply and sanitation in sub-Saharan Africa. *Health Policy and Planning* **2**(1): 70–79.
11. Nickson, A. (1998). The public-private mix in urban water supply. *Int. Rev. Admin. Sci.* **63**(2): 165–186.
12. Rameama (1997).

READING LIST

Ahmed, N. and Sohail, M. (2000). *Privatisation of KWSB—An Analysis*. City Press, Karachi, Pakistan.

Barlow, M. and Clarke, T. (2002). *Blue Gold: The Fight to Stop the Corporate Theft of the World's Water*. The New Press, Washington, DC.

Becker, M.L. (1993). The international joint commission and public participation—past experiences, present challenges, future tasks. *Natural Resour. J.* **33**(2): 235–274.

Bennett, A. (1998). Sustainable public/private partnerships for public service delivery. *Natural Resour. Forum* **22**(3): 193–199.

Bhattacharyya, A., Parker, E., and Raffiee, K. (1994). An examination of the effect of ownership on the relative efficiency of public and private water utilities. *Land Economics* **70**(2): 197–209.

Bhattacharyya, A., Harris, T.R., Narayanan, R., and Raffiee, K. (1995). Specification and estimation of the effect of ownership on the economic efficiency of the water utilities. *Regional Sci. Urban Economics* **25**(6): 759–784.

Briscoe, J. and Gann, H.A. (1995). Financing water supply and sanitation under Agenda 21. *Natural Resour. Forum* **19**(1): 59–70.

Brook Cowen, P.J. (1999). Lessons from the Guinea Water Lease. World Bank Public Policy for the Private Sector Note 78.

Brook Cowen, P.J. (1997). Getting the private sector involved in water: What to do in the poorest of countries? World Bank Public Policy for the Private Sector Note 102.

Brook Cowen, P.J. (1997). The private sector in water and sanitation—how to get started. World Bank Public Policy for the Private Sector Note 126.

Cain, L.P. (1997). Historical perspective on infrastructure and U.S. economic development. *Regional Sci. Urban Economics* **27**(2): 117–138.

Cashore, B. (2002). Legitimacy and the privatization of environmental governance: How non–state market–driven (NSMD) governance systems gain rule–making authority. *Governance* **15**(4): 503–529.

Cavill, S. and Sohail, M. (2003). Accountability in the provision of urban services. *Proceedings of the Institution of Civil Engineers* **156**(ME4): 235–244.

Cook, P. and Kirkpatrick, C. (1988). Privatisation in less developed countries: An overview. In: *Privatisation in Less Developed Countries*. P. Cook, and C. Kirkpatrick (Eds.). Harvester Wheatsheaf, London.

Correll, D. (1996). Public-private water partnerships benefit all of New Jersey. *Water, Eng. Manage.* **143**(9): 31–32.

Coyaud, D. (1988). Private and public alternatives for providing water supply and sewerage services. INU Discussion Note 31.

Crampes, C. and Estache, A. (1996). Regulating water concessions: Lessons from the Buenos Aires Concession. World Bank Public Policy for the Private Sector Note 91.

Crane, R. (1994). Water markets, market reform and the urban poor: Results from Jakarta. *World Development* **22**(1): 71–83.

Crosslin, R.L. (1991). Decision-support methodology for planning and evaluating PPPs. *J. Urban Planning Develop.* **117**(1): 15–31.

Dellapenna, J. (1994). Why are true water markets rare or why should water be treated as public property? In: *Joint Management of Shared Aquifers: Second Workshop*, M. Haddad and E. Feitelson (Eds.). 27 November–1 December.

Días A. and Ioannou, P.G. (1995). Debt capacity and optimal capital structure for privately financed infrastructure projects. *J. Construction Eng. Manage.* **121**(4): 404–414.

Drakeford, M. (1998). Water regulation and pre-payment meters. *J. Law Soc.* **25**(4): 558–602.

Easter, K.W. and Hearne, R. (1995). Water markets and decentralised water resources management: International problems and opportunities. *Water Resour. Bull.* **31**(1): 9–20.

Farade, T. and Sohail, M. (2003). Making regulatory mechanisms work: Lessons from cases of private sector participation. *Water Policy* **5**(3): 269–288.

Fass, S.M. (1993). Water and poverty: Implications for water planning. *Water Resour. Res.* **29**(7): 1975–1981.

Feigenbaum, S. and Teeples, R. (1983). Public vs. private water delivery: A hedonic cost approach. *Rev. Econ. Stat.* **65**(4): 672–678.

Feldman, R.D. (1993). Power and infrastructure privatization in Mexico. *Strategic Planning for Energy Environ.* **13**(2): 14–16.

Gentry, B. and Abuyuan, A. (2000). Global Trends in Urban Water Supply and Waste Water Financing and Management: Changing Roles for the Public and Private Sectors. Working Paper CCNM/ENV(2000)36/FINAL, OECD, Paris.

Gleick, P., Wolff, G., Chalecki, E.L., and Reyes, R. (2002). *The New Economy of Water: The Risks and Benefits of Globalization and Privatization of Fresh Water*. Pacific Institute, Oakland.

Gray, P. (1997). Colombia's gradualist approach to private participation in infrastructure. World Bank Public Policy for the Private Sector Note 113.

Haarmeyer, D. and Mody, A. (1998). Pooling water projects to move beyond project finance. World Bank Public Policy for the Private Sector Note 152.

Hall, D. (2002). Water in Public Hands. Public Services International Research Unit (Working Paper), Greenwich, UK.

Hall, D., Bayliss, K., and Lobina, E. (2002). Water privatization in Africa. Paper by the Public Services International Research Unit, University of Greenwich for the Municipal Services Project Conference, Johannesburg, South Africa.

Hazin, L.S. (1998). New strategy in urban water management in Mexico: The case of Mexico's Federal District. *Natural Resour. Forum* **22**(3): 185–192.

Hulme, D. and Montgomery, R. (1994). Cooperatives, credit and the poor: Private interest, public choice and collective action in Sri Lanka. *Marga: Quart. J.* **13**(3): 35–55.

Humphrey, C.E. (1990). *Privatization in Bangladesh: Economic Transition in a Poor Country*. Westview Press, Boulder, CO.

Idelovitch, E. and Ringskog, K. (1995). *Private Sector Participation in Water Supply and Sanitation in Latin America*. Directions in Development, World Bank, Washington, DC.

Irwin, T. (1997). Price structures, cross-subsidies, and competition in infrastructure. World Bank Public Policy for the Private Sector Note 107.

Kay, J.A. and Thompson, D.J. (1986). Privatisation: A policy in search of a rationale. *Econ. J.* **96**(3).

Kerf, M. and Smith, W. (1996). Privatizing Africa's infrastructure: Promise and challenge. World Bank Technical Paper 337, Africa Region Series, World Bank, Washington, DC.

Kikeri, S., Nellis, J., and Shirley, M. (1992). *Privatization: The Lessons of Experience*. Country Economics Dept, World Bank, Washington, DC.

Klein, M. (1998). *Bidding for Concessions—The Impact of Contract Design*. World Bank Public Policy for the Private Sector Note no. 158. Available at http://www.ppiaf.org

Krumholz, N. (1999). Equitable approaches to local economic development. *Policy Studies J.* **27**(1): 83–95.

Labonne, B. (1998). Public-private partnerships in natural resources management. *Natural Resources Forum* **22**(2): 75–76.

Lamberton, D.M. (1996). Infrastructure: A nebulous and overworked concept? *Int. J. Technol. Manag.* **12**(5–6): 696–703.

Lane, M. (1999). Trends in international water project procurement. *Proc. British Water Overseas Contracts and Conditions Conference*.

Lee, T. and Jouralev, A. (1992). Self-financing water supply and sanitation services. *CEPAL Rev.* (Santiago de Chile). **48**: 117–128.

Lee, T.R. (1996). Alternatives for private participation in the provision of water services. *Natural Resources Forum* **20**(4): 333–341.

Liddle, B.T. (1997). Privatization decision and civil engineering projects. *J. Manag. Engineer.* **13**(3): 73–78.

Lorrain, D. (1993). Urban services, the market and politics. In: *Private Financing of Public Infrastrucure: The French Experience*. C. Martinand (Ed.). Economica, Paris.

Lyonnaise des Eaux (1990). *Draft Concession Contract for Management, Operation and Maintenance of a Water Supply System*. Southern Africa.

Lyonnaise des Eaux (Coordinator) (1999). *Alternative Solutions for Water Supply and Sanitation in Areas with Limited Financial Resources*, France.

Maldonado, M. (1997). Public water in private hands. *Civil Engineer [New York]* **67**(1): 49–51.

Marvin, S. and Slater, S. (1997). Urban infrastructure: The contemporary conflict between roads and utilities. *Progress in Planning* **48**(4): 247–307.

McCarthy, S. and Tiong, L.K.R. (1991). Financial and contractual aspects of BOT projects. *Int. J. Proj. Manag.* **9**(4): 222–227.

McCoy Thompson, S. (1998). Public-private partnerships: Spreading the three R's. *Natural Resources Forum* **22**(2): 87–94.

Metzger, J.T. (1998). Remaking the growth coalition: The Pittsburgh partnership for neighbourhood development. *Economic Development Quarterly* **12**(1): 12–29.

Mody, A. (1996). Infrastructure delivery: New ideas, big gains, no panaceas. In: *Infrastructure Delivery: Private Initiative and the Public Good*, A. Mody (Ed.). World Bank Economic Development Institute, Washington, DC.

Montgomery, J.D. (1988). The informal service sector as an administrative resource. In: *Urban Services in Developing Countries: Public and Private Roles in Urban Development*, D.A. Rondinelli and G.S. Cheema (Eds.). MacMillan, London.

Montiel, R.P. and Barten, F. (1999). Urban governance and health development in Leon, Nicaragua. *Environ. Urbanizat.* **11**(1): 11–26.

Morris, N.G. and Parry-Jones, S.A. (1999). The affordability of water in an African town. *J. Charter. Inst. Water Environ. Manag.* **13**(1): 1–6.

Nath, S. (1994). Privatisation of urban public services: Cost recovery as a major constraint in India. *Public Enterprise* **14**(3–4): 432–445.

Neto, F. (1998). Water privatization and regulation in England and France: A tale of two models. *Natural Resources Forum* **22**(2): 107–117.

Nicholson, N. (1998). How Hardwired is Human Behavior? *Harvard Bus. Rev.* **76**(4): 135–147.

Padco, Inc. (2002). A Review of Reports by Private-Sector-Participation Skeptics. Discussion Draft prepared for the Municipal Infrastructure Investment Unit, South Africa and USAID.

Palmer, A. (1996). Linking external and internal relationship building in networks of public and private sector organizations: A case study. *Int. J. Public Sector Manag.* **9**(3): 51–60.

Ranasinghe, M. (1998). Thoughts on a method to analyse viability of private sector participation in new infrastructure projects in developing countries. *Impact Assessment and Project Appraisal* **16**(3): 203–213.

Rees, J.A. (1998). Regulation and private participation in the water and sanitation sector. *Natural Resources Forum* **22**(2): 95–105.

Reijniers, J.J.A.M. (1994). Organization of PPP projects: The timely prevention of pitfalls. *Int. J. Proj. Manag.* **12**(3): 137–142.

Rivera, D. (1996). *Private Sector Participation in the Water Supply and Wastewater Sector: Lessons from Six Developing Countries*. World Bank Directions in Development, Washington, DC.

Roger, N. (1999). Recent trends in private participation in infrastructure. World Bank Public Policy for the Private Sector Note no. 196. Available at http://www.ppiaf.org

Rogerson, C.M. (1996). Willingness to pay for water: The international debates. *Water SA* **22**(4): 73–380.

Rogozinski, J. (1999). *High Price for Change: Privatization in Mexico*. Inter American Development Bank.

Rondinelli, D.A. (1988). Increasing the access of the poor to urban services: Problems, policy alternatives and organisational choices. In: *Urban Services in Developing Countries: Public and Private Roles in Urban Development*. D.A. Rondinelli and G.S. Cheema (Eds.). MacMillan, London.

Rosell, E. (1994). The chickens can come home to roost: The anatomy of a local infrastructure crisis. *Urban Affairs Rev.* **30**(2): 298–306.

Roth, G. (1987). *The Private Provision of Public Services in Developing Countries*. Oxford University Press for the World Bank, New York.

Saghir, J., Sherwood, E., and Macoun, A. (1998). Management contracts in water and sanitation—Gaza's experience. World Bank Public Policy for the Private Sector Note no. 177. Available at http://www.ppiaf.org.

Schusterman, R. and Hardoy, A. (1997). Reconstructing social capital in a poor urban settlement: The integral improvement programme in Barrio San Jorge. *Environ. Urbaniz.* **9**(1).

Serageldin, I., Barrett, R., and Martin, J. (Eds.). (1994). The business of sustainable cities: Public-private partnerships for creative technical and institutional solutions: An associated event of the second annual World Bank Conference on Environmentally Sustainable Development. *World Bank Conference on Environmentally Sustainable Development*. World Bank, Washington, DC.

Sohail, M. and Baldwin, A.N. (2001). Partnering with the community—an option for infrastructure procurement. *Proc. Institution of Civil Engineers Municipal Engineer.* **1454**: 293–297.

Sohail, M. and Baldwin, A.N. (2003). Urban infrastructure procurement in low-income countries. *ICE Proc. Institute of Civil Engineers, Municipal Engineer, Engineering Sustainability* **156**(ES2): 0–1.

Sohail, M. and Baldwin, A.N. (2004). Performance indicators for 'micro-projects' in developing countries. *Constr. Manag. Econom.* **22**: 11–23.

Sohail, M. and Cavill, S. (2000). *Public Private Partnerships and Poor, Part B—Interim Findings and Case Studies*. WEDC, Loughborough.

Sohail, M. and Cotton, A.P. (2000). *Public Private Partnerships and Poor Interim Findings, Part A—Summary and Lessons Learned*. WEDC, Loughborough.

Sohail, M. and Aslyukivska, M. (Eds.). (2004). Tools for Pro-poor municipal PPP, United Nations Development programme Margraf Publishers, Frankfurt, Germany.

Solo, T.M. (1999). Small-scale entrepreneurs in the urban water and sanitation market. *Environ. Urbaniz.* **11**(1): 117–131.

Solo, T.M. (2003). *Independent Water Entrepreneurs in Latin America: The Other Private Sector in Water Services*. World Bank, Washington, DC.

United Nations (1992). Earth Summit Agenda 21, Chapter 33 (Finance). United Nations, Washington, DC.

Waddell, S. (2002). Core competences: A key force in business-government-civil society collaborations. *J. Corporate Citizenship* **7**: 43–56.

Webb, M. and Ehrhardt, D. (1998). Improving water services through competition. World Bank Public Policy for the Private Sector Note 164.

World Bank (1997). *Toolkits for Private Participation in Water and Sanitation*. The World Bank, Washington, DC.

World Bank (1997). *Toolkits for Private Sector Privatization in Water and Sanitation*. World Bank, Washington, DC.

World Bank (1998). *Global Development Finance 1998*. World Bank, Washington, DC.

World Bank (2003). Private Participation in Infrastructure data base. Available at http://ppi.worldbank.org/

World Bank (2004). *Global Development Finance 2004*. World Bank, Washington, DC.

Yepes, G. (1999). Do Cross-subsidies help the poor to benefit from water and wastewater subsidies? Lessons from Guayaquil, Ecuador. UNDP-World Bank Water and Sanitation Program.

APPENDIX A: OVERVIEW OF MODELS OF PRIVATE SECTOR PARTICIPATION IN WATER AND SANITATION PROVISION

Full Privatization (Divestiture)

Private company not only takes full responsibility for operation, maintenance, and investment, but ownership of infrastructure is transferred from the public to the private sector at an agreed fee. The government is responsible for regulation.

Partial Private-Sector Responsibilitys

Responsibility for service provision is shared between the private and public sectors, with differing levels of responsibility being delegated to the private partner depending on the contract type.

In all of the following models, ultimate ownership of assets remains with the public sector.

Service Contract

Service contracts are usually short-term agreements whereby specific operations and maintenance activities are contracted to the private sector. The public sector retains overall responsibility for the administration of the service.

Management Contract

A management contract entails private sector responsibility for utility operation and maintenance but without the obligation of investment or commitment of private investment capital.

Lease Contract (Affermage)

Under lease contracts, the private firm operates and maintains the utility at its commercial risk, deriving revenue directly from tariffs, but it does not invest in new infrastructure.

Concession Contract

Under concession contracts, the private company manages the infrastructure facility and operates it at its commercial risk and accepts investment obligations. The role of the government in concession contracts is predominantly regulatory.

Build-Own-[Operate]-[Train]-[Transfer]-Type Contracts (BOO/BOT/BOOT/BOTT)

These are similar to concession contracts, but they are usually used for greenfield projects as the private contractor is also responsible for constructing the infrastructure. At the end of the contract, the assets may either remain with the private company or be transferred back to the government.

Cooperative Model

The cooperative model is a type of government-owned public-limited company (plc) subject to the rules and regulations of other plcs and of which most shares are publicly owned (either by government or citizens/users).

Informal Sector Provision

Provision of water and sanitation services to the poor by "informal" and/or small-scale operators is common in most low- and middle-income countries, especially where the poor lack access to formal service provision. In an increasing number of cases, governments are supporting small-scale private initiatives to increase services provision to the poor.

Sources: Blokland et al. (6), Calaguas (7), Kempe and Schreiber (8), Johnstone and Wood (9), Lewis and Miller (10), Nickson (11), and Ramaema (12).

METHODS OF REDUCING RADON IN DRINKING WATER

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Since the late 1980s, radon has become a highly publicized health threat. This naturally occurring radioactive gas is seeping out of the earth's crust and into the basements of thousands of homes across the nation. Until recently, radon concerns have focused primarily on airborne radon; radon in drinking water was not considered a problem. Now, water tests reveal its presence, and many homeowners are asking water treatment dealers, "How can I reduce radon in my water supply?"

WATERBORNE RADON

Waterborne radon usually originates in deep wells that tap radon-contaminated groundwater. Radon increases household air levels during showering, laundering, and dishwashing. The EPA estimates that 2–5% of airborne radon comes from household water. They further estimate that even these small percentages increase the incidence of cancer. If radon is discovered in water, it is likely that radon is entering the house through the basement as well.

Currently, the EPA has not set official standards for either airborne or waterborne radon. EPA suggests that an airborne level of 4 pCi/L is a point at which remedial action should be taken. Recognize that for every 10,000 pCi/L in water, about 1 pCi/L will be released in the air. The EPA's proposed limit for radon in water is 300 pCi/L.

Detection and Testing

Radon and its daughters are radioactive—continually decaying and emitting radioactive particles called alpha and beta rays. Therefore, testing for radon in water requires special sampling and laboratory analytical techniques that measure its presence before it escapes from the sample. Direct water sampling is by far the most accurate testing method.

Treatment

Radon water treatment should remove radon before it becomes airborne.

Methods of Home Aeration

Home Aeration Units. Home aeration exposes the water to enough air so that radon can escape to the air before the water reaches the taps. Using new technological advancements in home aeration, these units can have radon removal efficiencies up to 99.9%. They are also ideal for high waterborne radon levels.

Spray Aeration Unit. A spray aeration unit, as shown in Fig. 1, sprays radon contaminated water into the tank using a spray nozzle. The increased surface area of the sprayed water droplets causes the radon to come out of solution, and the air blower carries the radon contaminated air to a vent outside the home. About 50% of the radon will be removed in the initial spraying. The water must be sprayed several times to increase removal efficiencies. To keep a supply of treated water, at least a 100-gallon holding tank must be used.

Packed Column Aeration Unit. In a packed column system, water moves through a thin film of inert packing material in a column. The air blower forces radon contaminated air back through the column to an outdoor vent. If the column is high enough, removal efficiencies can be between 90 to 95%. For a 6-foot column (shown in Fig. 2), the removal efficiency is around 95%. Packed columns become impractical if the radon level exceeds 20,000 pCi/L.

Shallow Aeration Unit. A final aeration system uses a shallow tray to contact air and water. Water is sprayed into the tray and then flows over the tray as air is sprayed up through tiny holes in the tray bottom (see Fig. 3). The system removes more than 99.9% of the radon and vents

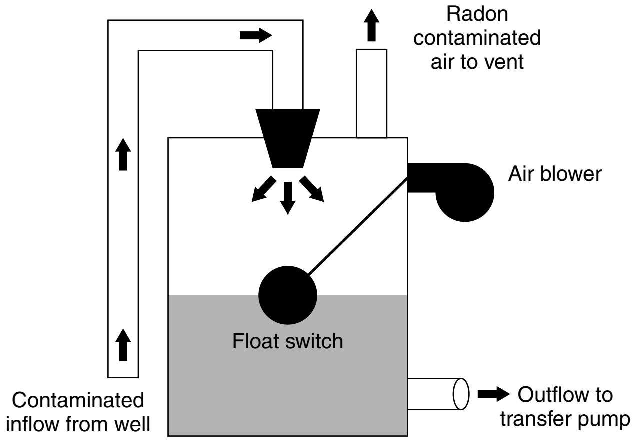

Figure 1. Radon removal using a home spray aeration system.

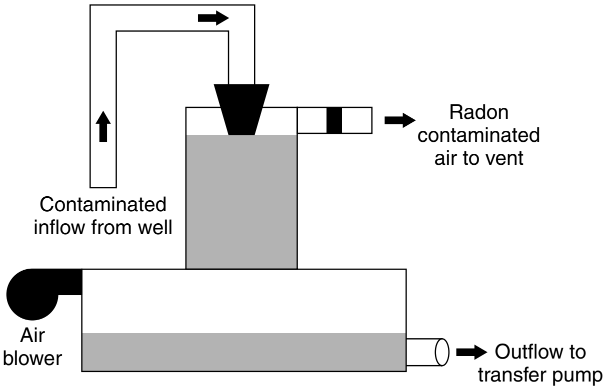

Figure 2. Radon removal using a packed column.

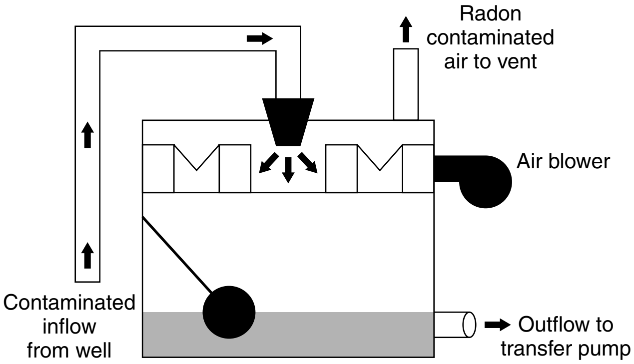

Figure 3. Radon removal by horizontally extended shallow aeration.

it outside the home. The treated water collects in the tank bottom and is pumped to the water pressure tank.

Advantages of this type of aeration include:

- Low pressure air blower
- No fouling problems in tray holes
- Small unit size

However, this unit uses 100 cubic feet per minute of air compared to the others, which can depressurize the basement.

Point-of-Entry Treatment

Another method for removing radon from water is a granular activated carbon (GAC) unit. Figure 4 shows a typical GAC unit.

For radon removal, GACs are constructed of a fiberglass tank containing granular activated carbon—a fine material that traps and holds the radon. Because of the carbon's fine particle size, it easily clogs with sediments or other contaminants in the water.

Important points to consider with GAC units are:

- Some GAC units come with a special backwashing feature for removing sediment, which eventually reduces the effectiveness of the carbon to remove radon.

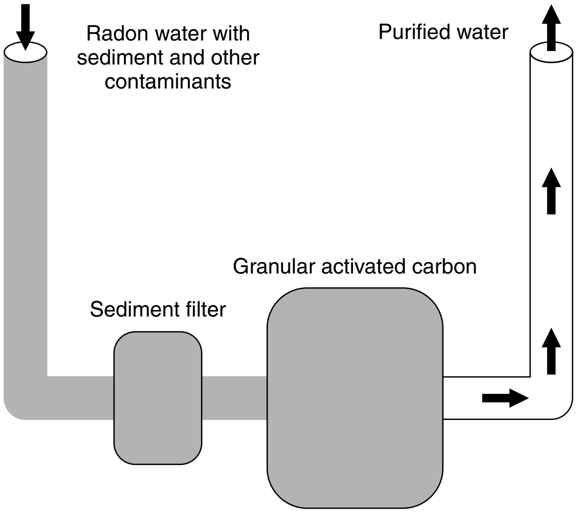

Figure 4. Treatment by activated carbon.

- Elimination of the sediment source or a sediment filter placed ahead of the GAC tank is the best protection against clogging.
- The maximum radon level at which a GAC unit operates effectively is uncertain. Some estimates show that it should not be used if waterborne radon levels exceed 30,000 pCi/L. Other experts say 5,000 pCi/L.
- It is important that the filter size matches the water use and conditions. According to the EPA, a 3-cubic-foot unit can handle as much as 250 gallons of water per day and effectively reduce radon levels. Typical water use in a home ranges from 50 to 100 gallons per person per day.
- GAC filter will remove radon indefinitely providing that sediments or organic pollutants have not clogged the filter.
- A major drawback to using a GAC filter is that if radon is present, the filter becomes radioactive as it picks up the gas. Lead-210 (a radon daughter) builds up on the carbon filter and then gives off its harmful radioactive rays, as it continues to decay.
- A GAC filter may produce a radiation problem when the device is used to remove other contaminants. For example, a GAC unit is installed to remove a pesticide without testing the water for radon. The GAC unit sits under the sink harmlessly removing the problem contaminant. Right? Wrong. Unfortunately, what the homeowner doesn't know is that the water supply has very high radon levels. So, while the GAC traps the pesticide, it also traps radon, thus producing a radioactive filter and a radiation hazard.
- Proper maintenance and handling of the GAC unit can minimize exposure risks. Redevelopment of the well intake or a sediment filter is vital to protecting the fine carbon from fouling and clogging; protected filters won't need to be changed as often. The water should also be periodically retested to insure that radon is still being removed.

WATER REUSE

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Water reuse is the general term applied to the act of recovering water from a process and reusing it in the same process, or another one, before discharging it. Some experts attach labels to this activity based on the specific use of the water: *Recycle* involves redirecting the recovered water back to the same process. *Reuse* means reusing the recovered water in a different application. *Recovery* generally refers to the technologies used to accomplish this.

Black water is defined as the effluent from toilets and garbage disposers in residences. *Gray water* in the residential environment typically refers to the effluent from bathing, showering, laundry, and dishwashing and other effluents from normal household activities. *Gray water* is distinguished from black water in that it contains much less organic loading and is expected to contain much less fecal coliform bacteria and other pathogenic organisms.

We all are familiar with the admonitions addressing the finite quality of water on this planet: the fact that only 1% is considered “fresh” (nonseawater), but is used for virtually all human activities and, as a result, is rapidly deteriorating in quality. The mindset is there, as are the technologies. The barrier is the commitment to make the economic investment.

From a technical standpoint, there are virtually no barriers to the quality improvement of either black water or gray water, even to the point of drinking water quality! Today it is possible to install a “black box” on the sewer line from residences and drink the treated water coming from it. Presently, the deterrents to this are economics and the “yuck” factor.

Drinking water regulations continue to place new standards for water quality, and industrial and commercial activities are requiring higher quality water in many applications. Due to population growth, water quantity requirements are also steadily increasing. For example, today it is estimated that one-fifth of the world’s population does not have access to safe drinking water; by 2025, the global population is expected to be 8.3 billion people (up from about 6.4 billion in 2004), and the usage of industrial water is expected to double by then. Interestingly, even in cities experiencing severe drinking water shortages, there always seems to be enough water to flush toilets.

Industries, in general, are very poor stewards of water conservation. Most water brought into the plant is used only once, even though that use may have had very little impact on water quality. In most of the industrialized world, we have labored under the misconception that our water supply was inexhaustible as well as inexpensive. This cost aspect has been exacerbated by the fact that, in many areas, the price of water has been partially subsidized by local government.

Undoubtedly, a paradigm shift is taking place with regard to water conservation and reuse. The barriers to reuse activity are

1. the “yuck” factor
2. lack of practical reuse technologies
3. economic factors
4. commitment to reuse

1. The average consumer recoils at the thought of drinking (or even reusing) “sewer water,” not considering the fact that the drinking water for one community is very likely the wastewater discharged from another community on the same river or lake. It is estimated that in major U.S. rivers, water is reused as many as 20 times by the time that river empties into the sea. Most “groundwater recharge” is treated municipal wastewater injected into groundwater supplies to provide sufficient storage capacity or to serve as a barrier to salt water intrusion from the oceans.
2. The key to water reuse is to have an arsenal of technologies available to remove hazardous or undesirable contaminants efficiently from the water supply. There is no single technology that efficiently removes all classes of contaminants; however, for the past century or so, there have been significant developments in treatment technologies that effectively reduce the concentration of virtually any contaminant to acceptable levels for any water use.

   There is little argument that reducing the huge variety of contaminants that may be encountered in typical wastewater, resulting from the combination of sewage, industrial wastewaters, and perhaps even effluent from surface water runoff, requires a stunning array of advanced technologies. The linchpins are the membrane separation technologies of reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. Whereas reverse osmosis has been around for more than 50 years, the others, most notably nanofiltration, are relatively new developments.

   By separating the treatment process into its key components, pretreatment, primary treatment, and posttreatment, it is now possible to create optimum technology trains that can purify the stream from virtually any source and condition it for virtually any reuse.
3. In addition to treatment technology costs, it is also necessary to factor in the fact that raw water costs are steadily increasing and will continue to do so, reflecting the diminishing supply and costs of meeting new regulations.
4. It is estimated that as of the year 2000, there were more than 10,000 water reuse systems installed in the United States, almost all of this recovered water was used to irrigate agricultural fields or residential and commercial landscaping. In California alone, it is estimated that 120 billion gallons per year are reused.

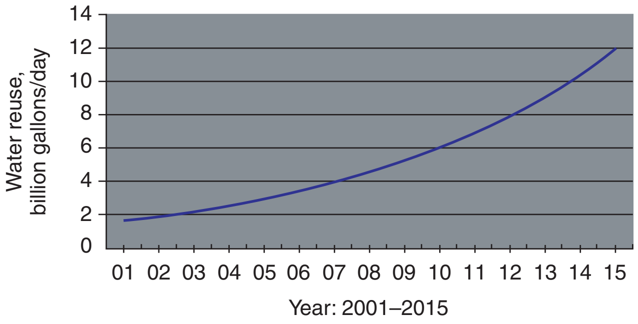

Figure 1. Projected water reuse in 21st century.

The rate of water reuse in the United States is expected to increase markedly over the next decade, as indicated by Fig. 1.

SPECIFIC TECHNOLOGIES

To understand the technologies most applicable to water reuse, it is necessary to understand the contaminants prevalent in water supplies. Contaminants can be categorized by their physical and chemical properties. Table 1 provides this classification.

Suspended Solids

Removing suspended solids from water supplies is probably the oldest water treatment procedure. Throughout history, humankind has used everything from containers of sand to cloth to charcoal to “clarify” water to make it look and taste better. The chronology of water treatment technology development also underscores the improvements to suspended solids removal processes; the latest is microfiltration.

Dissolved Organics

Removing dissolved organic contaminants requires the greatest variety of technologies, reflecting the diversity of dissolved organic chemicals. For most of these contaminants, there are several choices of technologies to effect removal. Some may involve adding chemicals, such as alum, powdered activated carbon, or an acid; other technologies may include physical separation as with a coalescer or ultrafiltration technology.

Dissolved Ionics (salts)

These are contaminants that have ionic charges and are almost all inorganic chemicals. The somewhat limited choice of removal technologies consists of membrane technologies of reverse osmosis, nanofiltration, and electrodialysis; adsorptive resin technology known as ion exchange and the hybrid of electrodialysis and ion exchange known as electrodeionization. Distillation is the oldest technology, mirroring the natural water cycle, but, because of its high energy cost, is now used only in specialized applications.

Table 1. Chemical Properties of Contaminants

Class	Typical Example
Suspended solids	Dirt, clay, colloidal materials
Dissolved organics	Trihalomethanes, synthetic organic chemicals, humic acids, fulvic acids
Dissolved ionics (salts)	Heavy metals, silica, arsenic, nitrate
Microorganisms	Bacteria, viruses, protozoan cysts, fungi, algae
Gases	Hydrogen sulfide, methane, radon

Microorganisms

Microorganism contaminants in most water supplies are from one or more of the following categories:

bacteria
viruses
protozoan cysts
fungi
algae

There are a number of disinfection technologies that inactivate or remove microorganisms. These include chemical (chlorine compounds and ozone). Certain heavy metals in solution inactivate microorganisms. The most common of these are silver for bacteria reduction and copper for algae inactivation. The most prevalent nonchemical technology is ultraviolet irradiation, although heat is still used occasionally in specialized applications, such as preparation of “water for injection” in the pharmaceutical industry. Many disinfectants are effective on only certain classes or types of microorganisms or under very specific conditions.

The most troublesome class of microorganisms is bacteria. Because bacteria are viable and grow under virtually any condition, they are impossible to eliminate completely. In most applications, the goal is to minimize bacterial growth so as not to interfere with the water use.

CONCLUSION

Water reuse is not an abstract concept; it is both a reality and a necessity. For the reasons cited, the requirements and opportunities for water reuse will continue to grow at an increasingly rapid rate.

ROOF DRAINAGE HYDRAULICS

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INTRODUCTION

Over the past decade, urban drainage systems have moved toward what are now commonly known as “sustainable urban drainage systems” (SUDS) or “best management practice” (BMPs). Fundamental to the implementation of these systems is addressing both runoff quantity and quality at a local level in a manner which may also have the potential to offer benefits to stakeholders. This has led to a change in the way new developments now look and interact within catchments. However, despite the availability of such tools to reduce, attenuate, and treat urban runoff, substantial areas of the urban environment are still 100% impermeable and drain rapidly, namely, roof surfaces. Normally, roof drainage systems do not always receive the attention they deserve in design, construction, and maintenance. Although the cost of a system is usually only a small proportion of a building's total cost, it can be far outweighed by the costs of the damage and disruption resulting from a failure of the system to provide the degree of protection required.

There are basically two different types of roof drainage system; conventional and siphonic (refer to Fig. 1). Conventional systems operate at atmospheric pressure, and the driving head is thus limited to the gutter flow depths. Consequently, conventional roof drainage systems normally require a considerable number of relatively large diameter vertical downpipes, all of which have to connect to some form of underground collection network before discharging to a surface drain. In contrast, siphonic roof drainage systems are designed to run full bore, resulting in subatmospheric pressures, higher driving heads, and higher flow velocities. Turbulent gutter conditions mean that there will always be a small percentage of entrained air within the system (typically 5%). Hence, siphonic systems normally require far fewer downpipes, and the depressurized conditions also mean that much of the collection pipework can be routed at high level, thus reducing the extent of any underground pipework.

Both types of drainage system comprise three basic interacting components:

- the roof surface
- the rainwater collection gutters (including outlets)
- the system pipework

Each of these components can alter the runoff hydrograph substantially as it is routed through the system. This text focuses on the role and performance of each of these components. As the principles of siphonic drainage are generally less well understood and certainly less well documented, particular emphasis placed on the performance of siphonic roof drainage systems.

ROOF SURFACE

The design of the roof surface is usually within the remit of the architect rather than the drainage designer. Notionally, there are three types of roof surfaces:

Flat Roofs

Flat roofs are normally associated with domestic properties in climates with low rainfall and with industrial buildings in developed countries. Such roofs are seldom truly "flat" but simply fall below the minimum gradient associated with sloped roofs in the jurisdiction under consideration; for example, in the United Kingdom, a flat roof is one whose gradient is less than 10° (1). Minimum gradients are usually specified to avoid any unwanted ponding (BS EN 6229:2003 specifies a 1 in 80 minimum gradient) and to help prevent the development of any adverse gradient due to differential settlement (2).

Although flat roofs can be problematic if not maintained properly, they are often preferred; they reduce the amount of dead space within the building and they attenuate flows more than sloped surfaces.

Sloped Roofs

Most residential and many commercial properties have sloped roofs. Such roofs are generally favored because their ability to drain naturally means that there is less risk of leakage. In temperate climates, their specification also means that snow loading is less of an issue. Once a rainfall is underway, the rate at which the runoff flows across a roof is a function of roof slope and roughness. Where rainfall data are available, runoff rates from roof surfaces may be readily assessed using kinematic wave theory (3).

Green/Brown Roofs (Sloped or Flat)

The oldest type of permanent roof is a green roof. These involve planting roof areas to attenuate and/or dissipate rainfall and can take the form of a rooftop garden with trees and shrubs (termed intensive) or a lightweight carpet of growth media and flora (termed extensive). The latter technology is already employed widely (e.g., the Rolls Royce plant at Goodwood; purportedly Europe's largest green roof). Many of these applications tend to focus on the aesthetic benefits such systems offer to high profile developments and are often installed to "green"

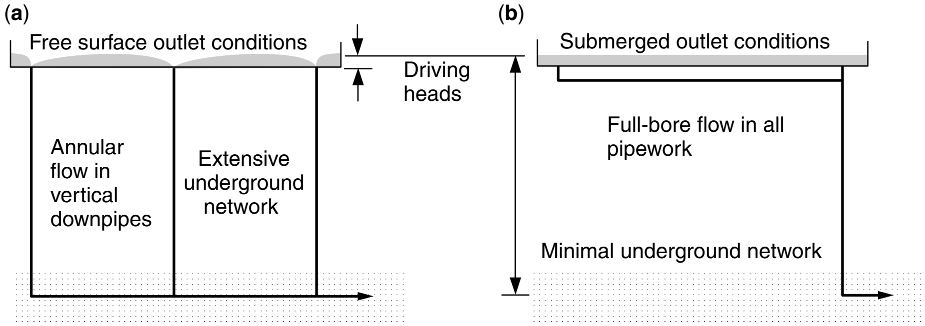

Figure 1. Schematics of a typical conventional (**a**) and (**b**) siphonic roof drainage system (at normal design condition).

a development and thus help secure planning consent in sensitive areas (4). However, as well as being aesthetically pleasing and hydraulically beneficial, green roofs may also offer thermal insulation (5), reduce the heat island effect, the phenomenon whereby absorption of solar radiation by urban surfaces causes a marked increase in ambient air temperature (6), provide acoustic damping, and extend the service life of the roof membrane (7–10).

Green roof systems are used extensively in Germany and to a lesser extent in North America, but again their specification is primarily due to a desire for a reduced aesthetic impact associated with a particular development. Germany probably has the most experience to date, a direct result of their use in the 1800s as a low fire risk alternative to tarred roofs in deprived urban areas (11). Currently, German research is focused predominantly on planting issues, and there is only a limited understanding of how the systems may be used to mitigate the impact of urban runoff. One research project, which ran from 1987–1989 in Neubrandenburg (8), found that an installed green roof with 70 mm of substrate could reduce annual runoff from a roof by 60–80%. Work in Vancouver (Canada), based on an uncalibrated computer model, suggests that for catchments where the roof area comprises 70% of the total surface, installing an extensive system could reduce total runoff to approximately 60% over 12 months (12). The same model was also used to assess specific synthetic rainfall; these results indicated that the catchment experienced increased runoff during longer rainfalls.

Neither of these studies detail how green roofs could be expected to perform during a particular rainfall or where efficiencies may be gained in the design of collection pipework. Limited testing in the United States (13), where green roofs are often irrigated, has indicated that runoff can be reduced by 65% during a single rain. The most authoritative design guidance for green roofs in the United States is produced by The New Jersey Department of Environmental Protection (14). This is focused on lightweight structures and gives guidance on how to ensure “rapid draining” where the rainfall return period exceeds 2 years.

Rainfall return periods are normally set within the context of failure probability and consequence. Conventional systems are usually designed assuming 100% runoff for a 2-minute storm; the 2-minute duration is selected because it is the typical time of concentration for conventional systems. Although advice is given in codes for setting higher runoff rates, there is little guidance on setting runoff rates below 100%. These observations mean that inadequacies are encountered if conventional codes are used to design green roofs:

- Runoff *coefficients* should be expected to be below that used for conventional roofs; 100% is used by BS EN 12056-3:2000 and 98.7% was recorded by Pratt and Parkar (15).
- Peak runoff *rates* are reduced; even where there is no infiltration, the surface roughness has a significant impact.
- Time of concentration is expected to be greater than 2 minutes; particularly relevant when designing collection pipework for large roof areas for public sector, commercial, and industrial properties.
- As with other elements of urban drainage design, it is not efficient for a complex system such as a green roof to be matched to a single rainfall. It is probable that the duration of runoff hydrographs will be orders of magnitude longer compared with conventional systems, and runoff interactions between independent rainfalls are probable; this may make a time-series approach more appropriate.

RAINWATER COLLECTION GUTTERS

The basic requirement for rainwater collection gutters is that they have sufficient flow capacity to accommodate flows from the design storm (16). Although it is common practice to install gutters at a slight gradient to prevent ponding, the nature of the construction industry and the process of settlement means that it is normal to assume that gutters laid at slack gradients are actually flat; for example, BS EN 12056-3:2000 stipulates that gutters at gradients less than 0.3% shall be treated as flat (17). In a level gutter, the water surface profile will slope toward the outlet, and it is the difference in hydrostatic pressure along the gutter that gives the incoming water the required momentum to flow toward the outlet (18).

Gutter Outlet Depths

Key to ensuring whether or not collection gutters have sufficient capacity are the conditions that occur at the gutter outlets. As well as affecting the flow rates entering the drainage system pipework, the outlet depths also affect upstream gutter depths (via the backwater surface profile). Hence, although the depth at a gutter outlet may not cause any particular problems, the greater depths at the upstream end of the gutter may result in overtopping.

Extensive experimental studies in the 1980s determined that the flow conditions in the vicinity of a gutter outlet in a conventional roof drainage system could be categorized as either “weir” type or “orifice” type, depending on the depth of water relative to the size of the outlet (19). At depths below that equivalent to half of the outlet diameter, the flow conditions are “weir” type, and outlet conditions are calculated using an appropriate sharp-edged weir equation (18). At higher flow depths, the flow effectively “chokes,” and the flow regime changes to “orifice” type; the outlet conditions are calculated by an appropriate sharp-edged orifice equation (18). Although conventional roof drainage systems are usually designed to ensure free discharge at gutter outlets, design restrictions may mean that the outlets cannot discharge freely; in such circumstances, additional gutter capacity (storage) is normally required to accommodate the resulting higher flow depths.

In siphonic roof drainage systems, the outlets are designed to become submerged to allow full-bore flow to develop and be sustained; if this is the case, the determination of outlet depth is complicated as the gutter conditions depend on downstream conditions (within the connected pipework) as well as gutter inflows. Recent experimental work has also indicated that conventional roof drainage systems incorporating "nonstandard" gutter sections, whose base width and height are significantly greater than the diameter of the outlet, can result in the development of full-bore flow in the vertical downpipe and siphonic action (20); for a given gutter section, the onset and extent of such conditions depend on the diameter of the downpipe. Similar phenomena have also been observed in "standard" gutter sections (semicircular and elliptical); in these cases, limited siphonic action occurs for only a short distance below the outlet (18).

Flow Division within Gutters

In terms of flow division between multiple outlets in a gutter under free discharge, it can be seen from Fig. 2a that the flow splits evenly in any given gutter section (between two outlets or between an end wall and an outlet), whether or not the gutter inflow is uniform or nonuniform. Figure 2b, c indicates the effect of outlet placement within a gutter; evenly spaced outlets require far less gutter capacity than those placed at gutter extremities.

Where outlets are not freely discharging, the flow division between multiple outlets in a gutter may not be as described, as the individual gutter sections may "hydraulically merge" to form one continuous channel and/or downstream system conditions may become significant. For example, the pipework in a siphonic system runs full bore when operating at or near its design point, and the flow division between outlets depends on the relative losses for each branch of the system.

Backwater Profiles

The water surface profile in gutters can only be assessed realistically by applying the momentum equation for channels with lateral input. In many cases, the low velocities associated with gutter flows mean that gutter friction losses are minor and may be ignored (18). If a gutter outlet allows free discharge and frictional effects are neglected, the backwater profile may be determined by applying Equation 1 to determine the horizontal distance (ΔL) between any given upstream depth (h_1) and downstream depth (h_2).

$$\Delta L = \int_{h_1}^{h_2} \left[\frac{\left(1 - \dfrac{Q^2 T}{gA^3}\right)}{\left(S_o - \dfrac{Q^2}{A^2 m C^2}\right)} \right] dh \qquad (1)$$

where Q = flow rate (m^3/s)
T = surface width (m)
g = gravitational constant (m/s^2)
A = flow area (m^2)
S_o = bed slope (-)
m = hydraulic mean depth (m)
C = Chézy coefficient (-)

This equation can be modified if frictional effects are significant (very long gutter lengths or very high flow velocities) or if the gutter outlet is not freely discharging.

Current Design Methods

The foregoing discussion has highlighted the key elements that should be considered when designing a rainwater gutter. However, without recourse to some form of numerical modeling, it is not feasible to calculate backwater surface profiles, and hence gutter capacities, for roof drainage systems; this is particularly the case for large commercial or manufacturing developments which may incorporate many kilometers of different types of guttering. Consequently, current gutter design methods for gutters installed in conventional drainage systems are based primarily on empirical relationships (19) and the assumption of free discharge at the outlet. For example, BS EN 12056-3:2000 specifies that the design capacity of a "short," level, semicircular gutter located on the eaves of

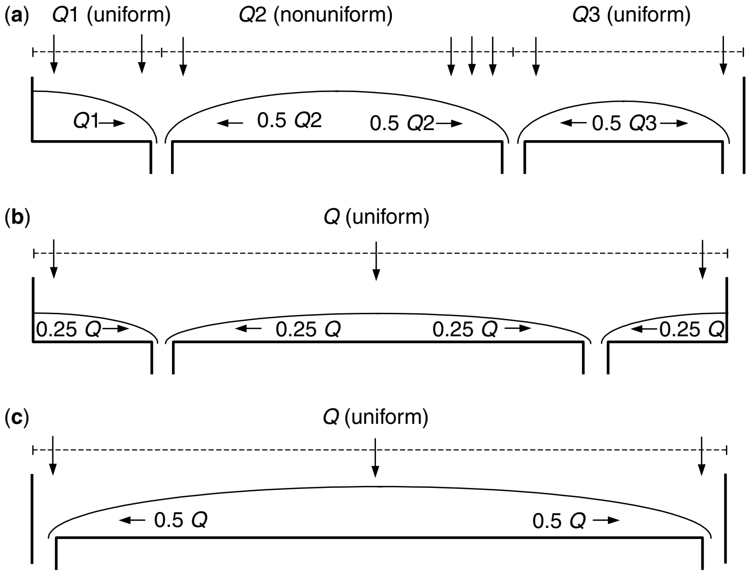

Figure 2. Effect of outlet positioning on flow division in gutters. (**a**) Flow division between multiple outlets in a gutter. (**b**) Flow division between evenly spaced outlets in a gutter. (**c**) Flow division between outlets positioned at gutter extremities.

a building (with outlets capable of allowing free discharge) is given by (17)

$$Q_{\mathrm{L}} = 0.9 \times Q_{\mathrm{N}} = 0.9 \times 2.78 \times 10^{5} \times A_{\mathrm{E}}^{1.25} \qquad (2)$$

where Q_{N} = notional gutter design capacity (L/s)
A_{E} = gutter cross-sectional area (mm^2)

Clearly not all gutters can be designed by application of Equation 2. For example, BS EN 12056-3:2000 (17) contains clauses to account for many eventualities, including

- location of gutter on building that may result in varying consequences of failure; eaves gutter, valley gutter, parapet gutter
- differently shaped gutter sections
- "hydraulically long" gutters (where frictional effects may be significant)
- gutters laid at a significant gradient
- changes in gutter alignment (bends, offsets, etc.)
- additional system elements, such as strainers or rainwater hoppers
- restricted flow at outlets
- gutters installed in siphonic roof drainage systems

In addition to the type of clauses listed above, BS EN 12056-3:2000 also allows designers to use data obtained from experimental testing of a particular arrangement (17).

Numerical Models

Numerical models have been developed that can accurately simulate the flow conditions in any type of gutter as a result of either steady or unsteady roof runoff. An example of this is incorporated into the "ROOFNET" model recently developed as part of an academic research project dealing with the effect of climate change on urban drainage (20). This model enables the user to specify data describing the relevant aspects of a particular installation, including details of the prevailing rainfall conditions, details of the roof surfaces to be drained, and details of the actual gutters. A kinematic wave model is then used to route the rainfall over the roof surfaces and into the gutters. A method of characteristics solution of the fundamental equations of one-dimensional flow in open channels is then used to route the runoff along the gutters to the outlets (21), at which point the flow enters the drainage pipework. The model automatically determines the flow conditions at the gutter outlets and, in addition to dealing with free discharge, can also simulate the effect of restricted flow and submerged outlet scenarios. Output includes depths, velocities, and flow rates along the gutter, as well as the location and severity of any gutter overtopping.

At present, models such as those described before are research tools; they are normally developed and used by universities for specific research projects. However, it is envisaged that such models may soon be used as diagnostic design aids, particularly for national code development.

SYSTEM PIPEWORK

The type and extent of pipework incorporated into a roof drainage system depends primarily on whether the system is conventional or siphonic.

Conventional Rainwater Systems

In conventional roof drainage systems, the aboveground pipework generally consists of vertical downpipes, connecting the gutter outlets to some form of underground drainage network, and offset pipes, used where the gutter overhang is significant. Note that an offset pipe is defined as a pipe with an angle less than 10° to the horizontal. The capacity of the system as a whole usually depends on the capacity of the gutter outlets rather than the capacity of the vertical downpipes.

The flow within vertical downpipes is normally free surface; BS EN 12056-3:2000 (17) specifies that downpipes run no more than 33% full; this effectively installs redundant capacity within the system. If the downpipes are sufficiently long (normally greater than 5 meters), annular flow may occur. Similarly, the flow within offset pipes will also normally be free surface; BS EN 12056-3:2000 (17) specifies that offsets run no more than 70% full, indicating the need to install all offsets at a gradient. The design of the pipework can either be undertaken using the design tables in BS EN 12056-3:2000 or by applying the Wyly–Eaton equation for vertical downpipes (22) and the Colebrook–White equation for offset pipes (23).

Siphonic Roof Drainage Systems

In contrast to conventional systems, siphonic installations depend on purging air from the system (priming) and subsequently establishing full-bore flow within the pipework connecting the outlets in the roof gutters to the downstream surface water sewer network (at ground level).

Current design practice assumes that, for a specified design storm, a siphonic system fills and primes rapidly with 100% water (24). This assumption allows siphonic systems to be designed using steady-state hydraulic theory. The steady flow energy equation is normally employed (25), and the elevation difference between the gutter outlets and the point of discharge is equated to the head losses in the system. Although this approach neglects the small quantities of entrained air that always enter a siphonic roof drainage system, it reportedly yields operational characteristics similar to those observed in laboratory test rigs in the fully primed state (25,26).

However, steady-state design methods are not applicable when a siphonic system is exposed to rainfall below the design criteria or with time-varying rainfall intensity. In the former case, the flow may contain substantial quantities of entrained air and exhibit pulsing or cyclical phases, a result of greatly varying gutter water levels and an indication of truly unsteady, transient flow. Such problems are exacerbated when the system incorporates more than one outlet connected to a single downpipe (multi-outlet system), as the breaking of full-bore conditions at one of the outlets (due to low gutter depths and air entry) is transmitted throughout the system and, irrespective of the gutter depths above the remaining outlet(s), results in cessation of fully siphonic conditions. As subdesign events are the norm, it is clear that current design methods may not be suitable for assessing the day-to-day performance characteristics of siphonic roof drainage systems. This is a major disadvantage, as it is during these events that the majority of operational problems tend to occur, for example, noise and vibration.

Despite any defects that current design methods may have, thousands of systems have been installed worldwide with very few reported failures. Where failures have occurred, they have invariably been the result of one or more of the following:

1. a lack of understanding of operational characteristics
2. poor material specification
3. installation defects
4. a poor maintenance program

In response to these perceived shortcomings, a series of research projects has recently been undertaken to augment the understanding of siphonic roof drainage systems and to develop numerical models for use as diagnostic design aids (27). The remainder of this section will present a selection of the salient points arising from this work.

In contrast to the assumption made in current design methods, the priming of a typical siphonic system actually found was as follows (refer to Fig. 3):

1. Flow conditions throughout the system are initially free surface (Phase 1).
2. Full-bore flow forms at some point within the horizontal pipework (Phase 1).
3. Full-bore flow conditions propagate downstream toward the vertical downpipe and upstream toward the gutter outlets (Phase 1).
4. Full-bore flow conditions reach the vertical downpipe, the downpipe starts to fill, and the system starts to depressurize (Phase 2).
5. Once the conditions throughout the downpipe are full bore, any remaining air pockets are purged from the system (Phase 2).
6. Full siphonic action occurs (Phase 3) and continues until the gutter depth(s) falls below the level at which air can enter the system.

The data shown in Fig. 4a illustrate the type of unsteady flow conditions that occur when a siphonic system is exposed to rainfall below the design point and the gutter flow depths are insufficient to sustain full siphonic action. The data shown in Fig. 4b illustrate the type of unsteady flow conditions that occur when an installed siphonic system is exposed to a “real” rainfall and the rainfall intensity varies with time.

Figure 5 shows an example of the output from one of the numerical models that has recently been developed (SIPHONET). As can be seen, the model can accurately simulate the priming of a siphonic system (0–32 s) as well as steady siphonic conditions (32–62 s). These data also illustrate that the model can simulate complex operating conditions, such as the rise in system pressure when the depth in gutter 1 drops below that necessary for full-bore flow, hence allowing air to enter the system and break the siphon (at approximately 62 s).

CONCLUSION

The text has illustrated how roof drainage systems are a key, but often overlooked, element of urban drainage infrastructure. It has also been shown that their design is a complex process, which relies heavily on gutter outlet performance. The following conclusions may be drawn with respect to the operation of roof drainage systems:

1. Their operation depends on three interacting components: the roof surface, the collection gutter, and the collection pipework.
2. Green or brown roofs provide an opportunity to reduce the flow from roof surfaces, improve urban aesthetics, and increase biodiversity.
3. Outlet conditions are key to understanding how a system performs.

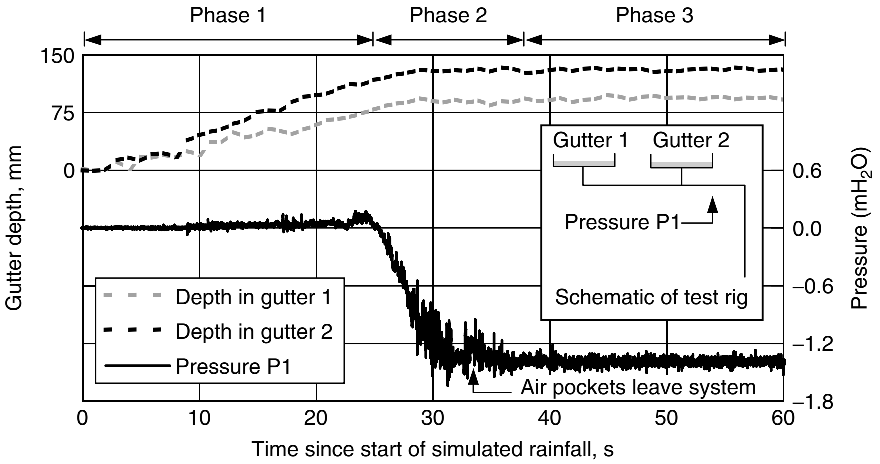

Figure 3. Priming of a laboratory siphonic drainage test rig (28).

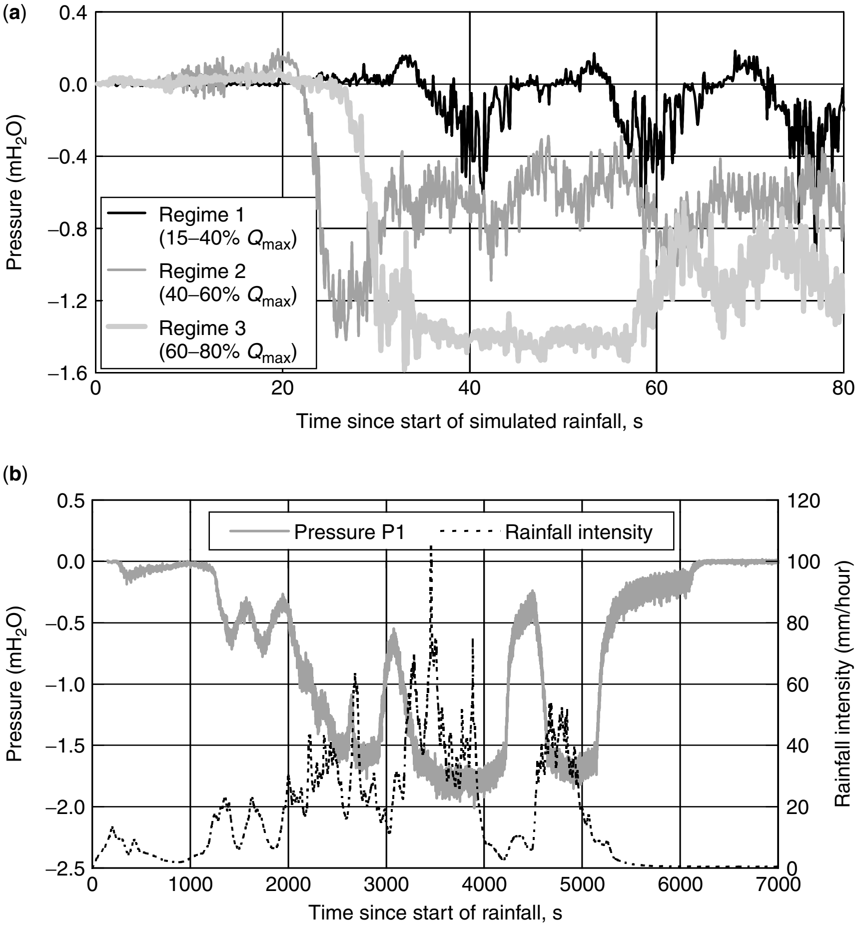

Figure 4. (**a**) Measured system pressures for subdesign rainfall within a laboratory siphonic drainage test rig (28). Note that data refer to the pressure P1, as indicated in Fig. 3. (**b**) Subdesign rainfall within an installed siphonic drainage system (28).

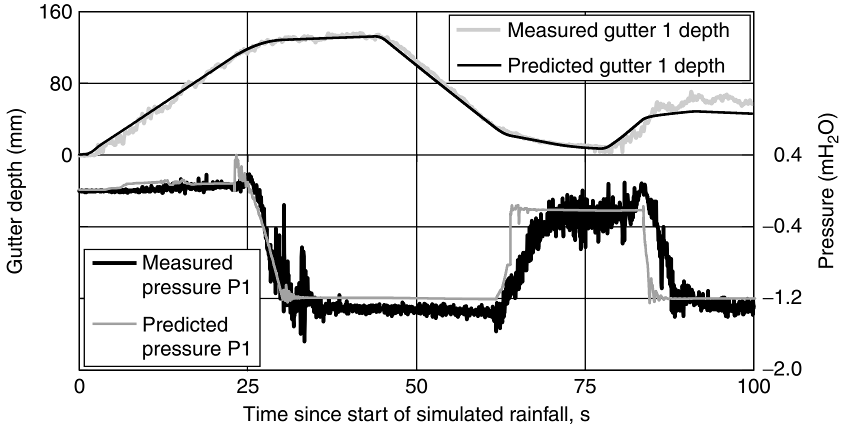

Figure 5. Measured and predicted system conditions within a laboratory siphonic drainage test rig: no inflow into gutter 1 between 62 and 82 s (28). Note that data refer to the system shown in Fig. 3.

4. Siphonic roof drainage systems present a more efficient way to drain large roof surfaces.
5. The design of siphonic roof drainage systems should consider subdesign rainfall and operational problems, such as blocked outlets.

THE FUTURE

Although green roofs are an attractive alternative, it is probable that conventional roof surfaces will continue to dominate domestic installations. However, it is likely that green roofs will experience a step-change in acceptance by the commercial sector once more becomes known about their performance and sustainability. Similarly, the efficiencies offered by siphonic systems means that they will continue to play a significant role in draining large commercial buildings, particularly if numerical models are applied diagnostically to improve performance and reduce costly system failures.

The biggest threat to roof drainage comes from climate change. Existing systems may not simply become more prone to flooding; changes in rainfall patterns may result in long periods of low precipitation, and self-cleansing velocities may be attained less frequently as a result. Furthermore, changes in wind patterns may also increase levels of rooftop debris and hence necessitate enhanced maintenance programs. As concern regarding climate change grows and the sustainability agenda widens, it is possible that harvesting roof runoff may become more widespread. At present, water consumption varies globally between 7 and 300 liters/household/day (L/h/d). In the United Kingdom, average consumption is 145 L/h/d, but only 1–2 liters may actually be consumed by humans, 30% may be used for WC flushing (29). Studies have shown that, when coupled with storage, roof rainwater harvesting has the potential to contribute substantially to domestic water usage in both developing and developed countries (30,31).

BIBLIOGRAPHY

1. BS EN 6229:2003. (2003). *Flat Roofs with Continuously Supported Coverings*, Code of practice, British Standards Publishing Limited (BSPL).
2. Simmons, T. (1994). Methods for designing proper roof drainage. *Prof. Roofing* 22–25.
3. Singh, V.P. (1996). *Kinematic Wave Modeling in Water Resources: Surface Water Hydrology*. John Wiley & Sons, New York.
4. Tarr, A.R. (2003). Green roof implementation: construction and contractor issues in the UK. *Green Roofs for Healthy Cities*. University of Sheffield.
5. Köhler, M. (2004). The multi-beneficiary system of green roofs: The green roof challenge to biophilic architecture and ecology. *Proc. Sheffield Conf. "Nature Enhanced"*.
6. Rosenfeld, A.H. et al. (1995). Mitigation of urban heat islands: materials, utility programs, updates. *Energy Build.* **22**(3): 255–265.
7. Hendricks, N.A. (1994). Designing green roof systems: A growing interest. *Prof. Roofing* 20–24.
8. Köhler, M., Schmidt, M., Paiva, V.L.A., and Taveres, S. (2002). Green roofs in temperate climates and in hot-humid tropics—far beyond aesthetics. *Environ. Manage. Health* **13**(4): 382–391.
9. Niachou A. et al. (2001) Analysis of the green roof thermal properties and investigation of its energy performance. *Energy Build.* **33**(7): 719–729.
10. Onmura, S., Matsumoto, M., and Hokoi, S., (2001), Study on evaporative cooling effect of roof lawn gardens. *Energy Build.* **33**: 653–666.
11. Köhler, M. (2004). Green roof technology—From a fire-protection system to a central instrument in sustainable urban design. *Second Green Roof Conf.*, Portland, Oregon.
12. GVRD. (2002). *Effectiveness of Stormwater Source Control*. Greater Vancouver Regional Sewerage and Drainage District.
13. PSU (2001). Online Research http://www.rps.psu.edu/0105/-roofs.html.
14. NJDEP (2000). *Standard for Rooftop Runoff Management*.
15. Pratt, C.J. and Parkar, M.A. (1987). Rainfall loss estimation on experimental surfaces. *Proc. Fourth Int. Conf. Urban Storm Drainage*, International Association of Hydraulic Runoff Research, Lausanne, Switzerland.
16. Beij, H. (1934). *Flow in Roof Gutters*. US Department of Commerce, Bureau of Standards: Research Paper RP644, Bureau of Standards Journal of Research, Vol 12.
17. BS EN 12056-3:2000. (2000). *GravitY Drainage Systems Inside Buildings*. Roof drainage, layout and calculation, British Standards Publishing Limited (BSPL).
18. May, R.W.P. (1995). *Design of conventional and siphonic roof drainage systems*, Public Health Services in Buildings—Water Supply, Quality and Drainage, IWEM Conference, London.
19. May, R.W.P. (1984). *Hydraulic Design of Roof Gutters*. Proceedings of the Institution of Civil Engineers, Part 2, Vol. 77.
20. Blanksby, J., Ashley, R., Saul, A.J., Cashman, A., Packman, J., Maksimovic, C., Jack, L., Wright, G., and Kay, D. (2004). Adaptable urban drainage (AUDACIOUS), *NOVATECH 2004: 5th Int. Conf. sustainable Tech. Strategies Urban Water Manage*.
21. Escarameia, M. and Swaffield, J.A. (1999). Prototype monitoring and numerical simulation of roof drainage gutter systems. *Proc. 8th Int. Conf. Urban Storm Drainage*, Sydney, Australia.
22. Wyly, R.S. and Eaton, H.N. (1952). *Capacities of Plumbing Stacks in Buildings,* National Bureau of Standards Building Materials and Structures, Report BMS 132.
23. Chadwick, A. and Morfett, J. (2004). *Hydraulics in Civil and Environmental Engineering*, 4th Edn. Spon Press.
24. Arthur, S. and Swaffield, J.A. (2001). Siphonic roof drainage: The state of the art. *Urban Water* **3**(1): 43–52.
25. May, R.W.P. and Escarameia, M. (1996). *Performance of siphonic drainage systems for roof gutters*. Report No SR 463. HR Wallingford.
26. Arthur, S. and Swaffield, J.A. (2001). Siphonic roof drainage system analysis utilising unsteady flow theory. *Build. Environ.* **36**(8): 939–948.
27. Wright, G.B., Swaffield, J.A., and Arthur, S. (2002). Investigation into the performance characteristics of multi-outlet siphonic rainwater systems. *Build. Serv. Eng. Res. Technol.* **23**(3): 127–141.
28. Swaffield, J.A., Wright, G.B., Jack, L.B., and Arthur, S. (2004). Pressure transient analysis to inform system design for building and roof drainage systems. *Proc. The Practical Application of Surge Analysis For Design And Operation, 9th Int. Conf.*
29. Butler, D. and Davies, J. (2004). *Urban Drainage*, 2nd Edn. Spon Press.
30. Thomas, T. (1998). Domestic water supply using rainwater harvesting. *Build. Res. Inf.* **26**(2): 94–101.
31. Fewkes, A. (2000). Modelling the performance of rainwater collection systems: towards a generalised approach. *Urban Water*, **1**(4): 323–333.

SEPTIC TANK SYSTEMS

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According to Wilson and Moore (1), a septic tank is an "underground vessel for treating wastewater from a single dwelling or building by a combination of settling and anaerobic digestion. Effluent is usually disposed of by leaching. Settled solids are pumped out periodically and hauled to a treatment facility for disposal." When properly

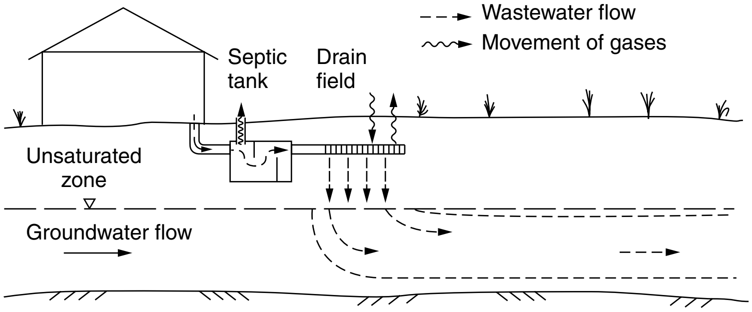

Figure 1. Components of septic tank systems (4).

sited, constructed, and maintained, septic systems can provide a low-cost environmentally responsible method of waste disposal. Improperly sited, constructed, operated, or maintained septic systems can, however, lead to water quality degradation and threats to public health. The basic components of a septic tank system are shown in Figs. 1 and 2. The septic tank is an enclosed receptacle designed to collect wastewater, segregate floatable solids, accumulate, consolidate, and store solids; wastewater treatment is provided by septic tank systems. The tank is the most important component used in these systems (2). The waste enters the tank near the top. There is a pair of baffles in the tank to keep the solids in the tank, preventing them from flowing out of the tank with liquids. Bacteria in the tank break down the solids as much as they can into a liquid form and this with the water leaves the tank on the other side of the baffles. The liquid then flows to a leaching field where the liquid enters the soil and is absorbed. If the bacteria cannot break the solids down, they will build up over time. If these solids are not removed by periodic pumping, the tank will allow solids to be washed out to the leaching field and begin to clog the soil. When the soil is clogged, the system stops working.

Septic systems fail for the following reasons:

1. Faulty design (leaching field that is too small).
2. Faulty installation (plugged lines or uneven grades).
3. Soil conditions (highly permeable soil or relatively impervious soil, less than 6 feet of unsaturated soil cover).
4. High water table less than 6 feet from the land surface.
5. Water overload.
6. Inadequate cleaning of the tank (should be pumped every 2–3 years).
7. Highly permeable soil.

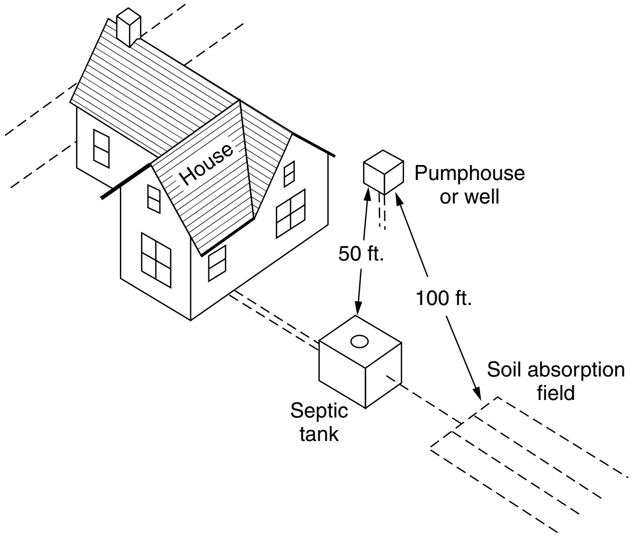

Figure 2. Setback distances (4).

It has been estimated that 25% of the U.S. population uses septic systems for treatment and disposal of their household sewage. Septic system technology is undergoing dramatic changes in efficiency and reduced contamination (2). The American Society of Testing and Material has prepared three standards for the treatment and disposal of on-site waste (D 5879-95, D 5921-96, D5925-96).

Bacterial and viral contamination from septic systems is the most common cause of drinking water contamination in the United States. The liquid effluent from septic systems follows the same path as precipitation moving into an unsaturated zone and aquifer. When the effluent reaches the water table, it moves downgradient to the point of discharge (lake, stream, wetland, and well). The location of the septic system in relation to the slope of the land surface is important because septic tank discharge follows the slope of the land surface. Wells downslope from septic tanks are subject to contamination (3).

The septic tank effluent can contain bacteria and also toxic materials and other contaminants. Some of the contaminants adhere to the soil and aquifer material or travel with the water.

Many septic systems are found in small rural homes sites and are commonly located on small narrow lots along a feeder highway. An increasing number of states are zoning suburban areas to limit the density of houses using septic tanks (4). Community sewer systems are used in some areas to substitute for septic systems.

Some banks require the prospective seller of rural property to provide proof of a bacteria-free water supply. Some sellers chlorinate the water to destroy the bacteria in the well. The bacterial contamination is in the aquifer, so this treatment lasts only a short time (5). The homeowner should have the well water analyzed at least once year for bacteria.

A buyer of rural property should determine the location of the well and the septic system. The buyer should also determine the age, maintenance, distance to the drinking water supply well, and depth to water at the septic system site. A wet area, lush vegetation over the leaching field, or odor of sewage is cause for further investigation. A water sample from the well at a septic system site should be obtained and analyzed for fecal coliform bacteria.

BIBLIOGRAPHY

1. Wilson, W. and Moore, J.E. (1998). *Glossary of Hydrology*. American Geological Institute, Denver, CO.
2. Bedinger, M.S. Fleming, J.S., and Johnson, A.I. (Eds.). (1997). *Site Characterization and Design of On-Site Septic Systems*. ASTM, Philadelphia, PA.
3. Waller, R.W. (1959). *Ground Water and the Rural Homeowner*. U.S. Geological Survey, General Interest Publication, Washington, DC.
4. Wyoming Department of Environmental Regulations (DER). (1998). *Septic Systems: Rural Wellhead Protection Fact Sheet*. Cheyenne, WY.
5. Covin, C. (1999). *Handbook of Groundwater Quality Protection for Farmers*. CSIR, South Africa.

DOMESTIC SOLAR WATER HEATERS

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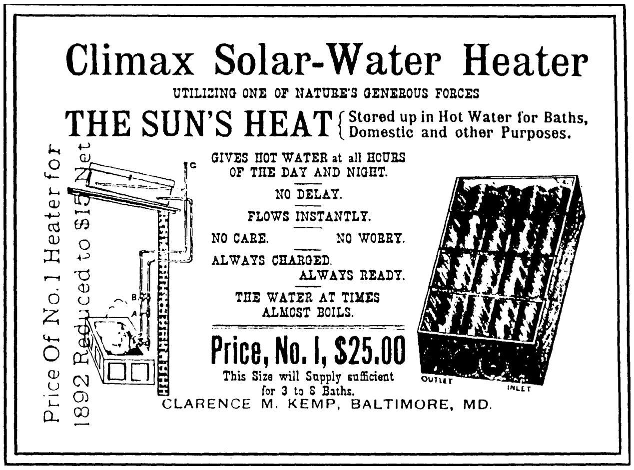
INTRODUCTION

Solar water heating systems convert solar radiation into useable thermal energy in the form of hot water. Domestic solar water heaters can provide households with a large proportion of their hot water needs while reducing the amount of conventional fuel used and hence reducing home energy costs. The amount of hot water produced will depend on the type and size of the system, the climate, and location for solar access. Over the years, a variety of system designs have been developed and tested to meet specific consumer needs and environmental conditions. The following article is a brief description of the many types of system in common use today.

The first solar water heaters consisted of exposed tanks of water left out to warm in the sun. Used on a few farms and ranches in the Southwestern United States in the late 1800s, they were reportedly capable of producing water hot enough for showering by the late afternoon on clear days (1). The first solar water heater, manufactured commercially under the trade name Climax Solar-Water Heater, was patented in 1891 (2). Figure 1 illustrates a reproduction of an advertisement for the Climax Solar-Water Heater. This water heater could be used from April to October in the State of Maryland in the eastern United States. It claimed to produce water hotter than 38 °C on sunny days even during early spring and in late autumn when daytime temperatures sometimes approached freezing.



Climax Solar-Water Heater

UTILIZING ONE OF NATURE'S GENEROUS FORCES

THE SUN'S HEAT { Stored up in Hot Water for Baths, Domestic and other Purposes.

GIVES HOT WATER at all HOURS OF THE DAY AND NIGHT.

NO DELAY.

FLOWS INSTANTLY.

NO CARE. NO WORRY.

ALWAYS CHARGED.
ALWAYS READY.

THE WATER AT TIMES ALMOST BOILS.

Price, No. 1, $25.00

This Size will Supply sufficient for 3 to 8 Baths.

CLARENCE M. KEMP, BALTIMORE, MD.

Price Of No.1 Heater for
1892 Reduced to $15 Net

Figure 1. Advertisement for the climax solar-water heater, 1892 (1).

Domestic solar water heaters can be categorized as being either active or passive and can be further grouped according to the configuration of the main solar water heating components: integral or distributed. Integrated systems combine the collector and storage functions in a single unit, whereas distributed systems have a separate solar collector and hot water store connected by a piping network. Distributed systems can be either active or passive. In active systems, a pump circulates the transfer fluid between the collector and the store. Integrated systems are almost always passive as they do not require external power.

THE INTEGRATED COLLECTOR/STORAGE SOLAR WATER HEATER

The most basic of solar water heaters is the integrated collector/storage solar water heating (ICSSWH) system or the integral passive solar water heater (IPSWH), commonly referred to as breadbox or batch water heaters. Kemp's early Climax Solar-Water Heater was an integrated system. A simplified diagram of a typical ICS solar water heating installation is shown in Fig. 2.

In its simplest form, the ICSSWH is a water tank painted black to absorb insolation (*in*cident *sol*ar radi*ation*). Variations consist of one or more tanks, painted black or coated with a selective absorbing surface, within a well-insulated box, possibly with reflectors and covered with single, double, or even triple layers of glass, plastic, or a combination of the two. Because of its simplicity, an integrated collector/storage system is easier to construct and install, which reduces maintenance and capital costs. In most climates, the large thermal mass of the store provides inherent resistance to freezing. However, the integrated unit has a significant problem because of its unique mode of operation.

The earliest systems suffered substantially from heat losses to ambient, especially at night and at noncollection periods, which meant no matter how effective the unit was in collecting solar energy, unless the hot water was fully withdrawn at the end of the collection period, losses

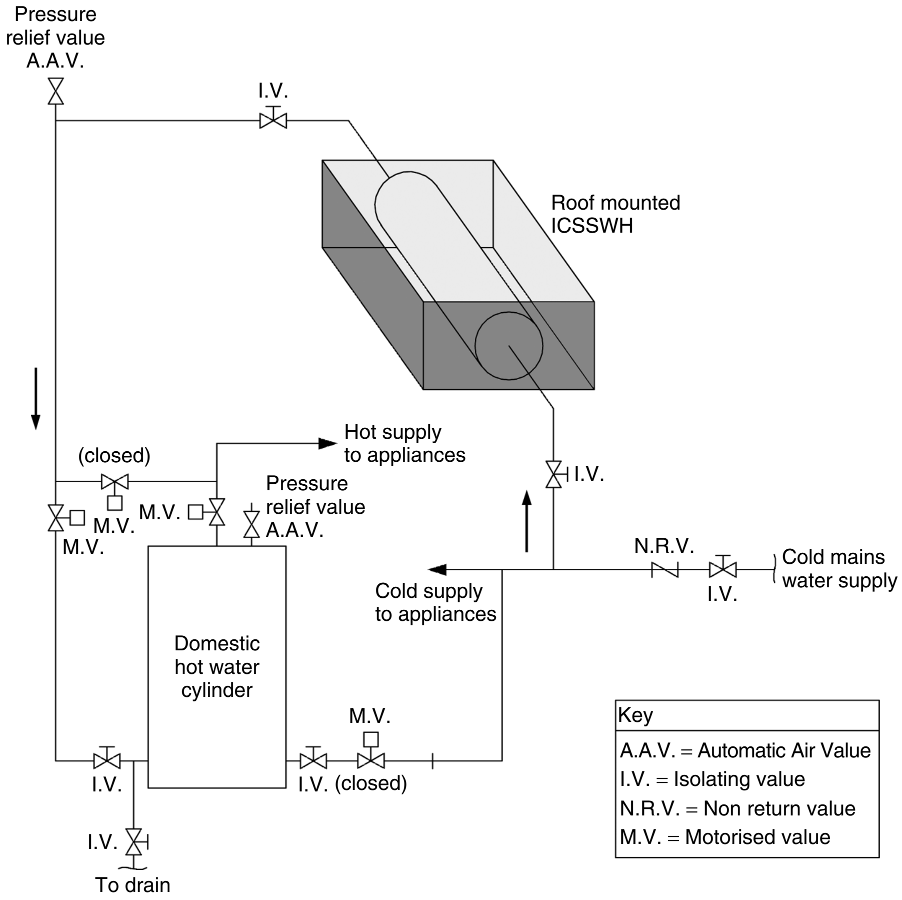


Figure 2. A simplified diagram of a typical roof-mounted ICS solar water heating installation.

to ambient led to only lukewarm water being available early the next day. This process reduced the overall solar fraction, which renders it less viable economically. Indeed this deficiency in the late nineteenth century led to the prominence of thermosyphon solar water heaters with diurnal heat storage to the detriment of the ICSSWH system. To overcome excessive heat loss and be in a position to compete with the more established distributed solar water heater systems, the ICSSWH design has had to evolve and incorporate new and novel methods of improving performance.

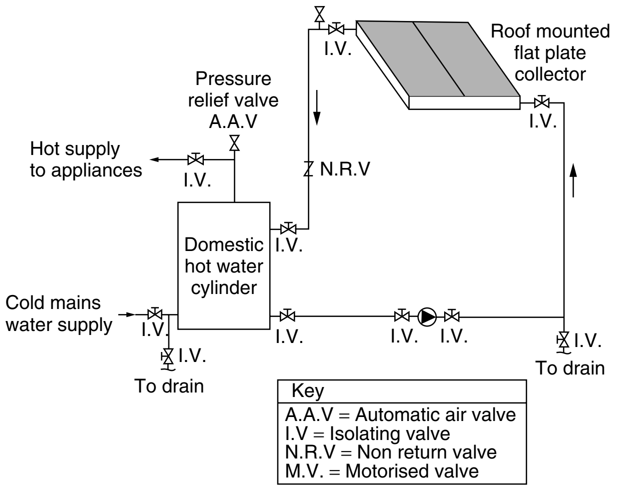


Figure 3. A simplified diagram of a typical roof-mounted distributed (flat-plate) solar water heating installation.

DISTRIBUTED SOLAR WATER HEATERS

Distributed systems consist of a separate solar collector and water store, with pipes connecting the collector(s) to and from store(s). As previously mentioned, these systems can be either active or passive, with the active system using an electric pump, and the passive system relying on buoyancy forces in the form of thermosiphonic action. Active systems also require more valves and control systems, which tend to make them more expensive than passive systems but generally more efficient. Figure 3 shows a simplified diagram of a typical roof-mounted distributed (flat-plate) solar water heating installation. Active systems are often easier to retrofit than are passive systems because their storage vessels do not need to be installed above or close to the collectors. In addition, a photovoltaic panel could power the pump, which results in stand-alone, proportional pump operation with reduced running costs.

Distributed solar water heaters can also be characterized as being direct (open loop) or indirect (closed loop). A direct system circulates incoming mains water through the collector and into the tank, whereas an indirect system transfers collected thermal energy via a heat exchanger to the domestic water. Indirect systems usually contain an aqueous antifreeze solution that flows through the heat exchanger immersed in the hot water store to provide protection from freezing. This process, however, results in reduced collection efficiencies over the direct system through lower specific heat capacities and losses during the heat exchange process.

Active Direct Systems

Active direct systems use pumps to circulate incoming mains water through the collector and back into the tank. This design is efficient and reduces operating costs but is not appropriate where water is hard or acidic because of scale buildup and corrosion. However, direct active systems are popular in regions that do not experience freezing temperatures (Fig. 4).

Active Indirect Systems

Active indirect systems pump the heat-transfer fluid (usually a glycol-water antifreeze mixture) through the collector and a heat exchanger transfers the heat from the fluid to the water that is stored in the tank. Heat exchangers can be double-walled vessels or have twin coil arrangements. Indirect glycol systems are popular in areas where temperatures regularly fall below zero because they offer good protection from freezing. However, antifreeze systems are more expensive to purchase and install and require regular checking and maintenance.

Indirect drainback systems do not use antifreeze mixtures, but they use pumped water as the heat-transfer fluid in the collector loop. When freezing conditions prevail or the system is not in use, the pump is switched off and the water in the collector is drained out, thus providing protection from freezing. The collector installation and plumbing arrangement must be carefully positioned to allow complete drainage and the pump must have sufficient head pressure to pump the water up to the collector each time the pump starts.

Thermosiphon Systems

A thermosiphon system relies on warm water rising, a phenomenon known as natural convection or buoyancy forces, to circulate water to and from the collector and tank. In this type of installation, the tank must be located above the collector. As water in the collector heats, it becomes less dense and naturally rises into the tank above. Meanwhile, cooler water in the tank flows downward into the collector, thus causing circulation throughout the system. Some forms of thermosiphon solar water heaters can be described as being compact. Compact systems are close-coupled thermosyphon flat-plate or evacuated-tube collector units fabricated and installed as a single item as opposed to a separate collector, store, and pipework. Thermosiphon systems are much cheaper than are active systems as no pump or controller is required and are ideal where a low-cost solar heater is required such as holiday houses and cabins, or countries where low-cost solar heating is required.

SOLAR WATER HEATING COLLECTORS

Basically three types of domestic solar collector are in common use today: flat-plate, evacuated-tube, and concentrating.

Flat-plate Solar Collector

The flat-plate system consists of a “flat” absorber panel through which water or conducting fluid passes. The panel may be of formed channels in a sandwich format or may be pipes connected to expanded absorber plates. Most

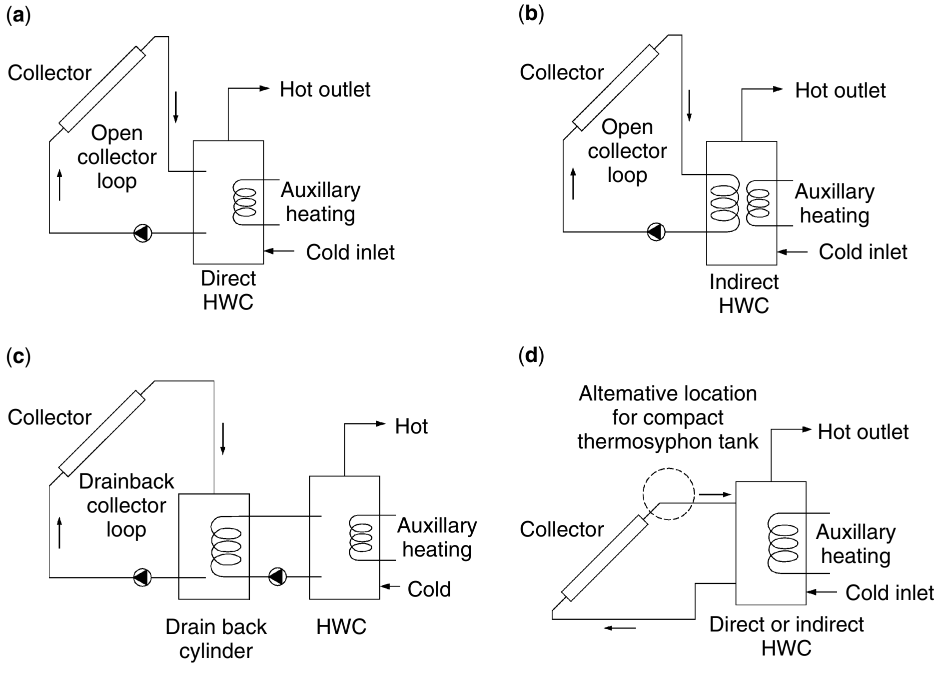


Figure 4. Schematic detail of common distributed solar water heating configurations: (**a**) active direct system, (**b**) active indirect system, (**c**) indirect drainback system, and (**d**) thermosiphon system.

absorbers are covered with a selective coating to improve solar radiation absorption and reduce long-wave radiative heat loss. As the fluid flows adjacent to the heated surface, it is heated. The absorber is mounted in an insulated, weatherproof unit, and the exposed collector aperture is covered with one or more transparent or translucent covers. The make-up of a typical flat-plate solar collector is shown in Fig. 5.

Evacuated-tube Collector

Evacuated-tube collectors are made up of rows of parallel, glass tubes, linked to a common flow (and return) manifold depending on the collector installed. Two types of evacuated-tube collector exist: glass/glass or metal/glass. The glass/glass collector consists of two concentric glass tubes. The inner tube is covered with a selective coating to improve solar radiation absorption and reduce long-wave radiative heat loss. The transparent outer tube forms a space between the two tubes that is evacuated to eliminate conductive and convective heat loss. The metal/glass collector consists of a copper plate attached to a heat pipe or water pipe mounted within a single evacuated glass tube. Again the absorber is coated with a selective coating to improve the collection performance. Figures 6 and 7 illustrate some common evacuated-tube collectors.

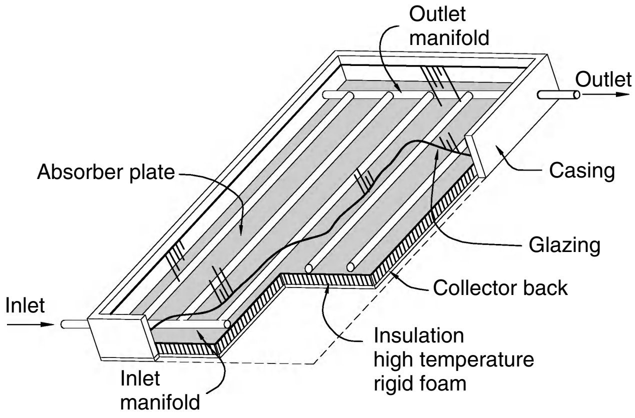


Figure 5. A typical flat-plate solar collector.

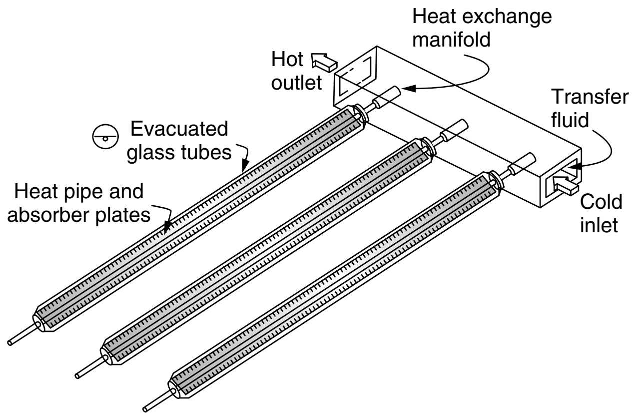


Figure 6. Metal/glass heat pipe evacuated-tube solar collector.

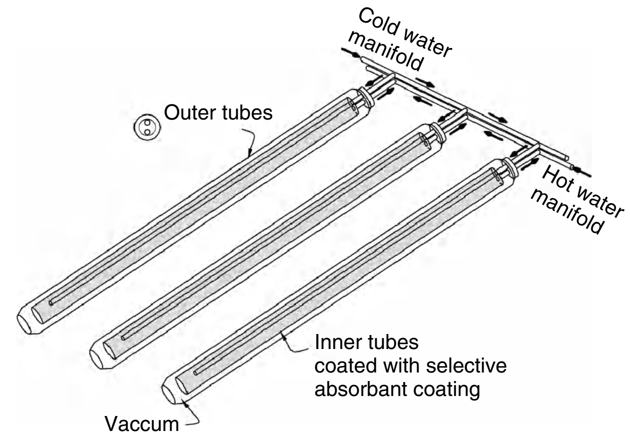


Figure 7. Metal/glass water pipe evacuated-tube solar collector.

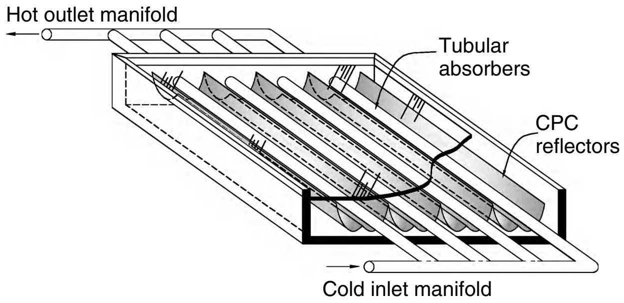


Figure 8. Diagram of a compound parabolic concentrating collector.

Concentrating collector

To increase the insolation on the absorber surface over that incident at the collector aperture, reflectors are employed in solar water heating systems. Concentrating reflectors can obtain higher temperatures on the absorbing surface than can those achievable by a flat absorber, and as the absorbing surface area is reduced relative to that of the aperture, a reduction in the overall heat loss from the system occurs, hence an improved thermal efficiency.

Internal reflectors are contained within the unit enclosure, whereas external reflectors are located outside the sealed casing. Reflecting concentrator designs for low-to-medium concentrations can be flat or curved, line-axis or line-focus (circular, parabolic or compound parabolic) reflectors, symmetrical or asymmetrical. The concentrating collector used for domestic applications usually incorporates a concentrating reflector in the form of parabolic trough or compound parabolic concentrating (CPC) collector, using highly reflective surfaces to concentrate the insolation onto the absorber. Most absorbers are tubular, although not exclusively. Figure 8 illustrates a CPC collector.

BIBLIOGRAPHY

1. Butti, K. and Perlin, J., (1981). *A Golden Thread*. Marion Boyars Publishers Ltd, London, UK.
2. Kemp, C.M. (1991). U.S. Patent 451384, April 28.

READING LIST

Duffie, J.A. and Beckman, W.A. (1991). *Solar Engineering of Thermal Processes*. John Wiley & Sons, New York.

Norton, B. (1992). *Solar Energy Thermal Technology*. Springer-Verlag London Ltd, London, UK.

HOUSEHOLD DRINKING WATER TREATMENT AND SAFE STORAGE

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Household water treatment is the decentralized treatment of drinking water in the home and safe storage is the protection of drinking water in specially designated household storage vessels prior to use. A safe water storage vessel is typically comprised of a container with a narrow mouth to prevent contact with potentially dipped cups or dirty hands, a lid, a spigot to access water and a flat base for easy water extraction. In many cultures and regions, household drinking water treatment and storage has been women's work based on traditional practices stretching back for millennia. For example, an ancient Indian medical text, the *Susruta Samhita*, compiled over several centuries and reaching its present form in about A.D. 300, includes the prescribed water treatment and handling practices as follows:

> Heat contaminated water by boiling on fire, heating in the sun, by dipping hot copper into it seven times, cooling in an earthen vessel and also scenting it with flowers of nagkesara, campaka, utpala, patala, etc. (Book 1, Chapter 45, Verse 12)

Moreover, home storage in various types of containers, including skin bags, ostrich eggs, vessels of wood, ceramic, metal, glass, or stone has been a traditional practice for hundreds or even thousands of years. Thus the twin concepts of household drinking water treatment and safe storage are not new. But there are new developments arising from a global need (Figs. 1–3).

Currently, about 50% of people worldwide are supplied with household connections that provide drinking water on tap in their homes. Sufficient, safe, acceptable, physically accessible, and affordable water for all is a fundamental human right essential to life and dignity. Tapped water for all is the long-term goal, but even among those with tap water today, the drinking water is not always considered safe, in terms of its water quality. In homes with a tapped water supply, household treatment devices typically provide a final "extra" step that begins with a well-protected source and includes a treatment process provided by a centralized water treatment system, administered by a municipal authority or private entity. In these cases, the purpose of the household treatment step is typically to improve the aesthetics of the water (e.g., chlorine odor or taste, hardness) and/or to remove certain harmful contaminants, including possible organic (e.g., benzene, toluene), inorganic (e.g., cadmium, lead), or microbiological (e.g., *Cryptosporidium, Giardia*) substances. These household drinking water

Figure 1. Ceramic filter—Nepal.

Figure 2. Ceramic candle filter by Katadyne, Switzerland.

Figure 3. Ceramic filter "filtron"—Ghana.

treatment devices take two forms—*point-of-entry* or *point-of-use*—depending on whether the device is installed at the point where the water main enters the home or whether the treatment unit is attached to or placed beside the kitchen faucet (i.e., at the point where drinking water is withdrawn). In such cases, household drinking water treatment in industrialized countries and regions is used to provide an additional barrier of safety to a water supply that has already received treatment upstream or is of known high quality.

Homes lacking a tapped drinking water supply via a household connection or lacking another form of "improved" water supply such as a public standpipe, a borehole, a protected dug well, a protected spring, or rainwater collection are more likely to bear the burden of water-related illnesses:

- 3.4 million deaths are water-related;
- 1.4 million children die annually of diarrhea, making this the third highest cause of illness and the sixth highest cause of mortality globally;
- 1.5–2 billion people are affected by intestinal parasites;
- 1.1 billion people lack access to safe drinking water;
- 2.6 billion people are without access to basic sanitation (1).

These combined conditions can be addressed and an improved quality of life can be realized by applying the same principles that brought about the industrialized world public health miracle of the nineteenth and twentieth centuries—a treated drinking water supply, sanitation, and good hygiene practices—to households globally.

Between 1990 and 2002, 1.1 billion more people worldwide gained access to improved water supplies. Yet that same number—1.1 billion or about one in six people—still lack access to improved water in 2004. Most of these people live in rural areas and urban and peri-urban slums. Their water needs are a focal point of international efforts to provide safe drinking water (2). For these 1.1 billion people, household water treatment and safe storage is not an additional barrier, post-treatment, as it is for those who purchase and use point-of-entry or point-of-use systems, but instead it may be their main barrier in the prevention of water-related illness. And these systems work! "There is now conclusive evidence that simple, acceptable, low-cost interventions at the household and community level are capable of dramatically improving the microbial quality of household stored water and reducing attendant risks of diarrheal disease and death" (3).

Moreover, we know that household drinking water treatment and safe storage, access to sanitation, and hygienic behavior are all interrelated activities. The combination of all these three main interventions will maximize health benefits to all. Household drinking water treatment and safe storage is one essential technology with a special role to play for households lacking a safe water supply. It was with this understanding that the World Health Organization formed the International Network to Promote Household Drinking Water Treatment and Safe Storage, a public–private partnership announced at the Kyoto World Water Forum in March 2003.

While we know that household water treatment and safe storage has been practiced locally and regionally, recognition of the role that household water treatment and safe storage can play globally in securing safe drinking water is a recent development dating to the 1990s. Research and development have been a process of adapting traditional wisdom and best engineering and public health practices, applied in settings that necessitate simple, low maintenance designs, use of local materials, applications under demanding local conditions, social acceptability, and economic sustainability. Research on cost effectiveness indicates that these household water treatment and safe storage practices can avert much of the burden associated with diarrheal disease at low cost(4).

Some of the treatment processes for household drinking water treatment and safe storage currently under investigation and/or in early stages of implementation include (see Figs. 4–6):

Sedimentation
Mechanical and/or biological filtration

Figure 4. Chlorine solution for household disinfection.

Figure 5. Safe water storage container.

Figure 6. Household arsenic filter (Kanchan arsenic filter—Nepal).

Cloth filters
Ceramic water filters
Intermittent household slow sand filters

Coagulation/flocculation

Metal salts (e.g., alum, ferric chloride, ferric sulfate)
Natural polymers
Mixtures of coagulants/flocculants, weighting agents, calcium hypochlorite

Adsorption

Arsenic remediation household systems
Fluoride remediation household systems

Ion exchange processes
Membrane/reverse osmosis processes
Oxidation processes
Disinfection

Chlorine and the safe water system
Solar UV or UV lamp disinfection
Heat disinfection or pasteurization

Distillation
Combined (multiple barrier) household treatment systems

Sedimentation + solar UV disinfection
Pretreatment filters (strung-wound + granular activated carbon filter + chlorine disinfection)
Pretreatment cloth + sand + ceramic candles with colloidal silver
Coagulation/flocculation + filtration + chlorine disinfection
Other combinations

Beyond inactivation and/or removal of microbiological contamination—which is the major concern for those lacking access to safe drinking water—appropriately designed household drinking water treatment can effectively remove physical substances (e.g., turbidity) and/or toxic chemicals (e.g., arsenic, fluoride, pesticides) as well as microbiological contamination by one or several of the processes listed above.

On every continent, there are promising household drinking water treatment and safe water storage options available. In the decade to come, we will witness new research, innovation, and scale-up of these systems from hundreds to thousands to millions to meet the enormous global need for clean, safe drinking water.

BIBLIOGRAPHY

1. WHO/UNICEF Joint Monitoring Programme on Water Supply and Sanitation (2004). *Meeting the MDG Drinking Water and Sanitation Target: A Mid-Term Assessment of Progress*. Available at http://www.who.int/water_sanitation_health/monitoring/jmp2004/en/.
2. Millennium Development Goal #7: to reduce by half the proportion of people lacking access to safe water and sanitation by 2015. Available at www.developmentgoals.org.
3. Sobsey, M. (2003). Managing water in the home: accelerated health gains from improved water supply. Available at http://www.who.int/water_sanitation_health/dwq/wsh0207/en/index.htm.

4. Hutton, G. and Haller, L. (2004). Evaluation of the costs and benefits of water and sanitation improvements at the global level. In: *Water, Sanitation and Health Protection of the Human Environment*. World Health Organization, Geneva, WHO/SDE/WSH/04.04. Available at http://www.who.int/water_sanitation_health.

VIRUS TRANSPORT IN THE SUBSURFACE

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BACKGROUND

The 1986 Safe Drinking Water Act (SDWA) amendments directed the EPA to develop national requirements for drinking water disinfection. The legislation required all public water supply systems to disinfect unless they fulfill criteria ensuring equivalent protection. To provide direction for the regulations associated with "acceptable" health risks to the public (4), the EPA established goals for maximum contaminant levels (MCLGs) of pathogenic microorganisms in drinking water, set or setting a level of zero for viruses (5,6).

On June 29, 1989, a Surface Water Treatment Rule (SWTR) was published addressing microbial contamination of drinking water from surface sources or from groundwater sources directly influenced by surface water, that had strict provisions for filtration and disinfection (5). On January 14, 2002, a SWTR was promulgated with special emphasis on the protozoan *Cryptosporidium* (7).

The development of a corresponding rule for groundwater, Ground Water Disinfection Rule (GWDR, later designated as the Groundwater Rule), to meet SDWA requirements began in 1987 and led to a published discussion piece (8) and a deadline for the GWDR proposal upon completion of the status of public health with respect to the microbial contamination of groundwater by conducting studies to generate a more careful nationwide picture of the problem. On May 10, 2000, "US EPA proposed to require a targeted risk-based regulatory strategy for all groundwater systems addressing risks through a multiple barrier approach that relies on five major components: periodic sanitary surveys of groundwater systems requiring the evaluation of eight elements and the identification of significant deficiencies; hydrogeological assessments to identify wells sensitive to fecal contamination; source water monitoring for systems drawing from sensitive wells without treatment or with other indications of risk; a requirement for correction of significant deficiencies and fecal contamination (by eliminating the source of contamination, correcting the significant deficiency, providing an alternative source water, or providing a treatment which achieves at least 99.99 percent (4-log) inactivation or removal of viruses), and compliance monitoring to insure disinfection treatment is reliably operated where it is used (9). The Ground Water Rule will be issued in 2005.

INTRODUCTION

More than 97% of all freshwater on the earth is groundwater. Of more than 100 million Americans who rely on groundwater as their principal source of potable water, over 88 million are served by community water systems and 20 million by noncommunity water systems (9). Historically, groundwater has been considered a safe source of drinking water which required no treatment. It has long been believed that this valuable resource was protected from surface contamination because the upper soil mantle removed pollutants during percolation. It was also believed that, even if contaminated, groundwater would be purified through adsorption processes and metabolism of indigenous aquifer microflora.

In the United States alone, the estimated annual number of reported illnesses resulting from contact with waterborne pathogens was as low as one million and as high as seven million between 1971 and 1982, and 51% of all waterborne disease outbreaks due to the consumption of contaminated groundwater (1). It is estimated that approximately 20–25% of U.S. groundwater sources are contaminated with microbial pathogens, including more than 100 types of viruses. A literature review by Craun (2) indicated that approximately one-half of the surface water and groundwater sources tested contained enteric viruses. Even 9% of conventionally treated drinking water (coagulation, sedimentation, filtration, postfiltration disinfection using chlorine/ozone) tested positive for enteric viruses.

Although water-transmitted human pathogens include various bacteria, protozoa, helminths, and viruses, agents of major threat to human health are pathogenic protozoa (*Cryptosporidium* and *Giardia*) and enteroviruses. Despite ample information regarding the fate of viruses in the subsurface, research on the persistency of pathogenic protozoa through passage in soil and groundwater is just now emerging. In the past, it was generally believed that pathogenic protozoa are confined to surface water. Contrary to that expectation, recent monitoring results from 463 groundwater samples collected at 199 sites in 23 of the 48 contiguous states suggested that up to 50% of the groundwater sites were positive for *Cryptosporidium, Giardia*, or both, depending on the parasite and the type of groundwater source (vertical wells, springs, infiltration galleries, and horizontal wells) (3).

Viruses are small obligate intracellular parasites that infect and sometimes cause a variety of diseases in animals, plants, bacteria, fungi, and algae. Viruses are colloidal particles, negatively charged at high pH (pH >7), ranging in size from 20 to 350 nm. The smallest unit of a mature virus is composed of a core of nucleic acid (RNA or DNA) surrounded by a protein coat. Due to this unique feature of viral structure and colloidal physicochemical properties, the transport of viruses in soil and ground water can act with a combination of characteristics ranging from those of solutes, colloids, and microorganisms.

Enteroviruses are a particularly endemic class of waterborne microorganisms that cause a number of ubiquitous illnesses, including diarrhea, gastroenteritis, and meningitis, to name only a few. Included in this group are poliovirus, hepatitis type A (HAV), Coxsackie virus A and B, and rotavirus. Although gastroenteritis is the most common disease resulting from these microorganisms, other associated illnesses include hepatitis, typhoid fever, mycobacteriosis, pneumonia, and dermatitis (10).

SOURCES OF VIRUSES

A number of avenues are available for the introduction of viruses to the subsurface, including land disposal of untreated and treated wastewater, land spreading of sludge, septic tanks and sewer lines, and landfill leachates.

Among these, septic systems may pose a significant chemical as well as biological threat to surface and groundwaters. One trillion gallons of septic-tank waste are released into the subsurface annually. Although phosphate and bacteria are ordinarily removed by soil, nitrate and viruses may escape these processes and move through the soil into the groundwater. The presence of viral particles is even more significant in the light of studies that indicate they are not necessarily inactivated in septic tanks and may move into the groundwater where they may survive for long periods of time.

It is a general consensus that the transport of pathogens in the subsurface depends on the extent of their retention on soil particles and their survival. Among the major factors that affect viral transport characteristics in the subsurface are temperature, microbial activity, moisture content, and pH. Among all the factors, temperature appears to be the only well-defined parameter that causes a predictable effect on viral survival. A direct relationship between a rise in temperature and viral inactivation rates ($K = \log$ inactivated/h) among various viruses has been suggested. Badawy et al. (11) stated that during the winter (4–10 °C), viral inactivation rates for coliphage, poliovirus, and rotavirus were 0.17, 0.06, and 0.10 per hour, respectively. Whereas, during the summer (36–41 °C), the inactivation rates for MS-2, poliovirus, and rotavirus were 0.45, 0.37, and 0.20 per hour, respectively. It should be pointed out that this information is based on ambient air. A more direct comparison would be correlation with temperatures in the subsurface. In this regard, the inactivation rates for enteroviruses are 0.06 (10–15 °C), 0.08 (15–20 °C), and 0.19 (20–25 °C). This worker also indicated that viruses may remain viable for 3 to 5 weeks on crops irrigated with sewage effluent, polio and Coxsackie virus up to 4 months on vegetables during commercial and household storage; and up to 30 days on vegetables stored at 4 °C.

Microbial ecology may also play an important role in the inactivation of waterborne viruses. For example, microbial activity could affect viral survival by the action of proteolytic enzymes of some bacteria and protozoa in destroying the viral capsid protein.

As discussed earlier, viral transport through porous media is controlled by sorption and by inactivation. However, adsorption of viruses to soil should not be confused with their inactivation because adsorption is not permanent and can be reversed by the ionic characteristics of percolating water. Viruses can remain infective after a travel distance of 67 meters vertically and 408 meters horizontally (12). The various forces involved in attaching viruses to soil particles include hydrogen bonding, electrostatic attraction and repulsion, van der Wals forces, and covalent ionic interaction.

EFFECT OF HYDROGEOLOGIC SETTINGS ON VIRAL MOVEMENT

The concentration and loading of viruses and the hydrogeologic setting through which they move will control the potential for viral migration to wells to a much greater extent than biological survivability. A hydrogeologic setting often consists of a soil underlain by unconsolidated deposits of sand, silt, and clay mixtures over rock. The setting further incorporates unsaturated and saturated zones.

All other factors being equal, the persistence of viruses at a well or other source of water is most likely where saturated flow transports large concentrations of the particles along short flow paths through media that contribute little to attenuation. Although the interrelated processes that control viral movement and persistence in the subsurface are not completely understood, some of the major hydrogeological factors that can be used to evaluate the potential for viral presence in groundwater wells include

- transport mechanisms (unsaturated versus saturated flow conditions),
- type of media through which the virus will travel (clays versus sands versus fractured media),
- length of the flow path to the extraction point (well), and
- time of travel.

Hydrogeologic settings that have shallow water tables are more susceptible to viral transport. Viruses are attenuated or immobilized by processes such as dessication, microbial activity, and stagnation. Further, viruses commonly bind to soil particles, fine-grained materials, and organic matter. The lower transport velocities associated with unsaturated conditions (e.g., move, stop, move cycle) allow these processes more time to occur. If viruses are introduced directly into the water table (such as from leaching tile fields associated with on-site sewage disposal) or if the volume of contaminants can maintain saturated flow conditions (such as in some artificial recharge situations), the potential for contamination increases. Where the viral concentration is high, the probability of contaminant migration increases regardless of the hydrogeologic setting. Therefore, in hydrogeologic settings that have deeper water tables and where contaminants are not introduced into the aquifer through saturated flow conditions, viruses are much less likely to survive transport to a well.

Hydrogeologic settings that have interconnected fractures or large interconnected void spaces that lack fine-grained materials have a greater potential for viral transport and well contamination. Karst aquifers, fractured bedrock, and gravel aquifers have been identified in the proposed GWDR as sensitive hydrogeologic settings (9).

In these settings, fractures and large void spaces allow rapid transport through the aquifer, thereby reducing the amount of time and particulate contact available for attenuation. Potential interaction with rock walls along fractures is reduced, and contact with fine-grained materials for potential sorption sites is minimal.

Similar to fractured rock aquifers, gravel aquifers that have only a small fine-grained fraction have little potential for viral sorption. However, as the amount of fine-grained material increases, effective grain size decreases, the potential for sorption increases, and travel times decrease. Finer grained aquifers and aquifers where void spaces are less interconnected or smaller are therefore less likely to transport viruses significant distances.

The potential for physical viral removal by filtration also appears to increase as grain size becomes smaller, although the filtration processes are not well understood due to their size. However, filtration of bacteria, which are larger than viruses, it has been shown is an effective removal mechanism.

Hydrogeologic settings, where fractures are not as interconnected or where more tortuous flow paths must be followed to reach a well, also allow greater viral removal. For example, in many rock aquifers, groundwater flow follows bedding planes that may result in an elongated indirect pathway to a well. In other rock aquifers, flow must travel around and through cemented portions of the matrix thereby increasing the flow path. Similarly, sand and gravel aquifers that have fine-grained materials in the matrix will have less direct flow paths as the water flows around the finer grained materials. Generally, it can be stated that tortuosity increases the length of the flow path and decreases the hydraulic conductivity, thus decreasing viral survival. Where finer grained materials are present or fractures are less interconnected, flow paths are also longer, thereby offering some protection to wells in more permeable units.

Hydrogeologic settings where time of travel is short have a greater potential for viral contamination. Where less permeable units (called aquitards) restrict or reduce vertical flow to underlying aquifers, time of travel is increased. Although inactivation rates, it has been shown, are extremely variable, time is a major factor affecting virus viability.

Due to the importance of hydrogeologic settings, the Proposed Ground Water Rule thoroughly addresses this issue to identify wells that are sensitive to fecal contamination. A component of the Proposed Ground Water Rule requires states to perform hydrogeologic assessments for the systems that distribute groundwater that are not disinfected (source waters that are not treated to provide 99.99% removal or inactivation of viruses). The states are required to identify sensitive hydrogeologic settings and to monitor for indicators of fecal contamination from sensitive hydrogeologic settings (see Ref. 9 for the complete proposed strategy).

VIRUS TRANSPORT MODELING

One method of addressing regulations for viral exposure, such as groundwater disinfection, the application of liquid and solid waste to the land, and wellhead protection zones, is using predictive viral transport models. Like most predictive modeling efforts, the results depend on the conceptual basis of the model as well as the quality and availability of input data. Clearly, a thorough understanding of the processes and parameters of viral transport are essential elements in their application.

Some of the more important subsurface viral transport factors include, soil water content and temperature, sorption and desorption, pH, salt content, organic content of the soil and groundwater matrix, virus type and activity, and hydraulic stresses. Berger (14) indicated that the inactivation rate of viruses is probably the single most important parameter governing viral fate and transport in ground water.

Some of the existing models require only a few of these parameters which limit their use to screening level activities, whereas others require input information which is rarely available at field scale and is usually applied in a research setting. One limitation of most models is that they have been developed for use in the saturated zone. It has been shown, however, that the potential for viral removal is greater in the unsaturated zone than in groundwater.

Setback Distances

Traditionally, state and county regulators have established fixed setback distances for all geologic settings in their jurisdictions. For example, the distance between a septic tank and a private well would, in many instances, be as little as 50 feet and would apply for tight clays as well as fractured rock. It would apply to areas where the water table is near the surface as well as at considerable depth. As discussed in this document, the travel time or transport distance of viral particles depends on a number of factors, including moisture content, geologic setting, type and depth of the soil overburden, and source loading, to name only a few.

Frequently, guidelines established as minimum distances became so standard that a well was often positioned precisely 50 feet from the septic tank. In the survey conducted as part of the proposed Ground-Water Treatment Rule, setback distances were quite variable (9). Some of the distances were presumably based on scientific principles, while others were holdovers from past practices.

One approach in determining setback distances for septic tanks in wellhead protection areas and bank filtration sites is to determine travel times using groundwater flow characteristics. This approach has been implemented in the Federal Republic of Germany, for example, where three concentric zones protect each drinking-water well. The zone immediately surrounding the well is faced with the most restrictive regulations which are founded on the belief that 50-day residence time is adequate for inactivation of any pathogen in contaminated water. However, a comprehensive study by Matthess et al. (15), involving the evaluation of the "50-day zone," concluded that the reduction of viruses by 7 log units (current regulations) requires a much longer residence time. Matthess et al. indicated that a reduction of 7 log units occurred in about 270 days (Haltern and

Segeberger Forest) in one study and about 160–170 days (Dornach) would be required, according to another study.

Another approach to this important issue is to consider the vulnerability to viral transport in the subsurface of portions of a state or county or of individual aquifers. Although there are a number of approaches to rank vulnerability, DRASTIC is one assessment methodology that uses hydrogeologic setting descriptions and a numerical ranking system to evaluate groundwater pollution potential (13). DRASTIC assumes that a potential contaminant will be introduced at the ground surface, have the mobility of water, and be flushed toward the aquifer by infiltration. Using existing information on variable scales, the methodology was designed to evaluate areas of 100 acres or larger.

DRASTIC is an acronym representing seven reasonably available factors that are used to develop a numerical score. They are **D**epth to water, net **R**echarge, **A**quifer media, **S**oil, **T**opography (slope), **I**mpact of the vadose zone media, and hydraulic **C**onductivity of the aquifer. DRASTIC uses a weighting system to create a relative pollution potential index that varies between 65 and 223; the higher numbers express greater vulnerability.

Although DRASTIC was not designed specifically to evaluate the movement of viruses in the subsurface, the major transport mechanisms and flow paths for viral transport are considered, and the flexibility of the systems' rating scheme allows many of these factors to be taken into account. For example, depth to water addresses saturated versus unsaturated flow conditions and their importance. Aquifer media, soil, and impact of the vadose zone media all are based on descriptive soil and rock terms that allow variation due to fracturing, grain size, attenuation mechanisms, and overall characteristics that affect flow. Topography addresses the tendency of viruses to be introduced into the subsurface or to be carried away by runoff. Hydraulic conductivity addresses the relative ease of a contaminant to move with the velocity of water through the aquifer.

Clearly, meaningful setback distances can be developed only by using scientific principles that allow the use of available knowledge. The establishment of setback distances from sources of viral contamination to points of extraction (wells) can be established using DRASTIC if both the hydrogeologic setting and sensitivity rankings are considered. For example, high pollution potential index signal the need for greater setback distances. However, the hydrogeologic factors that control viral movement must be evaluated within this context to establish reasonable numbers for setback distances. A matrix that incorporates the important DRASTIC factors can be used to establish setback distances that include the vulnerability concept. Setback distances must incorporate the knowledge of saturated flow, transport pathway length, transport velocities, media interaction, and potential attenuation mechanisms. These setback distances can be used on a regional scale but can be modified if site-specific information is available. The beauty of DRASTIC is that its rationale and sensitivity factors are easily displayed, so that it can be readily modified.

BIBLIOGRAPHY

1. CDC. (1991). Waterborne-disease outbreaks, 1989–1990 *MMWR* **40**(SS-3): 1–21.
2. Craun, G.F. (1989). Causes of waterborne outbreaks in the United States. *Water Sci Technol.* **24**: 17–20.
3. Hancock, C.M., Rose, J.B., and Callahan, M. (1998). Crypto and Giardia in US groundwater. *J. Am. Water Works Assoc.* **90**(3): 58–61.
4. Macler, B.A. (1996). Developing the ground water disinfection rule. *J. Am. Water Works Assoc.* **3**: 47–55.
5. U.S. EPA. (June 29, 1989). Drinking water; national primary drinking water regulations; filtration, disinfection; turbidity; *Giardia lamblia*, viruses, *Legionella*, and heterotrophic bacteria: final rule. *Fed. Reg.* **54**: 27486.
6. U.S. EPA. (June 29, 1989). Drinking water; national primary drinking water regulations; total coliforms (including fecal coliforms and *E. coli*): final rule. *Fed. Reg.* **54**: 27544.
7. U.S. EPA. (January 14, 2002). National primary drinking water regulations: long term 1 enhanced surface water treatment rule; final rule. *Fed. Reg.* **67**(9): 1844.
8. U.S. EPA. (1992). Draft Ground-Water Disinfection Rule. U.S. EPA Office of Ground Water and Drinking Water, Washington, DC, EPA 811/P-92-001.
9. U.S. EPA. (May 10, 2000). National primary drinking water regulations: ground water rule; proposed rules. *Fed. Reg.* **65**(91): 30202.
10. Bull, R.J., Gerba, C.P., and Trussell, R.R. (1990). Evaluation of the health risks associated with disinfection. *CRC Crit. Rev. Environ. Contr.* **20**: 77–113.
11. Badawy, A.S., Rose, J.B., and Gerba, C.P. (1990). Comparative survival of enteric viruses and coliphage on sewage irrigated grass. *J Environ Sci Health*. **A25**(8): 937–952.
12. Keswick, B.H. and Gerba, C.P. (1980). Viruses in groundwater. *Environ. Sci. Technol.* **14**(11): 1290–1297.
13. Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., and Hackett, G. (1987). *DRASTIC: A Standardized System for Evaluating Ground-Water Pollution Potential Using Hydrogeologic Settings*. EPA/600/2-87/035.
14. Berger, P. (1994). Regulation related to groundwater contamination: The draft groundwater disinfection rule. In: *Groundwater Contamination and Control*. U. Zoller (Ed.). Marcel Dekker Inc., New York, NY.
15. Matthess, G., Pekdeger, A., Zoller, U., and Schroeter, J. (1988). Persistence and transport of bacteria and viruses in groundwater—a conceptual evaluation. *J. Contam. Hydrol.* **2**: 171–188.

WINDMILLS

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Windmills are machines that convert the force of the wind into energy that is applicable to various tasks, like pumping water. Windmills that are used to pump water use the energy generated by these mills to turn the gears that propel the pump. These types of windmills, sometimes referred to as wind pumps, have been used for centuries and continue in use around the world.

A BRIEF HISTORY

The first documented use of windmills was in Persia around 500–900 A.D., however, it is widely accepted that they were invented in China more than 2000 years earlier (1). In these early windmills, vertical-axis systems were used for grinding grain and pumping water. In the vertical-axis system, the wind would have to hit the mill from a specific angle to get the desired effect; therefore, most of the area around the mill had to be shielded. Later, horizontal-axis systems were developed that proved to have greater structural efficiency. By tilting the blade to a certain degree, the system eliminated the dependence on the direction of the wind and harnessed the wind energy lost in the vertical-axis systems by the areas shielded. Horizontal systems were later used throughout Europe.

Windmill technology, it is believed was introduced in Europe in the eleventh century (2). Aiming to their lowlands, the Dutch set out to develop a more efficient windmill and in the process became the driving force behind wind-machine development. Although many innovations were made, one of the fundamental improvements was designing sails that allowed optimum aerodynamic lift. This improvement made the sails rotate faster, greatly increasing their efficiency and speed in completing the task at hand. Wind energy was applied to irrigation, pumping from local wells, and drainage pumping; this in turn made areas habitable and liberated workers from these labor-intensive jobs.

As Europeans sought to expand and colonize, they brought the windmill technology with them. The colonization of the Americas is a prime example. Without this technology, it would have been impossible for immigrants to settle in areas that lacked a constant water supply. Certain areas in Texas, for example, lacked the needed water supply to sustain life and allow cultivating of the land. The drive to expand into these areas helped to stimulate the need to refine the windmill to solve this problem. Daniel Halladay addressed this problem in 1854 by changing the European windmill so it could operate unattended and more efficiently (3). The changes that he made appealed to many companies and small communities without water systems by providing an inexpensive way to get the water they needed (Fig. 1).

Figure 1. Multi-sailed windmill.

By the early twentieth century, windmills were being mass-produced, and millions of them were being used around the world. However, in the 1930s, as other fuel resources such as oil were demanded, wind pumping systems were not as desirable because they were more expensive and not as reliable as these other fuels. This was true until the 1970s when a shortage of oil prompted communities to revisit the idea of wind energy.

Wind pumps are currently being used for crop irrigation, drinking water supply for communities, and even individual household water supply. Between 5,000 to 10,000 wind pumps are being installed worldwide each year, and the market for these is expected to increase as wind technology advances and becomes less expensive (4).

THE WIND PUMP: HOW IT WORKS

The wind pump has four main features the wind turbine, the tower, the actual pumping equipment, and the storage basin. These parts can be found in almost all wind pumps. They vary in design depending on the wind conditions in which they will be used. If the wrong design is used in strong wind conditions, the pump may move too fast and malfunction, and if the wind speed is low, it may not be able to function at all.

The horizontal-axis is the typical system used for wind turbines to pump water. The rotor does not have to follow any specific design but instead should be designed for the wind conditions in which it will be used. However, the pump tends to have more force when there are more blades. The next main part of the wind turbine is its transmission. The transmission of a wind turbine converts each rotation of the rotor into an up and down motion, driving the pump rod in and out of the well. The tail of the wind turbine is a piece that was added during the westward expansion in the United States. It allows the wind turbine to work without constant supervision by changing the direction of the rotor to keep it facing the wind.

A tower holds the wind turbine generally between 10 m and 15 m high (5). It holds up the wind turbine and stabilize its connection with the pumping parts of the machine. The tower has either a square or triangular base, and the pump rod that moves in and out of the well is positioned in the center of the tower. The well that the pump rod enters can either be a shallow hand-dug well or a deep-drilled well. If the latter is the case, the walls of the well should be lined with a water permeable material to prevent them from caving in. A pipe called the rising main lies in the center of the pump rod. Its function is to carry the water pumped up to the surface. The actual pump is at the bottom of the pump rod submerged in the water and is attached to the rising main. The pump fills with water during the downward motion of the pump rod and pushes the water into the rising main and up to the surface as the pump rod moves up.

Finally, all wind pumps should have a storage basin that can hold the excess water that is pumped. When the water moves up into the rising main, it is then redirected into the storage tank. This stored water is also essential to water pumping systems because wind energy cannot always be relied on, and having a surplus at hand is useful.

THE ADVANTAGES OF WIND PUMPS

There are many advantages to using wind energy for pumping water. First, wind pumps are environmentally friendly. As with the atmosphere, wind turbines will not contaminate the land, and in the case of water pumps, there is no chance the water will be contaminated as a result of a malfunctioning wind pump.

Wind turbines generally do not affect the wildlife that inhabits the area. Sheep, cattle, deer, and other wildlife are not bothered by the turbines, and in fact have been known to graze under them. The only argument that has been raised about this issue is the tendency for birds to collide with them. However, several studies suggest that the impact of the wind turbines on birds does not compare to that of other things, such as electrical lines and buildings.

Wind pumps are cost-efficient. After the initial cost of installation, the owner basically has an infinite source of energy for just the cost of maintenance. Whereas using a fossil fuel to work the pump would make the owner subject to its cost.

THE DISADVANTAGES OF WIND PUMPS

There are, however, a few setbacks in using wind energy for pumping water. Because the wind is not reliable, if water is needed on a day where there is little to no wind, obviously the wind pump will not be able to pump water. This problem can be solved by a storage basin, as explained earlier. Many people who inhabit areas around wind turbines complain about the noise that is created by the rotation of the rotor, but this generally applies only to many wind turbines grouped together. As the rotors are improved upon and become more aerodynamic, the noise level will decrease greatly.

BIBLIOGRAPHY

1. *Illustrated History of Wind Power Development*. (7 June 2001). http://relosnet.com/wind/early.html.
2. World Meteorological Organization. (1981). *Meteorological Aspects of the Utilization of Wind As An Energy Source*. No. 575, p. 44.
3. *The Handbook of Texas Online*. (6 June 2001). http://www.tsha.utexas.edu/handbook/online/articles/view/WW/aow1.html.
4. Wind Energy & Atmospheric Physics. *Review of Historical and Modern Utilization of Wind Power*. http://www.risoe.dk/vea-wind/history.htm.
5. Jenkins, N. et al. (1997). *Wind Energy Technology*. John Wiley & Sons, New York, pp. 116–117.

READING LIST

Andersen, P.D. (9 July 2001). Review of historical and modern utilization of wind power. *Wind Energy and Atmospheric Physics*. http://www.risoe.dk/vea-wind/history.htm.

British Wind Energy Association. (28 June 2001). *Wind Energy in Agriculture*. http://www.britishwindenergy.co.uk/you/agric.html.

Danish Wind Turbine Manufacturers Association. (28 June 2001). *21 Frequently Asked Questions About Wind Energy*. http://www.windpower.dk/faqs.htm.

Gipe, P. (1995). *Wind Energy Comes of Age*. John Wiley & Sons, New York.

Illustrated History of Wind Power Development. (7 June 2001). http://relosnet.com/wind/early.html.

Jenkins, N. and Walker, J.F. (1997). *Wind Energy Technology*. John Wiley & Sons, New York.

Larkin, D. (2000). *Mill: The History and Future of Naturally Powered Buildings*. Universe, New York.

Look Learn & Do. *A History of Windmills*. (7 June 2001). http://looklearnanddo.com/documents/history_winmills.html.

Windmills. *The Handbook of Texas Online*. (6 June 2001). http://www.tsha.utexas.edu/handbook/online/articles/view/WW/aow1.html.

World Meteorological Organization. (1981). *Meteorological Aspects of the Utilization of Wind as an Energy Source*, No. 575.

MIXING AND AGITATION IN WATER TREATMENT SYSTEMS

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Mixing is one of the primary processes involved in water and wastewater treatment. In this article, the state of the art in mixing and impeller design is presented.

INTRODUCTION

Stirring is provided in a wide variety of processes to blend constituents or to disperse one phase into another or several other phases. In a blend-type operation, the purpose is to obtain a homogeneous mixture, whereas in the dispersion process, the goals vary widely, depending also on the nature of the phases involved:

- in gas–liquid dispersions, gas is dispersed into fine bubbles which must be distributed as evenly as possible in the vessel to take part in a subsidiary process, for example, absorption and/or reaction with a dissolved component, as in water and wastewater treatment, or flotation of hydrophobic particles, among others;
- in solid–liquid distributions, it is necessary to provide the appropriate conditions for entraining all solid particles inside the bulk of the liquid, either from the bottom of the vessel or from the free surface of the liquid;
- in liquid–liquid dispersions, fine droplets of one of the liquids have to be dispersed inside the other liquid to produce an emulsion or for a polymerization, among others.

For each of these processes, a particular type of agitator is appropriate. These have evolved from the simple paddles used during the past centuries; modern flow visualization techniques (1) have helped in designing agitator blade shapes optimized for specific processes.

In the following sections, the main types of agitators are presented, according to the processes for which they are intended; this presentation is limited to turbulent flow, which is typical in water and wastewater treatment processes, and does not describe agitators designed for viscous liquids (anchors, gates, etc.).

TYPES OF IMPELLERS

An impeller is a pump; by its rotation, it draws liquid from its neighborhood and then ejects it at a relatively high speed. It is typically mounted on a shaft connected to a motor, and the shaft–impeller structure is inserted in the stirred tank either axisymmetrically or sideways. Close to the impeller blades, the rotation induces a tangential flow. Inside the bulk of the vessel, on the other hand, the action of the impeller induces flow circulation, which follows a pattern typical of the impeller type. Thus, we distinguish mainly radial and axial impellers, depending on the direction of the flow that emerges from the impeller-swept region.

Radial impellers eject a liquid stream radially. In a typical stirred vessel where the impeller is mounted on a shaft, is vertical and is usually centrally located, the ejected liquid flows from the edge of the impeller blades toward the vessel walls. There, it separates into two streams; one flows in the upper part of the vessel and one in the lower part of the vessel, thus forming two flow loops. The liquid from these two streams circulates in the upper and the lower parts of the vessel and eventually is drawn back into the agitator-swept region; two primary circulation loops are established inside the stirred tank.

Figure 1 presents some typical radial impellers. The Rushton turbine (RT; Fig. 1a) is one of the most widely used impellers due to its efficiency in gas–liquid and liquid–liquid mixing. Its construction is simple; usually it has six flat blades mounted on a flat disk. Figures 1b (SCABA 6SRGT turbine or Chemineer CD-6) and 1c (Chemineer BT-6) present two variants of the Rushton turbine, where blades have a parabolic shape, which is even more efficient than the RT, especially in dispersing gas inside a stirred vessel. Finally, the Narcissus (NS) impeller (2) produces an inverse radial flow; liquid is drawn in from its side and pumped out from its upper and lower parts.

Figure 2, which is a 2-D plot of composite radial and axial velocities U_{RZ}—which are obtained from the vector sum of the radial (U_{R}) and axial (U_{Z}) components of the local velocity vector—illustrates the typical radial flow patterns of the Rushton turbine—radial flow directed from the impeller toward the vessel walls—and of the Narcissus (NS)—radial flow directed toward the impeller. A similar double-loop circulatory flow pattern is induced by the SCABA turbine (3).

Axial impellers draw liquid mainly from one of their sides, top or bottom, and eject it from the opposite site; when liquid is ejected toward the bottom of the vessel, the impeller is said to work in the “down-pumping” mode, whereas when the liquid is ejected toward the surface of the liquid, this corresponds to the “up-pumping” mode. Often, liquid is also drawn from the side of the rotating impeller. Note that axial impellers are sometimes called “mixed-flow” impellers, too: in some cases, part of the ejected flow is directed sideways; this becomes more pronounced when the viscosity of the liquid increases (4).

Figure 3 presents some typical axial-flow impellers. The marine propeller (Fig. 3a) has been used for the propulsion of boats, and nowadays it is its sole application; far more efficient agitators have been designed for mixing liquids. Figure 3b shows the widely used pitched-blade turbine (PBT); the number of blades and their inclination usually characterizes the PBT more specifically, for example, the PBT in the illustration is referred to as a “4-45-PBT.” The Mixel TT has blades, which are wider than those of

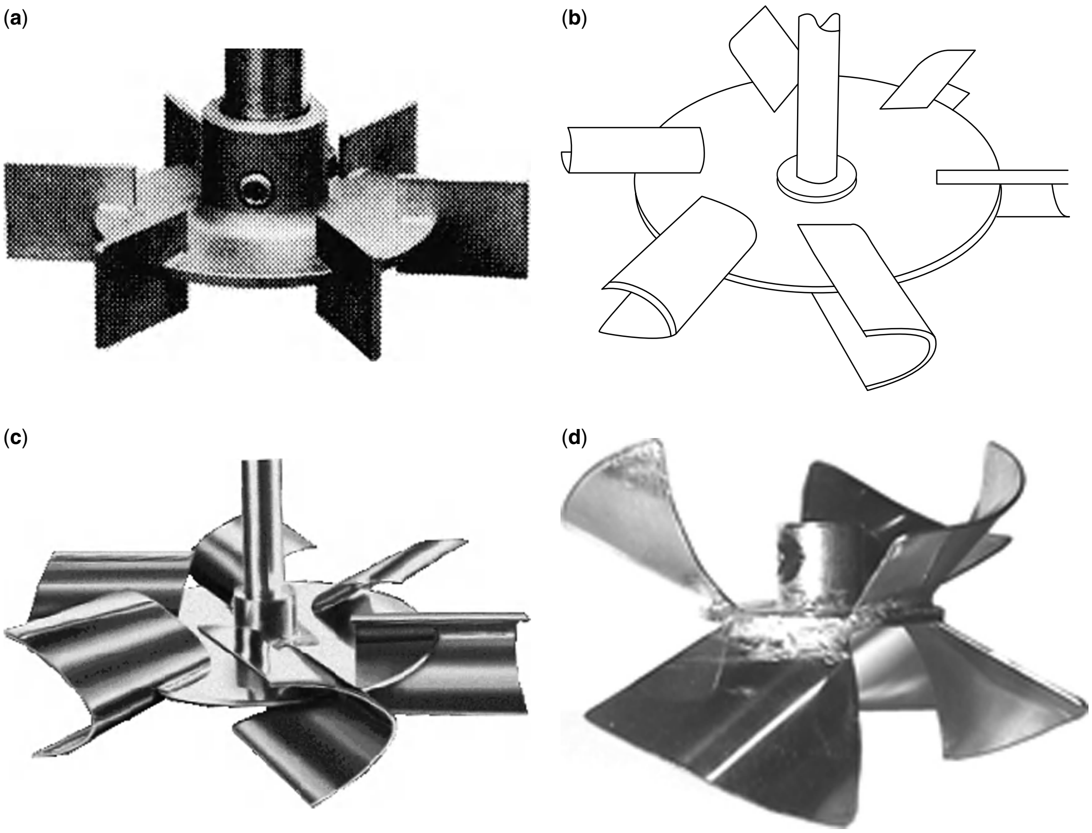

Figure 1. Radial agitators: (**a**) Rushton turbine; (**b**) SCABA 6SRGT (or Chemineer CD-6); (**c**) Chemineer BT-6; (**d**) Narcissus.

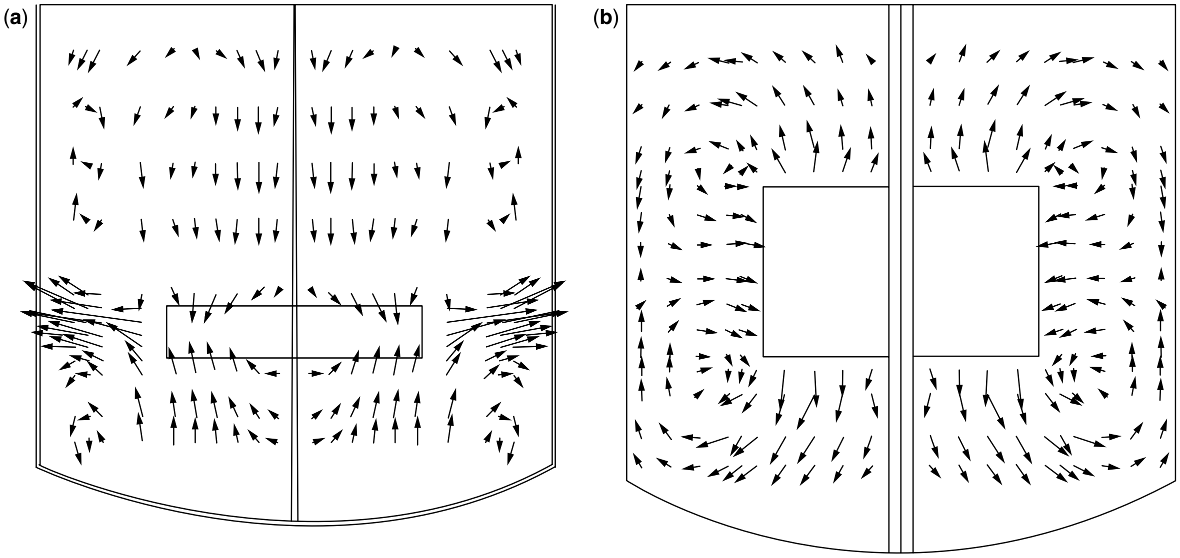

Figure 2. Flow patterns induced by radial impellers in a stirred tank: (**a**) Rushton turbine (4); (**b**) Narcissus (NS) impeller (2).

the PBT and are profiled to be more efficient in energy consumption.

The typical 2-D flow pattern induced by all axial-flow impellers in their usual configuration—"down-pumping"—is illustrated in (Fig. 4a). As already stated, liquid is drawn from the upper part and the side of the impeller and is ejected downward. A single circulation loop is established in all cases; liquid flows upward close to the vessel walls and returns toward the impeller. The velocities in the upper part of the vessel are typically rather slow: the U_{RZ} vectors are much shorter than those close to the upper and lower sides of the impeller.

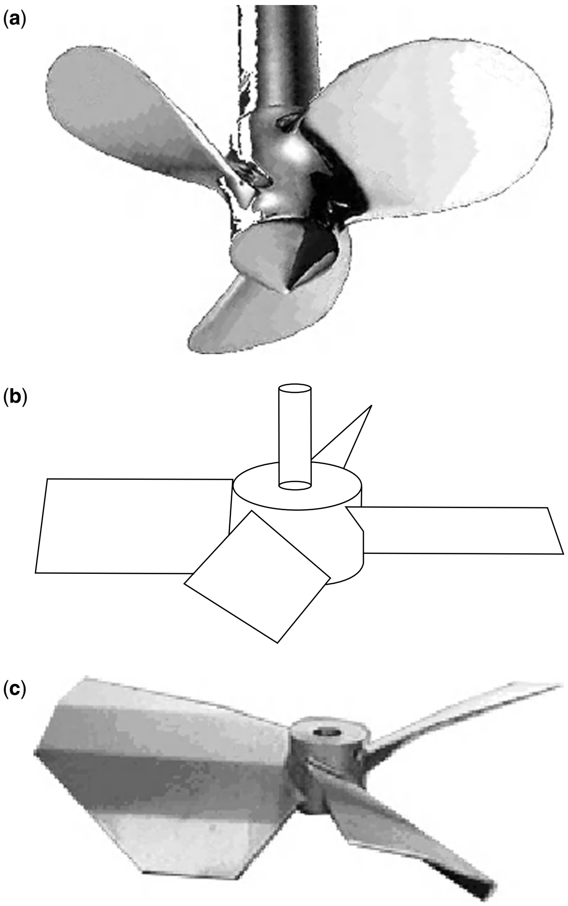

Figure 3. Typical axial-flow impellers; (**a**) marine propeller; (**b**) pitched-blade turbine; (**c**) Mixel TT.

Therefore, the liquid in the stirred tank may be divided into two regions: the first corresponds to the primary circulation loop, which is established around the impeller; liquid flows fast and results in an intensive mixing process. The liquid in the second region, located mainly in the upper part of the vessel, circulates slowly; therefore the mixing process is less intense and effective there; it is often necessary to add a second impeller on the same shaft, to enhance circulation and mixing in the upper part of the vessel.

The inverse configuration—“up-pumping”—again yields a single primary circulation loop, located around the impeller (Fig. 4b). A smaller, secondary circulation loop is established in the upper part of the vessel, achieving better overall circulation and mixing than the “down-pumping” mode.

Several other impellers have been tested and/or marketed, based on extensive hydrodynamic performance measurements, taking into consideration some optimization criterion; some of them are variants of the pitched-blade turbine; others have blade shapes originating from hydrofoils. Figure 5 illustrates some of these impellers.

The size and location of the impeller inside the stirred vessel are dictated by the process needs and affect its performance, for example,

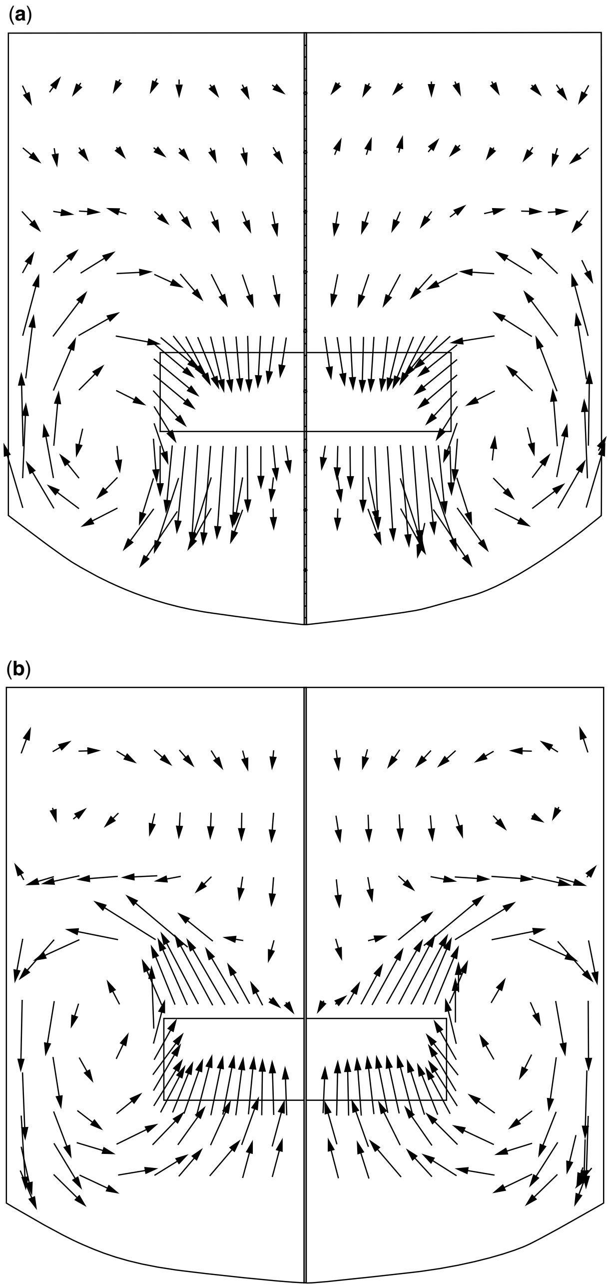

Figure 4. Flow patterns induced by axial impellers in a stirred tank: (**a**) Mixel TT in down-pumping mode [4]; (**b**) Mixel TT in up-pumping mode (5).

- to disperse gas effectively inside a stirred tank, it is necessary to use a radial agitator that has a large impeller diameter (D) to tank diameter (T) ratio, for example, $D/T = 1/2$, and to provide high rotational speed;
- if it is required to provide surface aeration to the stirred tank, the impeller is located close to the free liquid surface;
- if it is necessary to achieve an effective distribution of solid particles, an axial impeller having a reduced size ($D/T = 1/3$) should be used, located closer to the bottom of the vessel, having clearance (C), that is,

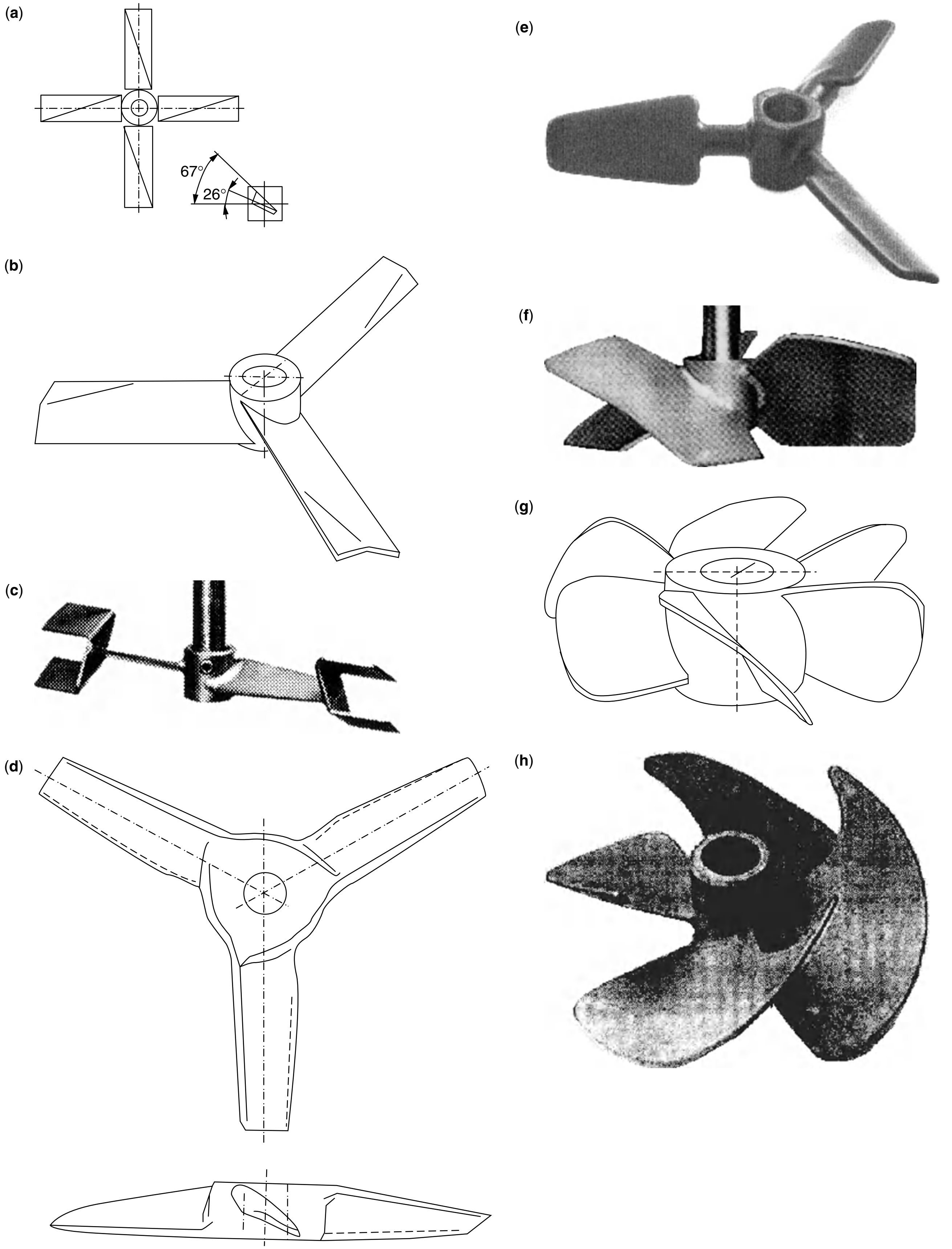

Figure 5. Examples of advanced impellers: (**a**) "Medek" PBT [6,7]; (**b**) Chemineer HE-3 [8]; (**c**) Ekato MIG; (**d**) Lightnin A-310; (**e**) DeDietrich hydrofoil; (**f**) Lightnin A-320; (**g**) Prochem Maxflo; (**h**) APV B2.

the distance from the bottom of the vessel, close to $T/3$ or even $T/4$.

When mixing is applied to rectangular troughs, the axis of the impeller is horizontally located at one end of the trough, and an axial-flow agitator with hydrofoil blades is used to induce longitudinal motion of the liquid in the trough.

PERFORMANCE DATA

The performance of the various impellers is characterized by quantitative criteria; some of these are power consumption, the amount of flow circulation caused by the pumping action of the impeller, the ability of the impeller to cause intense circulation in the stirred tank, and the time necessary to achieve homogeneity of the tank contents, among others.

The power consumption depends upon the impeller type; it has been found that in turbulent conditions, where the dimensionless Reynolds number (Re),

$$Re = \frac{\rho N D^2}{\mu} \tag{1}$$

is larger than about 4000, the dimensionless power number (Po),

$$Po = \frac{P}{\rho N^3 D^5} \tag{2}$$

is approximately constant and characterizes each impeller. Table 1 presents power numbers for a variety of commonly used impellers.

Another feature of impellers is the amount of fluid being "pumped out" of the agitator-swept region; from the flow rate of this stream (Q_p), another dimensionless number, the flow number, (Fl), which also characterizes impellers may be obtained:

$$Fl = \frac{Q_P}{ND^3} \tag{3}$$

Table 1 presents typical values of flow numbers for the most common types of impellers.

Table 1. Characteristics of Various Impellers

Type	D/T	C/T	Power Number (Po)	Flow Number (Fl)
A310 (Lightnin)	1/2	1/3	0.56	0.62
A315 (Lightnin)	NA[a]	NA[a]	0.75–0.80	0.73
A320 (Lightnin)	0.40	0.39	0.64	0.64
A410 (Lightnin)	0.40	0.40	0.32	0.62
4-45-PBT	1/3	1/3	1.25	0.77
6-45-PBT (down-pumping)	1/3	1/3	1.93	0.75
6-45-PBT (up-pumping)	1/3	1/3	2.58	0.68
6SRGT (SCABA)	1/3	1/3	2.8–3.0	NA[a]
BT-6 (Chemineer)	1/3	1/3	2.1	NA[a]
CD-6 (Chemineer)	1/3	1/3	2.8–3.0	NA[a]
HE-3 (Chemineer)	1/2	1/4	0.31	0.41
Marine propeller	1/3	NA[a]	0.89	0.79
Medek PBT	1/3	1/3	0.41	0.60
Mixel TT (down pumping)	1/2	1/3	0.74	0.67
Mixel TT (up-pumping)	1/2	1/3	0.67	0.61
Narcissus	1/3	1/3	1.14	0.31
MaxFloT (Prochem)	0.35	0.45	1.58	0.82
Rushton turbine	1/3	1/3	4.9–5.2	0.78

[a] NA: not available.

One of the purposes of an impeller is to create circulation inside a stirred vessel, so one quantitative characteristic of its efficiency is the spatial mean velocity achieved in the vessel. This mean velocity, compared to the velocity at the tip of the blades (V_{TIP}), yields the "agitation efficiency" (I_G) of each particular impeller (9).

Finally, the time to obtain vessel homogeneity is termed "mixing time" (t_{MIX}); it has been found that for a wide variety of impellers it may be correlated to the power number and to the impeller-to-vessel diameter ratio (10):

$$N\, t_{\mathrm{MIX}} = 5.3(Po)^{-1/3}\left(\frac{T}{D}\right)^2 \tag{4}$$

CONCLUSIONS

Mixing is used in a multitude of processes, including water and wastewater treatment, to achieve several goals: to disperse another phase—gas, liquid, or solid—into the bulk of the liquid; to homogenize the stirred tank contents; and to assist and promote a reaction between some of the dissolved and/or dispersed species, among others. This is usually achieved by using rotating impellers, whose blade design has been often optimized for particular processes. Radial impellers, such as the Rushton turbine, are more suitable for homogenization and for dispersing a second phase in liquids; however, they generate high-shear flows. Axial-flow impellers are more suitable for solids dispersion and for cases where shear-sensitive material exists in the liquid, requiring benign mixing conditions.

NOTATION

C: clearance of impeller (from midplane) to vessel bottom (m)
D: impeller diameter (m)
Fl: dimensionless flow number (-)
I_G: dimensionless agitation index (-)
N: impeller rotational frequency (Hz)
Po: dimensionless power number (-)
Re: dimensionless Reynolds number (-)
T: vessel diameter (m)
t_{MIX}: mixing time (s)
U: liquid velocity (m/s)
V_{TIP}: liquid velocity at the tip of the impeller blades ($= \pi ND$) (m/s)

GREEK LETTERS

μ: viscosity of liquid (Pa.s)
ρ: density of liquid (kg/m^3)

INDEXES

R: radial
RZ: composite radial-axial
Z: axial

BIBLIOGRAPHY

1. Mavros, P. (2001). Flow visualisation in stirred vessels. Review of experimental techniques. *Chem. Eng. Res. Des.* **79A**(2): 113–127.
2. Hristov, H.V., Mann, R., Lossev, V., and Vlaev, S.D. (2004). A simplified CFD for three-dimensional analysis of fluid mixing, mass transfer and bioreaction in a fermenter equipped with triple novel geometry impellers. *Food and Bioproducts Processing* **82**(C1): 21–34.
3. Khopkar, A., et al. (2004). Flow generated by radial flow impellers: PIV measurements and CFD simulations. *Int. J. Chem. Reactor Eng.* **2**: A18.
4. Mavros, P., Xuereb, C., and Bertrand, J. (1996). Determination of 3-D flow fields in agitated vessels by laser-Doppler velocimetry. Effect of impeller type and liquid viscosity on liquid flow patterns. *Chem. Eng. Res. Design* **74A**: 658–668.
5. Aubin, J., Mavros, P., Fletcher, D.F., Bertrand, J., and Xuereb, C. (2001). Effect of axial agitator configuration (up-pumping, down-pumping, reverse rotation) on flow patterns generated in stirred vessels. *Chem. Eng. Res. Des.* **79A**(8): 845–856.
6. Medek, J. and Fořt, I. (1991). *Relation between designs of impeller with inclined blades and their energetic efficiency*. *Proc. 7th Eur. Conf. Mixing*, Brugge, Belgium, Sept. 18–20, KVIV, vol. I, pp. 95–102.
7. Medek, J., Seichter, P., Rybníček, Z., and Chaloupka, Z. (1987). Czechoslovak patent no. 256630.
8. Ibrahim, S. and Nienow, A.W. (1995). Power curves and flow patterns for a range of impellers in Newtonian fluids $-40 < Re < 5 \times 10^5$. *Chem. Eng. Res. Design* **73**(A5): 485–491.
9. Mavros, P. and Baudou, C. (1997). Quantification of the performance of agitators in stirred vessels. Definition and use of an agitation index. *Chem. Eng. Res. Des.* **75A**: 737–745.
10. Ruszkowski, S. (1994). A rational method for measuring blending performance and comparison of different impeller types. *Proc. 8th Eur. Conf. Mixing*. Cambridge, UK, Sept. 21–23, IChemE, Rugby, pp. 283–291.

ARSENIC IN NATURAL WATERS

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INTRODUCTION

Arsenic is widely distributed in nature in air, water, and soil as a metalloid and as chemical compounds, both inorganic and organic (1). This class of compounds was known to the ancient Greeks and Romans both as therapeutic agents as well as poisons. This dual nature as useful substances as well as toxic matter to be controlled has grown over the centuries. Arsenic and arsenicals have widened use in commerce, but so have the recognition that their presence in drinking water, largely from natural sources, is a major public health problem around the world.

Acute and chronic arsenic exposure via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand, and Taiwan, where ground (well) water is contaminated with a high concentration of arsenic of 100 to more than 2000 μg/liter (ppb) (2). Studies have linked long-term exposure to arsenic in drinking water to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. Noncancer effects of ingesting arsenic include cardiovascular, pulmonary, immunological, neurological, and endocrine (e.g., diabetes) disorders (3). Besides its tumorigenic potential, it has been shown that arsenic is genotoxic (4,5). Given the importance of arsenic as a global environmental toxicant, we will summarize the geochemistry, natural distribution, regulation, anthropogenic sources, and removal mechanisms.

GEOCHEMISTRY

Average concentrations of arsenic in the earth's crust reportedly range from 1.5 to 5 mg/kg. Higher concentrations are found in some igneous and sedimentary rocks, particularly in iron and manganese ores. Common minerals containing arsenic are shown in Table 1. Arsenopyrite, realgar, and orpiment are the most important of these minerals, and they are commonly present in the sulfide ores of other metals, including copper, lead, silver, and gold. Arsenic may be released from these ores to the soil, surface water, groundwater, and the atmosphere.

Natural concentrations of arsenic in soil typically range from 0.1 to 40 mg/kg; an average concentration is 5 to 6 mg/kg. Arsenic can be released to ground or surface water by erosion, dissolution, and weathering. Geothermal waters can be sources of arsenic in groundwater.

In Yellowstone National Park, the arsenic concentrations in geysers and hot springs range from 900 to 3,560 ppb. Waters from these sources cause elevated arsenic levels in rivers downstream. Other natural sources include volcanism and forest fires. Volcanic activity appears to be the largest natural source of arsenic emissions to the atmosphere, estimated variously between 2,800 to 44,000 metric tons annually. The relative contributions of volcanic sources, other natural sources (Table 1), and anthropogenic sources to the atmosphere have not been definitively established.

The predominant forms of arsenic in groundwater and surface water are arsenate (V) and arsenite (III). Examples

Table 1. Common Minerals of Arsenic[a]

Arsenopyrite, $FeAsS$	Smalite, $CoAs_2$
Lollingite, $FeAs_2$	Cobaltite, $CoAsS$
Orpiment, As_2S_3	Gersdorffite, $NiAsS$
Realgar, As_4S_4	Tennantite, $4Cu_2SAs_2S_3$
Chloanthite, $NiAs_2$	Proustite, $3Ag_2SAs_2S_3$
Niciolite, $NiAs$	Enargite, $3Cu_2SAs_2S_5$

[a] Reference 3.

of inorganic arsenic compounds found in the environment include oxides (As_2O_3, As_2O_5), and sulfides (As_2S_3, AsS, $HAsS_2$, $HAsS_3{}^{3-}$). Inorganic arsenic species that are stable in oxygenated waters include arsenic acid [As(V)] species (H_3AsO_4, $H_2AsO_4{}^-$, $HAsO_4{}^{2-}$ and $AsO_4{}^{3-}$). Arsenous acid [As(III)] is also stable as H_3AsO_3 and $H_2AsO_3{}^-$ under slightly reducing aqueous conditions. Arsenite is generally associated with anaerobic conditions. Oxidation state, oxidation–reduction potential, pH, iron concentrations, metal sulfide and sulfide concentrations, temperature, salinity, and distribution and composition of biota appear to be the significant factors that determine the fate and transport of arsenic. In surface waters, additional factors include total suspended sediment, seasonal water flow volumes and rates, and time of day.

Sorption of arsenic to suspended sediment may strongly affect the fate and transport of arsenic in surface water systems (6). Where pH and arsenic concentrations are relatively high and total suspended sediment levels are relatively low, sorption processes may be less important. However, where suspended sediment loads are higher, arsenic concentrations are lower, and pH levels are lower, arsenic is more likely to be present in the suspended particulate phase rather than in the dissolved phase. Particulate phase arsenic may settle to bottom sediment in reservoirs and areas of low flow levels. In deeper lakes, remobilization of arsenic from sediment may be minimal, whereas in shallower lakes, arsenic may be remobilized faster from wind-induced wave action and high-flow scouring. Diurnal changes of as much as 21% in arsenic concentrations have been observed in rivers, attributable to pH changes due to sunlight and photosynthesis.

NATURAL DISTRIBUTION

A survey of arsenic concentration in natural waters is of importance relative to the desirable maximum limit of 10 ppb or less for human consumption. An attempt has been made to quantify the global element cycle for arsenic, based on published data (1). Arsenic concentrations in environmental media are presented in Table 2.

Table 2. Arsenic Concentrations in Environmental Media[a]

Environmental Media	Arsenic Concentration Range	Units
Air	1.5–53	ng/m^3
Rain from unpolluted ocean air	0.019	μg/L (ppb)
Rain from terrestrial air	0.46	μg/L
Rivers	0.20–264	μg/L
Lakes	0.38–1,000	μg/L
Ground (well) water	<1.0–>1,000	μg/L
Seawater	0.15–6.0	μg/L
Soil	0.1–1,000	mg/kg (ppm)
Stream/river sediment	5.0–4,000	mg/kg
Lake sediment	2.0–300	mg/kg
Igneous rock	0.3–113	mg/kg
Metamorphic rock	0.0–143	mg/kg
Sedimentary rock	0.1–490	mg/kg
Biota—green algae	0.5–5.0	mg/kg
Biota—brown algae	30	mg/kg

[a] Reference 7.

In addition to geochemical factors, microbial agents can influence the oxidation state of arsenic in water and can mediate the methylation of inorganic arsenic to form organic arsenic compounds (8). Microorganisms can oxidize arsenite to arsonate and reduce arsenate to arsenite or even to arsine (AsH_3). Bacteria and fungi can reduce arsenate to volatile methylarsines. Marine algae transform arsenate into nonvolatile methylated arsenic compounds such as methylarsonic acid [$CH_3AsO(OH)_2$] and dimethylarsinic acid [$(CH_3)_2AsO(OH)$] in seawater. Freshwater and marine algae and aquatic plants synthesize complex lipid-soluble arsenic compounds (9). Organic arsenical compounds were reportedly detected in surface water more often than in groundwater. Surface water samples reportedly contain low but detectable concentrations of arsenic species, including methylarsonic acid and dimethylarsinic acid. Methylarsenicals reportedly comprise as much as 59% of total arsenic in lake water. In some lakes, dimethylarsinic acid has been reported as the dominant species, and concentrations appear to vary seasonally from biological activity within waters.

REGULATIONS

In the United States, the Safe Drinking Water Act (SDWA) of 1974 called for establishing Maximum Contaminant Levels (MCL) as national drinking water standards and required the Environmental Protection Agency (EPA) to revise the standard periodically. Based on a Public Health Service standard established in 1942, the EPA established a standard of 50 μg/liter (50 ppb) as the maximum arsenic level in drinking water in 1975. In 1984, the World Health Organization (WHO) followed with the same 50 ppb recommendation. Since that time, rapidly accumulated toxicity information prompted a revision of the standard, and a provisional guideline of 10 ppb was recommended by WHO in 1993. In January 2001, EPA published a revised standard that would require public water supplies to reduce arsenic to 10 ppb by 2006. Perceived hardships in implementation and uncertainty in setting the standard at 3, 5, 10, or 20 ppb has led the EPA to announce temporary delays in the effective date for the January 2001 rule to allow for further cost–benefit analysis and public input. The rule is significant because it is the second drinking water regulation for which the EPA has used its discretionary authority under the SDWA to set the MCL higher than the technically feasible level, which is 3 ppb for arsenic, based on the determination that the costs would not justify the benefits at this level.

ANTHROPOGENIC SOURCES

Arsenic is released from a variety of anthropogenic sources, including metal and alloy manufacturing, petroleum refining, pharmaceutical manufacturing, pesticide manufacturing and application, chemical manufacturing, burning of fossil fuels, and waste incineration.

Most agricultural uses of arsenic are banned in the United States. However, sodium salts of methylarsonic acid are used in cotton fields as herbicides. Organic arsenic is also a constituent of feed additives for poultry and swine and appears to concentrate in the resultant animal wastes. About 90% of the arsenic used in the United States is for the production of chromated copper arsenate (CCA), the wood preservative. CCA is used to pressure treat lumber and is classified as a restricted use pesticide by the EPA. A significant industrial use of arsenic is in the production of lead-acid batteries; small amounts of very pure arsenic metal are used to produce gallium arsenide, which is a semiconductor used in computers and other electronic applications. The U.S. Toxics Release Inventory data indicated that 7,947,012 pounds of arsenic and arsenic-containing compounds were released to the environment in 1997; most of that came from metal smelting. The data did not include some potentially significant arsonic sources associated with herbicides, fertilizers, other mining facilities, and electric utilities.

REMOVAL MECHANISMS

At the regulated maximum arsenic level of 10 ppb, the U.S. EPA estimated that 5% of all U.S. community water systems would have to take corrective action to lower the current levels of arsenic in their drinking water. In high arsenic areas of the world, the need for removal from water supplies is even more acute.

Due to their predominance in natural waters, arsenic(V) acid (H_3AsO_4) and arsenous(III) acid ($HAsO_2$) and their salts can serve as the model for these and alkylated species for consideration of removal mechanisms. The pK values of arsenic acid = 2.26, 6.76, 11.29 (10) and arsenious acid = 9.29 (10) or 8.85 (11) are of prime importance in determining the degree of ionization at the pHs of the water from which removal strategies are considered. It is readily apparent that at a natural pH of 7 to 8, arsenic acid is extensively ionized as the divalent ion; arsenious acid remains largely un-ionized.

Due to the ionic charge, arsenate(V) is more easily removed from source waters than arsenite(III). In particular, activated alumina, ion exchange, and reverse osmosis may achieve relatively high arsenate removal rates, but they show lower treatment efficiencies for arsenite. Elevating the pH such as by caustic injection into reverse osmosis system feedwater would be one approach to greater removal of arsenite(III) compounds. Arsenite can also be oxidized to arsenate to improve removal efficiencies. In water that contains no ammonia or total organic carbon, chlorine rapidly (in less than 5 seconds at chlorine concentrations of 1.0 mg/L) oxidizes approximately 95% of arsenite to arsenate. Monochloramine at a concentration of 1.0 mg/L oxidized 45% of arsenite to arsenate. Potassium permanganate performs this oxidation rapidly; oxygen does so slowly unless activated by light and sensitizer.

In contrast to other heavy metals, As^{3+} and As^{5+} are not precipitated as hydroxides, only as sulfides. Alkyl and arylarsonic acids are precipitated by quadrivalent metals such as tin, thorium, titanium, and zirconium. The tendencies of dissolved arsenic species to adsorb on inorganic particle surfaces such as iron, ferric hydroxide, iron oxide, alumina, sulfur, and sulfides allow for removal strategies involving fixed-bed reactors or adsorption/coagulation/filtration schemes. Sulfate, fluoride, and phosphate ions are known to be strong competitors of arsenic adsorption in some systems.

BIBLIOGRAPHY

1. Matschullat, J. (2000). Arsenic in the geosphere—a review. *Sci. Total Environ.* **249**(1–3): 297–312.
2. Tchounwou, P.B., Wilson, B., and Ishaque, A. (1999). *Rev. Environ. Health* **14**(4): 211–229.
3. Various reports available from the US-Environmental Protection Agency website: www.epa.gov/safewater/arsenic.html and the World Health Organization website: www.who.int/water_sanitation_health/water_quality/arsenic.htm.
4. Basu, A., Mahata, J., Gupta S., and Giri, A.K. (2001). *Mutat. Res.* **488**(2): 171–194.
5. Gebel, T.W. (2001). *Int. J. Hyg. Environ. Health* **203**(3): 249–262.
6. Nimick, D.A., Moore, J.N., Dalby, C.E., and Savka, M.W. (1998). *Wat. Res. Research* **34**(11): 3051–3067.
7. US-Environmental Protection Agency. (2000). *Arsenic Occurrence in Public Drinking Water Supplies*, EPA-815-R-00-023, December 2000, available from EPA Website (Ref. 3).
8. Tamaki, S. and Frankenberger, W.T., Jr. (1992). *Rev. Environ. Contam. Toxicol.* **124**: 79–110.
9. Shibata, Y., Morita, M., and Fuwa, K. (1992). *Adv. Biophys.* **28**: 31–80.
10. Lide, D.R. (Ed.). (1995). *CRC Handbook of Chemistry and Physics*, 76th Edn. CRC Press, New York, pp. 8–43.
11. Meites, L. (Ed.). (1963). *Handbook of Analytical Chemistry*. McGraw-Hill, New York, pp. 1–29.

EVALUATION OF MICROBIAL COMPONENTS OF BIOFOULING

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Detecting the occurrence of biofouling and assessing its impact involve a range of analytical techniques, including informed observation and inspection of well components, interpretation of hydraulic and water quality testing, and direct analysis of microbial components of biofouling. The latter is the subject of this article.

SYMPTOMS: INDIRECT ANALYSIS

Symptoms can be used as qualitative indicators of biofouling but not specifically of the microbial component. Observable symptoms include the following:

- clogging (both formation/well and pump/discharge systems).

- corrosion
- alteration of water quality in pumped samples
- distinct coating on surfaces visible during inspections, such as borehole television surveys.

Such symptoms are indications of biofouling and should trigger analysis to determine the nature of the biofouling.

DIRECT ANALYSIS OF MICROBIAL BIOFOULING AND COMPONENTS

Standard Methods

Some existing "standard methods" for analyzing aspects of biofouling are described in:

- ASTM Test Method for Iron Bacteria in Water and Water-Formed Deposits (D 932) (1)
- Section 9240—Iron and Sulfur Bacteria, *Standard Methods for the Examination of Water and Wastewater* (APHA-AWWA-WEF, currently 20th ed. Supplement) (2).
- Additional *Standard Methods* (Part 9000) microbiological methods (and others accepted by technical and regulatory bodies) for analysis of heterotrophic bacteria and specific groups of interest such as the total coliform group. All relevant aquatic and public health microbiological methods are applicable in identifying microbiological components of biofouling.
- Microscopic particulate analysis (MPA) ((2), consensus method) can identify biofilm components as part of its larger scope and represents a systematic approach.

Microscopic Examination and Analysis. The presence of filamentous (e.g., *Leptothrix, Thiothrix,* or *Crenothrix*) or stalked (*Gallionella*) iron or sulfur bacterial forms is accepted as a positive indicator of biofouling. Examination by light microscopy has traditionally been the method of choice for confirming and identifying these "iron bacteria" or "sulfur bacteria" (1,2). However, the absence of such visible structures does not necessarily mean the absence of biofouling:

1. Samples may not include enough recognizable materials to provide the basis for a diagnosis of biofouling.
2. Samples examined may not include the filamentous or stalked bacteria normally searched for in such analyses. It is generally understood that the morphologically distinct types are only part of the biofouling present.
3. Analysts vary in their skill and opinions in interpreting what they see.

In addition, the existing standard microscopic tests (1,2) are specified as qualitative. Attempts have been made to quantify degrees of biofouling by microscopy. However, spatial variations and the pulsating, three-dimensional nature of active biofilms make them unreliable (4). An available semiquantitative method using microscopy is described by Barbic et al. (5).

Culturing Methods for Detection. Culturing enriches biofouling microflora that cannot be identified microscopically and helps provide more complete information on the nature of biofilm samples. It can also be used to draw reasonable conclusions about biofouling in the absence of microscopy. *Standard Methods* (2) describes a range of media formulations, and more for other purposes are found in other sections of Part 9000. With regard to Section 9240 formulations, a number of limitations have been identified. These weaknesses have all been recognized by the *Standard Methods* Section 9240 joint technical group:

- No reported effort has been made to standardize these media with reference cultures from well water. Thus the efficiency of recovery of iron-precipitating bacteria from groundwater samples remains unknown at present (4) but is probably very low.
- Except for the modified Wolfe's medium for *Gallionella* enrichment (6), the environmental conditions for growth in these media do not seem to match well with groundwater environmental conditions (7,8).
- Useful Mn-precipitation media have been one area of weakness in common practice (7), although they are being refined (9).
- The available sulfur oxidizer media are still nonisolating, enrichment media.
- Employment of all of these culture methods requires preparation from raw materials (no packaged agar or broth media specific to IRB are available), sterilization, and maintenance in a microbiological laboratory by a skilled person. Thus, they are rarely used in operational practice.

Cultural Media Improvements. An important innovation of the last 20 years in biofouling cultural recovery has been the development of prepackaged cultural media that permit (1) practical use in operational monitoring in addition to more academic analyses and (2) recovery of a range of microflora, resulting in a more complete understanding of the microbial ecology of wells and more refined maintenance and management of water quality (see entry GW-1311 Well Maintenance). Two groups using slightly different approaches developed these methods independently:

MAG Method (MAG Laboratorio Ambiental, La Plata, Argentina). MAG tests for heterotrophic iron-related bacteria (IRB) and sulfate-reducing bacteria (SRB) consist of a prepared liquid medium contained in small septum bottles (10,11). The MAG medium for iron-related heterotrophic bacteria (BPNM-MAG) uses ferric ammonium citrate [like W-R and R2A + FAC (7)] and the SRB medium (BRS-MAG) uses Postgate C medium under a reducing atmosphere, supplemented with iron filings (11). Inoculation of a single bottle provides a presence-absence (P-A) result. Dilution to extinction provides a semiquantitative (MPN) result (11).

BART Method. Currently, the most commonly used cultural approach for routine biofouling monitoring is the Biological Activity Reaction Test (BART^{TM}) Method (Droycon Bioconcepts Inc., Regina, Saskatchewan).

- BART tubes contain dehydrated media formulations and a floating barrier device, which is a ball that floats on the hydrated medium of the sample.
- These devices and their proposed use are described in detail in Cullimore (12). They can be used as an enrichment method to provide a presence-absence (P-A) or semiquantitative (MPN) detection of biofouling factors (7,12–14).

BART tubes are available in a variety of media mixtures. The IRB-BART^{TM} test, for example, is designed to recover microaerophilic heterotrophic Fe- and Mn-precipitating microorganisms and is (like the BPNM-MAG test) derived from the W-R iron bacteria medium (15). This method, which is gaining wide operational acceptance as a means of detecting and characterizing biofouling symptoms, has provided useful qualitative information in well biofouling in various field trials (7) and has proven useful in a range of applications.

These methods have proved to be significant advances in making microbial ecology an important factor in routine operational monitoring as they

1. Reliably provide results to the level of detection needed to make operational decisions.
2. Are relatively easy to use and interpret.
3. Offer a means for precise scientific characterization of the microbial system if properly used and interpreted within their limitations.

At present, neither of these systems is included in *Standard Methods*, although they have become operationally de facto standard methods within the water operational and hydrogeologic communities (16). A definitive comparability test among these and various *Standard Methods* media is yet to be conducted.

Hybrid Methods. A subcategory of cultural methods consists of field-usable enrichment procedures to increase the potential for successful detection by microscopy. For example, Alcalde and co-workers (10,17) describe a simple enrichment and staining technique to enhance the numbers and visibility of filamentous bacteria on glass slides.

Nonculturing Biofouling Analytical Methods. All cultural enrichment methods recover only a fraction (1% is an often cited value) of microflora in environmental samples. Employing a range of cultural media and using media that better approximate ideal growth conditions (and making them easier to use) helps to overcome these problems; however, many microflora types may remain unrecoverable. Nonculturing analytical methods that directly detect interpretable evidence of microflora bypass these limitations.

Phospholipid Fatty Acid (PLFA) or Phospholipid Fatty Acid Methyl Ester (PL-FAME) Analysis. The method described by White and Ringelberg (18,19) and its variations provide a nonculturing method of characterizing the microbial components of environmental samples (solids such as sediment cores as well as fluids). In PLFA or PL-FAME, "signature" lipid biomarkers from the cell membranes and walls of microorganisms are extracted from the sample. Particular types of biomarkers are linked to groups of microorganisms. Amounts of biomarkers can be reliably associated with viable biomass, and compound ratios can be linked to community nutritional status. Once extracted from cells with organic solvents, the lipids are concentrated and fractionated using gas chromatography/mass spectrometry (GC/MS). A profile of the fatty acids and other lipids is then used to determine the characteristics of the microbial community. This "fingerprint" represents the living portion of the microbial community because phospholipids degrade rapidly following cell death (20).

A variation is TC-FAME (total-cell FAME), in which the lipids of whole cells are extracted and characterized from microbial isolates. These fatty acid profiles are compared to libraries of known isolates to identify unknowns in environmental samples or pure cultures.

Adenosine Triphosphate (ATP) and Adenylate Kinase (AK) Detection. ATP is ubiquitous in cellular life and can be detected rapidly using bioluminescence methods. The ATP bioluminescence test (21), detects ATP, which is present only in living cells. The amount of light emitted in the reaction can be correlated with the amount of ATP that can be extracted from a known number of bacteria. The test is rapid (<1 minute) and can be conducted with convenient test kits. Differences in ATP amounts occur by cell type and by growth phase and nutrient availability (22), and 10^5 cells/mL is the lower detection limit, requiring concentration for lower concentrations (*Standard Methods* Section 9211 C). The AK test detects a cellular enzyme (adenylate kinase-catalyzing ATP) that is present at a fairly consistent level in cells of all growth phases except spores, and the process (also rapid) can detect cells at 10 cells/mL (22). These tests are primarily useful in determining the total numbers of cells in a sample. What this means depends on the nature of the sample, but the ATP or AK result can be used for comparisons and in making operational or treatment decisions.

Nucleic Acid Testing. To identify biofouling microbial constituents definitively, genetic testing is used. Nucleic acids extracted are compared to libraries of sequences. Among the most useful procedures in groundwater microbial analysis is 16S rRNA community structure analysis (20). This method permits identifying microbes within complex environmental samples (such as biofilms), typically expressed as percent homology with known groups, but it is possible to identify isolates to the strain level.

Analytical Choice Considerations

All available analytical methods have their limitations. Fortunately, the strengths and weakness of microscopy and cultural enrichment appear to be complementary (7), so they are best used in tandem. The best use of BART or MAG methods is as indications of:

1. early detection or confirmation of probable biofouling and MIC conditions,
2. the presence of viable bacterial types in both liquid and extracted or eluted solids samples, and
3. relative "aggressivity" or activity of biofouling and corrosion-inducing communities.

Standard or heterotrophic plate counts (HPC) have often been used in water analysis for quantitative results. The validity of HPC has been called into question on the viability issue and because agar plates are an osmotically hostile environment. The actual organisms recovered in HPC testing can also vary widely among locations, seasons, and consecutive samples at a single location (23). Also, unamended HPC media tell little about what the recovered bacteria are doing in the environment. For these reasons, cultural methods developed for biofouling analysis are preferred, but HPC can be used if calibrated for specific applications and as a gauge to interpret some BART or MAG results.

PL-FAME provides a nonculturing method that can reliably assay the types of microflora (some of which are nonviable or dormant) in a range of samples, including biofilm samples, and their relative health and vigor. ATP/AK methods provide rapid cells-per-unit counts of living microflora reliable within a margin of error, which can also be conducted under field conditions in certain circumstances.

Where genetic identification is important (as when pathogen presence is suspected or to be ruled out), 16S rRNA analysis identifies all bacterial types. Both PL-FAME and 16S rRNA analyses are relatively expensive, although information-rich.

Sampling Methods

A serious limitation in biofouling monitoring is that recovering "representative" samples of biofouling microflora is difficult. Pumped (grab) sampling is the easiest way to obtain samples for analysis from wells or sample taps in pipelines. However, if pumping fails to detach and suspend biofilm particles, they will not be available for collection and analysis. Thus, a presumption of "probably absent" based on lack of recovery of microscopically visible particles (per Section 9240 or D 932) or cultural recovery may be a false negative. To improve the odds in recovery, it is useful to employ one or more of the following:

1. Filtration or centrifugation as recommended in *Standard Methods* increases the odds of recovering material useful for microscopic identification.
2. Time-series sampling: Cullimore (12) describes a time-series pumped-sampling procedure (similar to familiar procedures for groundwater quality analysis) that attempts to overcome the randomness of grab sampling. The time-series sampling approach, which includes taking replicates of samples at each sampling step, helps to overcome the statistical limitations of random, pumped, grab sampling for culture analysis.
   - This information can be used in assessing the microbial ecology in the well and the aquifer adjacent to the well (12). This procedure can be incorporated into a step-drawdown pumping test procedure.
   - Analysis of samples taken at various points in a groundwater-source system (flow-series instead of time-series) permits developing a profile of the microbial ecology of the system.
3. Collection of a biofilm on immersed surfaces can provide essentially intact biofilms for analysis. These methods are also adaptable for collecting samples of inorganic encrustations.

Several experimental designs for collecting biofilm organisms have been presented in the literature since at least the 1920s. Recent methods and equipment for biofilm coupon collection are summarized in Smith (7).

Sampling methods are closely linked to analytical methods:

- Pumped sampling is used for cultural enrichment (MAG or BART) or noncultural analysis of water (e.g., PL-FAME or ATP/AK).
- Time-series or flow-series sampling permits spatial analysis of results.
- Collection on surfaces is preferred for microscopy samples.
- Collection of solids provides samples that can be examined microscopically or extracted for culturing (qualitative) and nonculturing assay.
- All are practical in the operational setting (7,24).

PRACTICAL ISSUES IN MAINTENANCE MONITORING IMPLEMENTATION AND INTERPRETATION

Successful control of biofouling and associated changes in water quality, such as increased turbidity or alteration of metals content, depends very much on preventive or early warning monitoring (see MW-76, Well Biofouling and GW-1311, Well Maintenance). Among applications of microbiological analysis, biofouling monitoring of groundwater systems is a case study of methods in transition attempting to meet user needs. In contrast to available detection methods for microflora of concern to human health, convenient methods yielding information useful to formulate a response to biofouling have not been readily available to operators of groundwater systems until very recently.

At present, biofouling analytical methods remain at best semiquantitative and offer results that require expert interpretation. Consistency in usage and cross-correlation with other information (e.g., biochemical, physicochemical water quality and mineralogy) are keys to extracting the maximum information from biofouling analysis for a particular situation.

BIBLIOGRAPHY

1. ASTM D 932. *Test Method for Iron Bacteria in Water and Water-Formed Deposits*. American Society for Testing and Materials, West Conshohocken, PA.
2. APHA-AWWA-WEF. (1998). Section 9240. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. American Public Health Assn., Washington, DC.
3. U.S. EPA, 1992. *Consensus Method for Determining Groundwaters Under the Direct Influence of Surface Water Using Microscopic Particulate Analysis*, Method 910992029. Office of Drinking Water, Washington, DC.
4. Tuhela, L., Smith, S.A., and Tuovinen, O.H. (1993). Flow-cell apparatus for monitoring iron biofouling in water wells. *Ground Water* **31**: 982–988.
5. Barbic, F., Bracilovic, D., Djorelijevski, S., Zivkovic, J., and Krajincanic, B. (1974). Iron and manganese bacteria in Ranney wells. *Water Res.* **8**: 895–898.
6. Hanert, H.H. (1981). The genus *Gallionella*. In: *The Prokaryotes: A Handbook on Habitats, Isolation and Identification of Bacteria*, M.P. Starr et al. (Eds.). Springer-Verlag, Berlin, Chap. 40, pp. 509–521.
7. Smith, S.A. (1992). *Methods for Monitoring Iron and Manganese Biofouling in Water Supply Wells*. AWWA Research Foundation, Denver, CO.
8. Hallbeck, L. (1993). *On the Biology of Iron-Oxidizing and Stalk-Forming Bacterium Gallionella ferruginea*. Department of General and Marine Microbiology, University of Göteborg, Göteborg, Sweden.
9. Emerson, D. and Ghiorse, W.C. (1992). Isolation, cultural maintenance, and taxonomy of a sheath-forming strain of *Leptothrix discophora* and characterization of manganese-oxidizing activity associated with the sheath. *Appl. Environ. Microbiol.* **58**: 4001–4010.
10. Alcalde, R.E. and Gariboglio, M.A. (1990). Biofouling in Sierra Colorado water supply: A case study. *Microbiol. Civ. Eng., FEMS Symp. No. 59*, P. Howsam (Ed.). E.& F.N. Spon, London, pp. 183–191.
11. Gariboglio, M.A. and Smith, S.A. (1993). *Corrosión e encrustación microbiológica en sistemas de captación y conducción de agua - Aspectos teóricos y aplicados*. Consejo Federal de Inversiones, San Martin, C.F., Argentina.
12. Cullimore, D.R. (1993). *Practical Ground Water Microbiology*. CRC Lewis, Boca Raton, FL.
13. Mansuy, N., Nuzman, C., and Cullimore, D.R. (1990). Well problem identification and its importance in well rehabilitation. In: *Water Wells Monitoring, Maintenance, and Rehabilitation*, P. Howsam (Ed.). E.&F.N. Spon, London, pp. 87–99.
14. Walter, D.A. (1997). *Geochemistry and Microbiology of Iron-Related Well-Screen Encrustation and Aquifer Biofouling in Suffolk County*, Long Island, New York, Water Resources Investigation Report 97-4032. U.S Geological Survey, Coram, NY.
15. Cullimore, D.R. and McCann, A.E. (1977). The identification, cultivation, and control of iron bacteria in ground water. In: *Aquatic Microbiology*, F.A. Skinner and J.W. Sewan (Eds.). Academic Press, New York, pp. 219–261.
16. Smith, S.A. (1996). Monitoring biofouling in source and treated waters: Status of available methods and recommendation for standard guide. In: *Sampling Environmental Media*, ASTM STP 1282, J.H. Morgan, (Ed.), American Society for Testing and Materials, West Conshohocken, PA, pp. 158–175.
17. Alcalde, R.E. and Castronovo de Knott, E. (1986). *Occurrence of iron bacteria in wells in Rio Negro (Argentina)*, *Proc. Int. Symp. Biofouled Aquifers: Prevention and Restoration*, D.R. Cullimore (Ed.), American Water Resources Association, Bethesda, MD, pp. 127–136.
18. White, C.D. and Ringelberg, B.D. (1992). *Signature Lipid Biomarker Analysis*. Center for Environmental Biotechnology Standard Operating Procedures. University of Tennessee, Knoxville, TN
19. White, D.C. and Ringelberg, D.B. (1997). Utility of the signature lipid biomarker analysis in determining the *In Situ* viable biomass, community structure, and nutritional/physiological status of deep subsurface microbiota. In: *The Microbiology of the Deep Terrestrial Subsurface*, P.S. Amy and D.L. Haldeman (Eds.). CRC Press Lewis, Boca Raton, FL, pp. 119–136.
20. USEPA NRMRL undated. *Innovative measures of treatment performance*. National Risk Management Research Laboratory, U.S. EPA, Cincinnati, OH.
21. Picciolo, G.L., Chapelle, E.W., Deming, J.W., Thomas, R.R., Nible, D.A., and Okrend, H. (1981). *Firefly luciferase ATP Assay Development for Monitoring Bacterial Concentration in Water Supplies*, EPA-600/S2:81-04. U.S. Environmental Protectional Agency, Cincinnati, OH.
22. Biotrace International (2003). Biochemical Indexes, Issue Ref MLM177 TEP004 Issue no. 002, Biotrace International. http://www.biotrace.com.
23. WHO (2002). *Heterotrophic Plate Count Measurement in Drinking Water Safety Management*, WHO/SDE/WSH/02.10. Report of an expert meeting, Geneva, April 24–25, 2002, World Health Organization, Geneva.
24. Smith, S.A. (1995). *Monitoring and Remediation Wells: Problems Prevention and Cures*. CRC Lewis, Boca Raton, FL.

THREAT AGENTS AND WATER BIOSECURITY

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THE NATURE OF THE THREAT

This article focuses on biological agents that can be maliciously introduced into potable water supplies and emphasizes those that would most likely be used, what the state of knowledge is on disinfection and/or inactivation protocols, and existing methods for detecting these agents.

The anthrax bioterror event that occurred in the eastern United States in the fall of 2001 provided graphic evidence of the considerable economic and public health impact that deliberate release of a pathogenic agent could engender, even in a technologically advanced nation. The event brought increased awareness of the perils of threat agents to public health and security personnel and led to the implementation of methods to determine when these agents may be present and to ameliorate their effects. The water industry (here used to refer principally to potable water suppliers) has been no exception; as part of the Public Health Security and Bioterrorism and Response Act (H.R. 3448) of 2002, all utilities providing water to 3300 people or more are required to have an emergency response plan in the event of a terror attack on their infrastructure.

In the light of the increased demands these new regulations make on the water industry, it is reasonable to ask, how real is the threat? Undoubtedly, some information on this topic is classified and not available to the general public, but there are indications that militant Islamic groups, such as Al Qaeda, are contemplating the use of threat agents and/or chemicals to compromise potable water supplies in the United States. Accordingly, managers and supervisors of water utilities may find it prudent to have some knowledge of potential threat agents, how they can be detected, and how they may be removed or inactivated when found.

THREAT AGENTS THAT MAY BE INTRODUCED INTO WATER SUPPLIES

Traditional lists of biological threat agents include both viruses and bacteria and the toxins that may be elaborated by some of these organisms. The list of viruses usually includes hemorrhagic fever- and encephalitis-causing viruses such as Venezuelan equine encephalitis (VEE), Ebola virus (EB), and Rift Valley fever virus (RVF). Perhaps the most worrisome virus is smallpox (Variola), enormous quantities of which were created by a clandestine bioweapons program in the former Soviet Union. Most of the world's population lacks immunity to smallpox and would thus be exceptionally vulnerable to infection (1).

Bacterial agents (and their diseases) include *Yersinia pestis* (plague), *Bacillus anthracis* (anthrax), *Francisella tularensis* (tularemia), *Coxiella burnetii* (Q fever), and *Burkholderia pseudomallei* (glanders or melioidosis). The category of toxins includes staphylococcal enterotoxins A and B; the botulinum toxin of *Clostridium botulinum*; ricin; which is produced by the castor bean; and trichothecene mycotoxins, which are extracted from fungi and gained notoriety in the late 1970s as the "yellow rain" used by Soviet-supplied forces in battlefields in Cambodia and Laos (2).

SURVIVAL OF THREAT AGENTS IN WATER

Generally, little is known about the survivability of threat agents in chlorinated or nonchlorinated water, how readily they disperse in water, and whether exposure to water alters their infectivity for the worse (or better, as the case may be). Conducting experiments with virulent strains of threat agents almost always requires use of dedicated Biosafety Level 3/4 laboratory facilities, which places sizeable constraints on the ability to carry out assays to answer these questions. Therefore, it often is necessary to extrapolate data derived from work done with related species, or avirulent strains, of these threat agents.

Some bacterial species that can be used as threat agents are "naturally" encountered in water and have been implicated in small but well-studied disease outbreaks. A waterborne outbreak of tularemia occurred in Chlumcany, Czech Republic, in 2000; 96 people became ill and contaminated water, used for drinking and food preparation, was the vehicle of infection (3). Other documented cases of tularemia linked to contaminated water were observed in Kosovo (4) and Norway (5), and it was hypothesized that an outbreak of oropharyngeal tularemia in Turkey in 2001 was caused by ingestion of nonchlorinated reservoir water (6). Laboratory experiments conducted by Forsman et al. (7) found that cells could be cultured in water devoid of carbon sources and maintained at 8 °C for up to 70 days postinoculation, indicating that *F. tularensis* can survive immersion in an aquatic environment for an appreciable length of time.

Outbreaks of melioidosis have been linked to the ingestion of water contaminated with *Burkholderia pseudomallei*; in Australia in 1997, seven culture-confirmed cases were identified in a small (300 people) rural community served by capped borehole wells 2 km distant (8). Chlorine levels in potable water samples were undetectable prior to the presumed exposure period, reflecting failure to treat water adequately before consumption.

A helpful overview of the ability of conventional water chlorination/disinfection protocols to inactivate threat agents is summarized in Burrows and Renner (9). The ability of some pathogens, such as spores of *B. anthracis*, to remain viable following typical chlorination regimens is a troubling but unavoidable facet of dealing with incidents of bioterorrorism aimed at potable water distribution networks (Fig. 1).

Note that for some agents, exposure to chlorine is bacteriostatic rather than lethal; though log reductions in the numbers of viable bacteria may be achieved, a remnant population may survive and can grow when chlorine concentrations decrease. For example, after 30 minutes of exposure, two strains of *B. pseudomallei* survived exposure to 1000 ppm chlorine; another could survive 300 ppm, but not 500 ppm (10). The utility of alternative methods, for such as chloramines, ozone, peroxides, UV radiation, metal ions, and electrochemistry, water disinfection may offer distinct advantages over chlorine (11). However, the paucity of experiments using actual threat agents requires us to extrapolate results achieved with conventional waterborne pathogens to gain insight as to how well these methods would inactivate species such as *B. anthracis, F. tularensis*, and poxviruses.

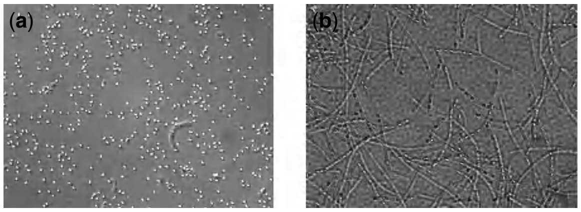

Figure 1. Nomarski interference contrast microscopy images of *Bacillus anthracis* Sterne strain spores: panel A, the comma-shaped organism in the center of the image is a vegetative cell, and vegetative cells (panel B), 1000X magnification (panel A photograph, courtesy of Jeffrey Karns).

MONITORING WATER FOR THREAT AGENTS: RECOVERY FROM SOURCE AND FINISHED WATERS

Successful monitoring of source and finished waters for threat agents is a two-component process: first, the organisms must be removed or isolated from the water samples, usually via filtration or other selective separation protocols. Second, the recovered organisms must be detected and their identity confirmed with a sufficient degree of reliability and accuracy to allow water utility managers to make decisions with confidence.

Approaches to establishing potable water security must deal with three segments of the water delivery system: the source water supply, the water purification/treatment facility, and the distribution network that brings water to individual buildings and homes. The water industry has considerable expertise in detecting select pathogens in source water, such as *Giardia* and *Cryptosporidium*, via protocols such as the U.S. EPA Method 1623, which involves capsule filter-mediated recovery of oocysts from 10 L volumes of water. However, source waters may contain appreciable numbers of naturally occurring flora that can confound detection efforts; they may also contain high concentrations of particulate matter that can impede filtration protocols for pathogen recovery from large volumes of water.

Recovery of viral threat agents presents greater difficulties than for bacterial agents because they are considerably smaller (except for poxviruses, which may approach 0.2–0.3 μm in length) and require culture in living cells to reproduce. As with protozoa, the water industry, private and academic laboratories, and agencies such as the U.S. EPA, have made considerable efforts to develop protocols for isolating enteric viruses from large volumes of water, and these protocols may be useful in dealing with agents such as poxviruses and hemorrhagic fever viruses.

Little is known about the behavior of biological toxins in source waters, particularly when large quantities of the toxins may be deliberately introduced into reservoirs close to intake pipes. The stability of toxins in such an environment is poorly understood. However, larger utilities continuously monitor source water for chemical contaminants (metals, organics, solvents, etc.) and provide some measure of confidence in the industry's ability to adapt preexisting assays for detecting threat toxins. Analytical chemistry protocols, such as gas or liquid chromatography and mass spectrometry, as well as immunoassays and bioassays, can be used in a comprehensive monitoring strategy (12).

Monitoring operations at the second and third segments of the water delivery system—the purification facility and the distribution network—are more difficult targets for bioterror attacks, because they have a more highly supervised structure and offer fewer opportunities for unobserved, deliberate introduction of pathogens. However, deliberate contamination at these segments of the delivery system has far more troubling aspects than for source waters because the infectious dose is comparatively more concentrated in finished water and this water is destined for direct (and indirect) consumption by the public. However, by containing disinfecting agents, "in plant" finished water is less likely to permit survival of infectious agents; by the time it reaches the household tap, potable water may support pathogen viability. For example, in experiments conducted in collaboration with Dr. Kalmia Kniel at the University of Delaware, we have found that raccoonpox virus can survive over two month's exposure in tap water, as measured by its ability to cause lytic infection of Vero cells. These experiments are preliminary, but they indicate a need to learn more about poxvirus survival in finished water (Fig. 2).

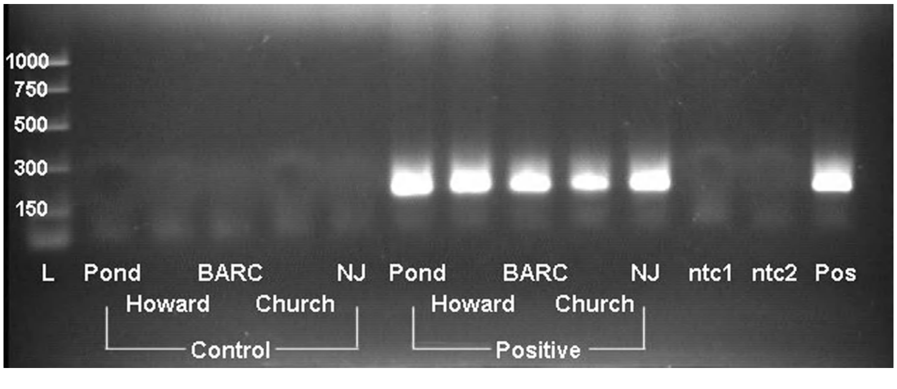

Figure 2. Polymerase chain reaction (PCR) assay conducted on Vero cell supernatant following infection with raccoonpox virus (RPV). RPV ($\sim 1 \times 10^6$ plaque-forming units) was incubated in 2 mL volumes of water from various sources: pond water and water from taps in Howard County, Maryland; the Beltsville Agricultural Research Center (BARC), Maryland; and a home in New Jersey, for 70 days at room temperature. Two hundred μL portions of the water were then mixed with a cell culture medium and applied to Vero cells for 1 hour; after that the medium was replaced and the Vero cells maintained at 37 °C and 5% CO_2. The supernatant (200 μL) was collected after 5 days and subjected to DNA extraction and nested PCR using the hemagglutinin primers of Ropp et al. (13). Control samples represent unspiked tap water samples. Lanes ntc1 and ntc2 represent PCR negative controls and lane Pos is the PCR positive control. Lane L is the DNA ladder, with rung sizes indicated.

MONITORING WATER FOR THREAT AGENTS: IDENTIFYING THREAT AGENTS

Once threat agents have been recovered from source or potable waters, they must be identified. Note Despite significant advances in detection technologies, sponsored in large part by U.S. government Department of Defense research initiatives, there is no single method currently that can reliably and reproducibly detect all potential threat agents in water samples in real time with any appreciable degree of sensitivity and specificity. The lack of such a method obviously presents the water industry with major challenges in monitoring potable water supplies for potentially harmful organisms and/or toxins.

Detection methods can be classified into three broad categories; the first includes traditional detection methods, which offer some advantages: they are often relatively inexpensive to perform, require modest training of the individuals performing the tests, and have standardized methods that have been reproduced by many laboratories over lengthy periods of time. For bacterial pathogens such as anthrax, traditional methods involving culture of vegetative cells on agar, the appearance and morphology of colonies on the agar, and the light microscopy features of the cells comprising the colonies offer a convenient and affordable means to monitor water for this agent (Fig. 3).

The same approach can be used with some degree of success for *Francisella and Burkholderia*, among others. As always, the type of water sampled can influence the sensitivity and specificity of the detection method; when closely related waterborne flora can be mistaken for threat agents, traditional methods must be augmented by other detection protocols to avoid generating false-positive results.

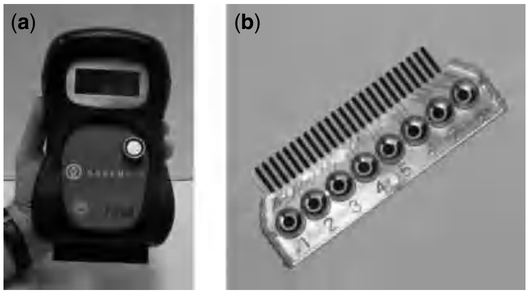

Figure 4. The Anzenbio PDS-8 instrument is a novel platform for field-based detection of toxins and pathogens. The detector (panel A) can be held in one hand and presents data to the end user via the inset LCD screen. The biosensor chip (panel B) is part of a disposable cartridge that is inserted into the detector. Up to six different samples (plus one positive and one negative control) can be analyzed on the chip, using a proprietary antibody-mediated, electrochemical format. The assay can be completed in as few as 2 hours (photo courtesy of Linda Williams, Anzenbio).

The second category of detection approaches involves immunologic methods, which are mediated by antibodies; the formats for such methods can be quite varied and include enzyme-linked immunosorbent assay (ELISA), immunochromatographic lateral flow assay, immunomagnetic separation-electrochemiluminescence (IM-ECL), and time-resolved fluorescence assay (14). Compared to traditional protocols, antibody-based detection methods provide greater specificity and sensitivity, timeliness, and ease of

Figure 3. Photograph of bacterial colonies grown from stream water spiked with spores of *B. anthracis* Sterne strain on red blood cell agar plates. The large black arrow indicates a colony of *B. anthracis*; the smaller black arrow indicates a colony of a related *Bacillus* spp. Note the lytic zone surrounding this colony, a feature that can be used to differentiate between colonies of *anthracis* and those of other spore-forming members of waterborne flora.

use. Emerging technologies in this field seek to miniaturize the assay to the point where it can be done in the field or on site; one example of such an emergent technology is provided in Fig. 4.

Immunologic methods for the detecting bacterial, protozoal, and viral pathogens have been reported in the literature; in one of the more recent reports, Tims and Lim (15) detected purified *B. anthracis* spores in less than one hour, using a portable fiber-optic biosensor. Immunologic methods are particularly useful in detecting toxins, which are often proteins and thus not easily amenable to molecular biology-based detection (16).

Immunologic assays do possess some drawbacks. The specificity of the antibodies used to mediate detection is a critical factor; too poor a specificity means that false-positive signals can be generated from organisms that are closely related to the pathogen of interest. And, in general, antibody-based assays may not provide as great a degree of sensitivity as their molecular counterparts.

Molecular biology-based assays, such as PCR, have come into the forefront of pathogen detection technologies. By targeting regions of DNA intrinsic to particular species or strains of microorganisms, molecular methods can provide a high degree of specificity and sensitivity. There is a substantial and ever-increasing body of scientific literature on the use of molecular techniques for detecting and characterizing conventional waterborne pathogens. Many water quality laboratories in the United States, Europe, Australia, and Asia now use these methods routinely and readily adopt new instrumentation and procedures as their testing needs evolve.

Drawbacks of molecular detection techniques include high setup and maintenance costs, which translate into a higher cost per assay than traditional protocols, and the need for more training for laboratory personnel. Nonetheless, the enhanced detection capability of molecular protocols has led to their adoption by U.S. Department of Defense agencies as the first choice for threat agent identification. A detailed recitation of existing threat agent detection protocols is beyond the scope of this article; readers are directed to the paper by Firmani and Broussard (17) for a comprehensive overview of this evolving topic.

FUTURE DIRECTIONS FOR BIOSECURITY OF WATER RESOURCES

As this article is written in early fall 2004, there are encouraging signs that government agencies responsible for regulating water quality are moving to enhance the ability of the industry to respond to threats directed against water resources.

One of these efforts is being mounted by the U.S. EPA, which in July 2004 began testing three competing platforms for the rapid detection of threat agents in water under the aegis of the Environmental Technology Verification (ETV) program. All three platforms, the Idaho Technology, Inc. Ruggedized Advanced Pathogen Identification Device (RAPID), the Applied Biosystems 7000 Sequence Detection System, and the Agilent Bioanalyzer used by Invitrogen Corporation, rely on PCR to mediate amplification and identification of pathogen DNA in real time. These instruments will be tested by the Battelle laboratory's Advanced Monitoring Systems Center using the bacterial threat agents *Bacillus anthracis, Francisella tularensis, Brucella suis, E. coli*, and perhaps *Yersinia pestis*. The platform performing best in sensitivity and specificity may be designated the rapid detection method of choice for utilities and agencies contemplating enhancements of their biosecurity capabilities.

Other U.S. EPA initiatives, such as the Water Quality Protection Center and the Drinking Water Systems Center, are working to provide the industry with up-to-date technologies for providing safe and wholesome water to their customers. Industry organizations such as the International Water Association, the American Water Works Association, the Water Environment Foundation, the European Water Association, and the Australian Water Association are actively funding research and development to provide improved biosecurity resources to their subscribers. All of these developments should assist water quality managers as they deal with the challenge presented by this potential threat to human health.

BIBLIOGRAPHY

1. McClain, D.J. (1997). Smallpox. In: *Medical Aspects of Chemical and Biological Warfare*. F.R. Sidell, E.T. Takafuji, and D.R. Franz (Eds.). Borden Institute, Washington, DC, pp. 539–559.
2. Wannemacher, R.W., and Wiener, S.L. (1997). Trichothecene mycotoxins. In: *Medical Aspects of Chemical and Biological Warfare*. F.R. Sidell, E.T. Takafuji, and D.R. Franz (Eds.). Borden Institute, Washington, DC, pp. 665–676.
3. Pazdiora, P., Moravkova, I., Nocarova, D., Velkoborska M., and Valeckova, K. (2002). A waterborne epidemic of tularemia in Chlumcany. *Epidemiol. Mikrobiol. Immunol.* **51**: 23–25.
4. Reintjes, R. et al. (2002). Tularemia outbreak investigation in Kosovo: Case control and environmental studies. *Emerg. Infect. Dis.* **8**: 69–73.
5. Hoel, T., Scheel, O., Nordahl, S.H., and Sandvik, T. (1991). Water- and airborne *Francisella tularensis* biovar palaearctica isolated from human blood. *Infection* **5**: 348–350.
6. Gurcan, S., Tatman-Otkun, M., Otkun, M., Arikan, O., and Ozer, B. (2004). An outbreak of tularemia in Western Black Sea region of Turkey. *Yonsei Med. J.* **45**: 17–22.
7. Forsman, M., Henningson, E., Larsson, E., Johansson, T., and Sandstrom, G. (2000). *Francisella tularensis* does not manifest virulence in viable but non-culturable state. *FEMS Microbiol. Ecol.* **31**: 217–224.
8. Inglis, T. et al. (1999). Acute melioidosis outbreak in Western Australia. *Epidemiol. Infect.* **123**: 437–443.
9. Burrows, W.D. and Renner, S.E. (1999). Biological warfare agents as threats to potable water. *Environ. Health Perspect.* **107**: 975–984.
10. Howard, K. and Inglis, T. (2003). The effect of free chlorine on *Burkholderia pseudomallei* in potable water. *Water Res.* **37**: 4425–4432.
11. Morato, J., Mir, J., Codony, F., Mas, J., and Ribas, F. (2003). Microbial response to disinfectants. In: *The Handbook of Water and Wastewater Microbiology*. D. Mara and N. Horan (Eds.). Elsevier, New York, pp. 657–693.

12. Gullick, R.W., Grayman, W.M., Deininger, R.A., and Males, R.M. (2003). Design of early warning monitoring systems for source waters. *J. Am. Water Works Assoc.* **95**: 58–72.
13. Ropp, S.L., Jin, Q., Knight, J.C., Massung, R.F., and Esposito, J.J. (1995). PCR strategy for identification and differentiation of smallpox and other orthopoxviruses. *J. Clin. Microbiol.* **33**: 2069–2076.
14. Peruski, A.H. and Peruski, L.F., Jr. (2003). Immunological methods for detection and identification of infectious disease and biological warfare agents. *Clin. Diagn. Lab. Immunol.* **10**: 506–513.
15. Tims, T.B. and Lim, D.V. (2004). Rapid detection of *Bacillus anthracis* spores directly from powders with an evanescent wave fiber-optic biosensor. *J. Microbiol. Methods* **59**: 127–130.
16. Kijek, T.M., Rossi, C.A., Moss, D., Parke, R.W., and Henchal, E.A. (2000). Rapid and sensitive immunomagnetic-electrochemiluminescent detection of staphylococcal enterotoxin B. *J. Immunol. Methods* **236**: 9–17.
17. Firmani, M.A. and Broussard, L.A. (2003). Molecular diagnostic techniques for use in response to bioterrorism. *Expert Rev. Mol. Diagn.* **3**: 605–616.

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GRANULAR ACTIVATED CARBON

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Activated carbon is the generic term used to describe a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. Activated carbon is distinguished from elemental carbon by the removal of all noncarbon impurities and the oxidation of the carbon surface (1). Activated carbon has the highest volume of adsorbing porosity of any substance known to humans (5 grams of activated carbon can have the surface area of a football field). It can be defined as (2):

> Activated carbon is a crude form of graphite, with a random or amorphous structure, which is highly porous, over a broad range of pore sizes, from visible cracks and crevices, to cracks and crevices of molecular dimensions.

The use of activated carbon is not new. The Egyptians used carbonized wood around 1500 B.C. as an adsorbent for medicinal purposes as well as a purifying agent. The ancient Hindus in India used charcoal for filtration of drinking water. However, the basis for industrial production of active carbons was established in 1900–1901 in order to replace bone char in the sugar refining process (3).

Active carbons can be prepared from a wide range of carbonaceous materials, which include coconut shells, wood char, lignin, petroleum coke, bone char, peat, saw dust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, and waste rubber tire. (Table 1). The range of raw materials is diverse and widespread and greatly influenced by the need to produce low-cost carbon. Among the most commonly used raw materials, precursors for the production of commercially activated carbons are wood (130,000 tons/year), coal (100,000 tons/year), lignite (50,000 tons/year), coconut shell (35,000 tons/year), and peat (35,000 tons/year) (4,5).

TYPES OF ACTIVATED CARBONS

Based on the physical properties, activated carbons can be classified into the following broad categories:

Powdered Activated Carbon (PAC)

These activated carbons are made in the powders or fine granules according to the requirement. Powdered activated carbons have a diameter between 15 and 25 μm. These carbons provide a large internal surface with a small diffusion distance.

Granular Activated Carbon (GAC)

Granular activated carbon (GAC) is commonly used for the purification of liquids and gases. Granular activated carbon adsorbs a vast variety of dissolved organic materials, including many that are nonbiodegradable. GAC removes organic contaminants from water/wastewater by the adsorption process of the attraction and accumulation of one substance on the surface of another. Granular activated carbons typically have surface areas of 500–2000 m^2/g, with some reported as high as 3000 m^2/g. Much of the surface area available for the adsorption in granular activated carbon particles is found in the pores within the granular carbon particles created during

Table 1. Source Materials Used for the Preparation of Activated Carbons

Bagasse
Bark
Beat-sugar sludge
Blood
Blue dust
Bones
Carbohydrates
Cereals
Coal
Coconut coir
Coconut shell
Coffee beans
Corn Cobs and corn stalks
Cottonseed hulls
Distillery waste
Fertilizer waste slurry
Fish
Fruit pits
Fuller's earth
Graphite
Human hairs
Jute stick
Kelp and seaweed
Leather waste
Lignin
Lignite
Lampblack
Leather waste
Molasses
Municipal waste
News paper
Nut shells
Oil shale
Olive stones
Palm tree cobs
peat
Petroleum acid sludge
Petroleum coke
Potassium ferrocynide residue
Pulp-mill waste
Reffination earth
Refinery waste
Rice hulls
Rubber waste
Saw dust
Scrap tires
Spent Fuller's earth
Sunflower seeds
Sugar-beet sludge
Tea leaves
Rubber Tires
Wheat straw
Wood

the activation process. GAC have relatively larger particle sixes than powdered activated carbon and therefore provide a smaller external surface. These carbons are preferred for all the sorption of gases and vapors. GAC are also used in water/wastewater treatment, deodorization, decolorization, and separation of components in flow systems.

Spherical Activated Carbon (SAC)

These carbons are prepared from small spherical balls wherein pitch is melted in the presence of naphthalene or tetorlin and converted into spheres. These spheres are then contacted with naptha solution, which extracts naphthalene introduced into the porous structure. These porous spheres are then heated between 100 and 400 °C in the presence of an oxidizing agent. The oxidized spheres are then heated between 150 and 700 °C in the presence of ammonia to introduce nitrogen into spheres followed by activation in steam or CO_2.

Impregnated Activated Carbon (IAC)

In chemical activation, a catalyst may be impregnated into the feedstock. The most commonly used chemical activants include $ZnCl_2$, H_3PO_4, H_2SO_4, KOH, K_2S, and KCNS. In this process, a near-saturated solution of catalyst-impregnated feedstock is dried to influence pyrolysis in such a way that tar formation and volatilization can be kept at a minimum. The resulting product is then carbonized. Silver impregnated activated carbons are used for purification of domestic water.

Polymer Coated Activated Carbons (POAC)

In this process, porous carbon can be coated with biocompatible polymers resulting in a smooth and permeable coat without blocking the pores. It is well documented in literature that activated carbons possess a highly developed porous system. These pores are produced during the activation process of carbonized residue when spaces between elementary crystalline are cleared of carbonaceous compounds and nonorganized carbon.

The precursors used for the production of activated carbons have a large effect on the pore size distribution, surface area, and other physical and chemical properties. Table 2 sums up some of the basic differences between the raw materials used for the production of some important activated carbons, whereas the properties of some commercially available carbons with their sources as collected from literature are presented in Table 3.

METHODS FOR ACTIVATED CARBON DEVELOPMENT

The methods for the development of activated carbons are nearly as widespread as their potential uses and source materials (6). However, the basic steps most commonly used in the preparation of activated carbons are precursor material preparation, palletizing, low-temperature carbonization, followed by chemical or physical activation (Fig. 1). A number of methods were used for the preparation of activated carbons from waste materials from time to time using different activation parameters. Different steps/activation parameters used for the preparation of some of the activated carbons are presented in Table 4. Although the list is not complete, it will provide a general idea of the different methods used for the production of activated carbons.

Raw Materials

The selection of an appropriate raw material (Table 1) for the development of granular activated carbon is the most important aspect. The following points must be considered before selecting any raw material for the production of activated carbons:

1. Industrially inexpensive materials with high carbon and low inorganic content should always be preferred.
2. The impurities in raw materials should be kept at a minimum because after the activation process, many of these may be present in the carbon at higher concentrations than the precursors materials.
3. Importance should be given to the precursors having high density and sufficient volatile content. The volatile results in porous char, whereas high density favors the enhancement of structural strength of the carbon needed to withstand excessive particle crumble during use.
4. The raw material should be available in abundance locally.

The raw materials used for the preparation of activated carbons vary with their applications. A comparison of some of the raw materials is presented in Table 2.

Table 2. Basic Differences in Precursor Materials Used for the Production of Activated Carbons

Raw Materials	Percent Carbon	Percent Volatile Matter	Ash Percent	Density (kg/m3)	Activated Carbon Texture	Applications
Hard wood	40–42	55–60	0.25–1.2	0.50–0.8	Soft with large pore volume	Liquid phase adsorption
Soft wood	40–45	55–60	0.25–1.0	0.40–0.50	Soft with large pore volume	Liquid phase adsorption
Nut shells	40–45	55–60	0.40–0.60	1.4	Hard with large multi pore volume	Vapor phase adsorption
Lignite	50–70	25–40	5–6	1.0–1.40	Hard with small pore volume	Liquid phase adsorption
Soft coal	60–80	25–30	2–12	1.25–1.50	Medium hard with medium micropore volume	Liquid and vapor phase adsorption
Semihard coal	70–75	1–15	5–15	1.45	Hard with large pore volume	Vapor phase adsorption
Hard coal	85–95	5–10	2–15	1.50–2.0	Hard with large pore volume	Vapour phase adsorption

Table 3. Properties of Some Selected Activated Carbons Gathered from the Literature

Types of Carbons	Raw Material	Surface Area, BET (m^2/g)	Total Pore Volume (ml/g)	Iodine Number (mg/g)	Ash (%)	Uniformity Coefficient	pH_{zpc}	Moisture as Packed (%)	Effective Size, mm	Apparent Density
F-100	Bituminous coal	850–900	—	850		2.1	9.0	2	0.8–1.0	—
F-200	Bituminous coal	714	—	850		1.9	8.2	2	0.55–0.75	—
F-300	Bituminous coal	950–150	0.85	900	9	2.1	9.8	2	0.8–1.0	0.5 g/cc
F-400	Bituminous coal	1050–1200	0.94	1000	5.4	1.9	10.40	2	0.55–0.75	27
F-816	Bituminous coal	—	—	900	9	1.4	—	2	1.3–1.5	—
F-820	Bituminous coal	—	—	900	—	1.5	—	2	1.0–1.2	—
Centaur HSV	Bituminous coal	—	—	800	7	—	—	4	—	0.56 g/cc
Nuchar SN	Wood	1400–1800	—	900	3–6	—	4.0	10	—	337–369 (kg/m^3)
Nuchar SA	Wood	1400–1800	—	900	3–6	—	4.0	10	—	337–369 (kg/m^3)
Nuchar W	Wood	1400–1600	—	900	—	—	—	10	—	240–305 (kg/m^3)
HD-4000	Lignite coal	625	0.93	647	23	1.44	—	8	0.74	0.40 g/ml
Draco KB	Hard wood	1500	1.8	—	2	—	—		—	0.45 g/cc
Norit GAC 840 R	Reactivated Carbon	—	—	800	—	—	—	2	—	0.48 g/cc
Norit PAC 20 B	Coal	—	—	800	—	—	—	3	—	
HD-C	Lignite coal	556		500		—	—	4	—	0.51 g/cc
Norit GAC 1240	coal	1100	0.95	1020		1.8	—	2	—	0.50 g/cc
Barnebey & Sutcliffe SE	Coconut shell	1100–1200	—	1050	2–3	—	—	—	—	—
Barnebey & Sutcliffe PE	Coconut shell	1100–1200	—	1050	2–3	—	—		—	—
Barnebey & Sutcliffe KE	Coconut shell	1150	—	—	5	—	—		—	0.48 g/cc
Barnebey & Sutcliffe UU	Coconut shell	1150	—	—	5	—	—	5	—	0.4–0.8 g/cc
Pica POU/POE GX203	Coconut shell carbon	700–2200	—	1150	5	—	—	5	—	0.45–0.54 g/cc
Pica POU/POE NC 506	Coconut shell carbon	700–2200	—	1100	4	—	—	3	—	0.41–0.45 g/cc
Cameron PACarb	Resinous wood charcoal	—	—	500	8	—	—	3	—	0.45 g/cc
Selecto ABA 4000 LC		300–500	0.35–0.55	—	—	—	—		—	—
Witco 517	Petroleum	1050	—	1000	0.5	1.4	—	1	0.89	0.52 g/cc

Carbonization

Carbonization, sometimes called charring, converts the organic material into primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalline carbon.

In carbonization, the material is heated slowly in the absence of air. In this process, most of the noncarbon elements, hydrogen, and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting materials. The important parameters, which determine the quality and quantity of the carbonized product, are (a) rate of heating, (b) final temperature, and (c) soaking time.

Activation

The activation is carried out basically to enlarge the diameters of the pores, which are created during the carbonization process, and to create some new porosity, which results in the formation of a well-defined and readily accessible pore structure with large internal surface area. During the activation process, the spaces between the elementary crystallites become cleared or less organized loosely bound carbonaceous material. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphite planes constitute the porous structure, with large internal surface area (24). There are two types of activation, which are used to impart a porous structure within a starting material of relatively low surface area, namely thermal/physical or chemical activation.

Physical or Thermal Activation. Physical or thermal activation occurs after initial treatment and palletizing; it involves carbonization at 500–600 °C to eliminate the bulk of the volatile matter followed by partial gasification using mild oxidizing gas such as CO_2, steam, or fuel gas at 800–1000 °C to develop the porosity and surface area (25). An example includes the gasification of the carbonized material with steam, and carbon dioxide occurs by the following endothermic reactions:

$$C + H_2O \longrightarrow CO + H_2 \text{ (29 kcal)}$$

$$C + CO_2 \longrightarrow 2CO \text{ (39 kcal)}$$

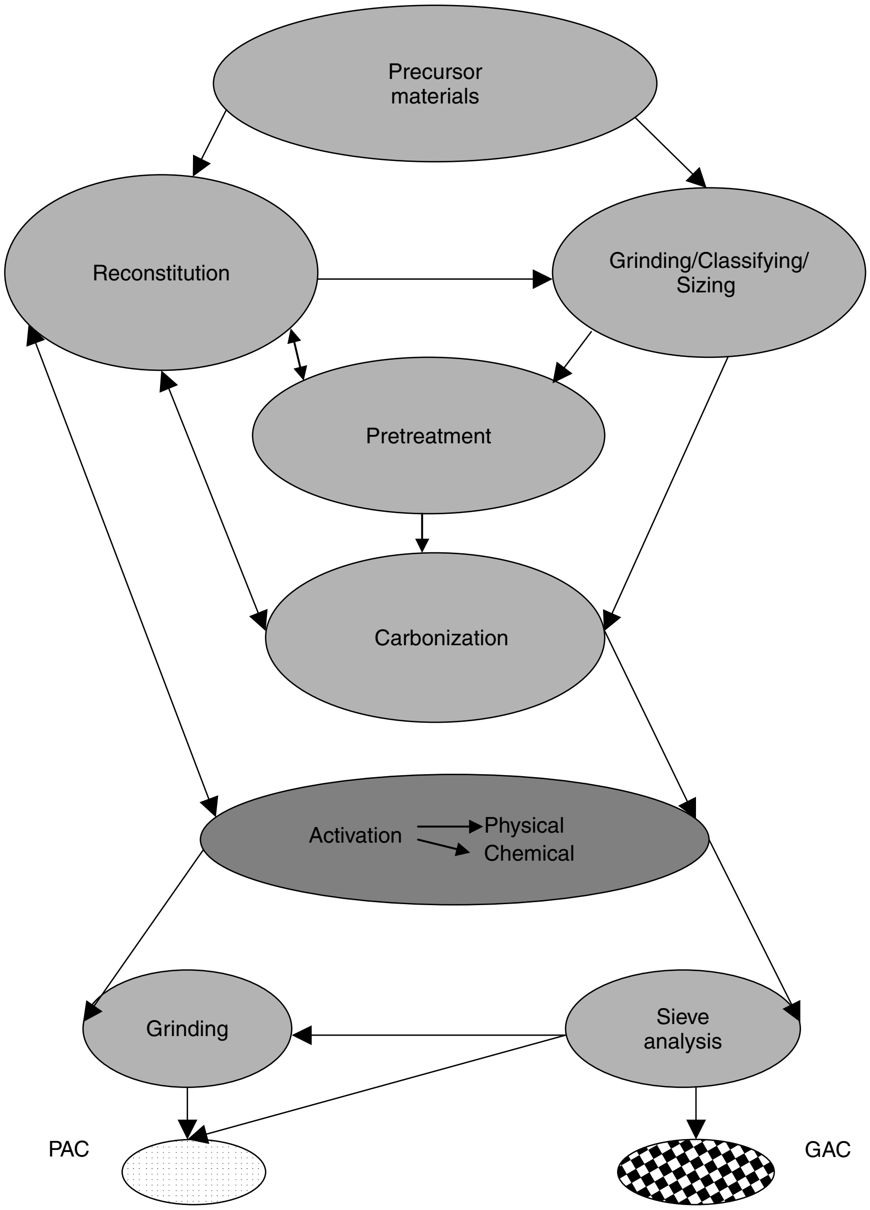


Figure 1. Various steps used in the activated carbon production.

$$CO + H_2O \longrightarrow CO_2 + H_2 \text{ (10 kcal)}$$

The H_2O molecule is smaller than the CO_2 molecule and thus diffuses faster into the pores of the carbon. Consequently, a reaction with steam is faster than that of CO_2. It has been reported in literature that a decrease in the reaction rate with CO_2 activation on carbon-containing wastes is nearly two times less than that of steam. When air or oxygen is used as an activating agent, problems develop because of the exothermic nature of the reactions of carbon with air (oxygen), and thus it is difficult to control. Despite these problems, several researchers have used the same for the activation of their products.

Chemical Activation. The second type of activation involves the incorporation of inorganic additives or metallic chlorides, such as zinc chloride or phosphoric acid, into the precursor before the carbonization (6). It has been reported that carbons with well-developed porous structure, mainly meso and microporous, can be produced by $ZnCl_2$ incorporation. KOH activation has also been shown to successfully increase the surface area and pore volume of active carbons (20,26)

Many other chemicals, such as ammonium salts, borates, calcium oxide, ferric and ferrous compounds, manganese dioxide, nickel salts, hydrochloric acid, nitric acid, and sulfuric acid, have also been used for the activation purpose.

The basic difference between physical and chemical activation is the number of stages required for activation and the temperature at which the activation takes place. Chemical activation is a one-step process, whereas physical activation is a two-step process, including carbonization and activation. The temperature required in physical activation (800–1000 °C) is higher than that of chemical activation (200–800 °C).

Table 4. Some Chemical Activant-Feedstock Couples [Extended Form of (4)]

Feedstock	Activant	Conditions	Reference
Coconut shell	Con. H_2SO_4	1.5 parts by weight H_2SO_4 for 24 hrs at 140–160 °C: steam activation at 1 Kg/m^2 pressure for 30 min.	7
Agricultural by products such as almond shell, olive stones and peach stones	—	Heating in CO_2 at 1123K	8
Coconut shell	Con. H_2SO_4	1.0 parts by weight H_2SO_4 for 24 h at 150 °C	9
Fertilizer slurry	H_2O_2/H_2O, N_2	450 °C, 1 h	10
Palm tree cobs	H_3PO_4/H_2SO_4	730 °C, 6 h	11
Coconut shell	H_3PO_4	450 °C	12
Petroleum coke	KOH/H_2O	700–850 °C, 4 h	3
Raffination earth	H_2 SO_4	10% v/v,350 °C	13
Algerian coal	KOH/NaOH	930 °C	14
Pine saw dust	$Fe(NO_3)_3/CO_2$	850 °C, 1 h; 825 °C, 6 h	15
Almond and pecan shells	H_3PO_4	Chemical activation with H_3PO_4/Physical CO_2	16
Eucalytus woodchars	—	CO_2 activation, 400–800 °C	17
Bituminous coal	$ZnCl_2$	N_2/400–700 °C	18
Coal or coconut shell		Phosgene or chlorine gas at 180 °C	19
Petroleum coke	KOH	Dehydration at 400 °C followed by activation in 500–900 °C	20
Lignite	Na_2MoO_4/ $NaWO_4$/ NH_4VO3/ $(NH_4)_2MoO_4$/ $FeCl_3$/ $Fe(NO_3)_3$	Inert atmosphere/600–800 °C	21
Peanut hulls	H_2SO_4	150 °C, Sodium bicarbonate	22
Coconut shell and cocnut shell fibers	H_2SO_4	600 °C	23

Thus, the activated carbons can be prepared by either physical/chemical activation or a combination of both with well distributed porosity and high surface area.

Characterization of GAC

The effectiveness of activated carbon as a unit process in the treatment of water/wastewater/industrial effluents requires the best selection of an appropriate activated carbon. Following are some of the important properties used for the selection of suitable activated carbon for specific treatment:

Density. The density of carbon can be expressed in several different ways. The two most important among these are apparent and particle densities.

Apparent Density. Apparent density has little role in initial evaluation of an activated carbon, but it has an important role in the regeneration process. It is defined as the mass of carbon per unit volume that can be packed into an empty column. It is expressed in grams per cubic centimeter or pounds per cubic foot.

Particle Density. Particle density is defined as the ratio of the mass of dry and unloaded carbon particles to the total volume of the particles, including pore volume.

Higher density GAC is preferred because of the following reasons:

1. High density GAC has more carbon structure.
2. The high density GAC figured that, for each cubic meter of volume, more GAC could be installed.
3. Bituminous coal-based GAC provides a much denser material than lignite or subbituminous coal.

Moisture. It is important only for shipping and manufacturing purposes. It is defined as the percent by mass of water adsorbed on activated carbon.

Hardness and Attrition. It is an important factor in system design, filter life, and product handling. Large differences exist in the hardness of activated carbons, depending on the raw materials used and activity level (Tables 2 and 3). It is defined as the resistance of a granular activated carbon to the degradation action of steel balls in a Ro–Tap machine. It is calculated by using the mass of granular carbon retained on a particular sieve after the carbon has been with steel balls.

Sieve Analysis. It is very useful in carbon production evaluation. It is also important in the evaluation of purchased carbon to the specifications. The distribution of particle sizes in a given sample is obtained by mechanically shaking a weighed amount of activated carbon through a series of test sieves and determining the quantity retained by or passing given sieves.

Abrasion Number. The abrasion number is important in evaluating the ability of a carbon to withstand attrition. It is defined as a measure of the resistance of the particles to degrade on being mechanically abraded, which is measured by putting a carbon sample with steel balls in a pan on a Ro–Tap machine. In other words, it is defined as the ratio of the final average (mean) particle diameter to the original average (mean) particle diameter times 100.

Ash Percent. The ash percent is very important in the evaluation of the raw materials and the manufacturing process. It is the residue that remains when the carbonaceous portion is burned off. The ash contained mainly has silica, alumina, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered to be an impurity. It can be measured by the change in weight by burning the carbon sample to constant weight at 800 °C.

pH. The effect of the carbon on pH of a volume of water is very much dependent on the relative quantities of both activated carbon as well as water. The pH effect can be studied by putting 1.0-gram carbon with 50 ml of de-ionized water and heating to 90 °C followed by cooling to 20 °C and measuring the pH of the supernatant.

Effective Size, Mean Particle Diameter, and Uniformity Coefficient. It is used to establish the hydraulic conditions of an adsorber column. Measurement of the gradation of carbon particles plays an important role in the evaluation of head loss in the flow through granular beds. The mean particle diameter can be calculated as follows:

First the average particle diameter (d) of each sieve used for the particle distribution is calculated by using the following equation:

$$d = w \times n$$

where w is the percent of the total weight retained by a particular sieve and n is the average of the mesh opening of the sieve that contained w and the sieve used immediately above.

By using this d, the mean particle diameter can be calculated as:

$$\text{Mean particle diameter} = \text{sum of all diameters divided by } 100$$

It is very important to note here that the smallest sieve is not considered in calculating the mean particle diameter.

The effective size can thus be calculated by using the cumulative percentage of carbon passing each size and plotting the sieve opening in millimeters (ordinate) versus the cumulative percentage (abscissa) on a semilogarithmic scale. Thus, the effective size is the opening in millimeters, which passes 10% of the total material. The 60% passing sieve size divided by the effective size gives the uniformity coefficient. The 50% passing sieve size is approximately the mean particle diameter. The uniformity coefficient is basically a dimensionless factor, which indicates the degree of uniformity of GAC. A value of one indicates that all parameters are identical in size, whereas greater values relate to a higher degree of variation.

Surface Area. Total surface area is very important to characterize porous solids. Large surface area is generally a requirement for a good adsorbent. However, the total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species. Surface area determination relies on the accurate knowledge of the average area. It is determined by the sorption of nitrogen gas into the carbon and is expressed in square area per gram of carbon. The most widely accept method is the BET nitrogen adsorption method.

Pore Size Distribution. Activated carbon is a complex network of pores of different sizes and shapes. The shapes include cylinders, rectangular cross sections, and other irregular shapes and constrictions. The identification of different sizes is called the pore size distribution.

The pore size distribution is very much dependent on the source materials and method of activation. According to IUPAC accepted criteria (27), activated carbons have a trimolecular distribution of pore sizes (Fig. 2), as discussed below.

Macropores. These are the pores having diameter greater than 50 nm (Fig. 2). Their pore volume varies from 0.2 to 0.5 cm^3/g and surface area lies between 0.5 and 2 m^2/g. Such low value of surface area renders them of little use in adsorption except for large adsorbate molecules.

Mesopores. These pores have diameter ranging between 2 nm and 50 nm (Fig. 2). The pore volume of these pores varied from 0.02 to 0.01 cm^3/g. The surface area constituted by these pores lies between 10 and 100 m^2/g. The capillary condensation with the formation of a meniscus of adsorbate mainly takes place in these pores.

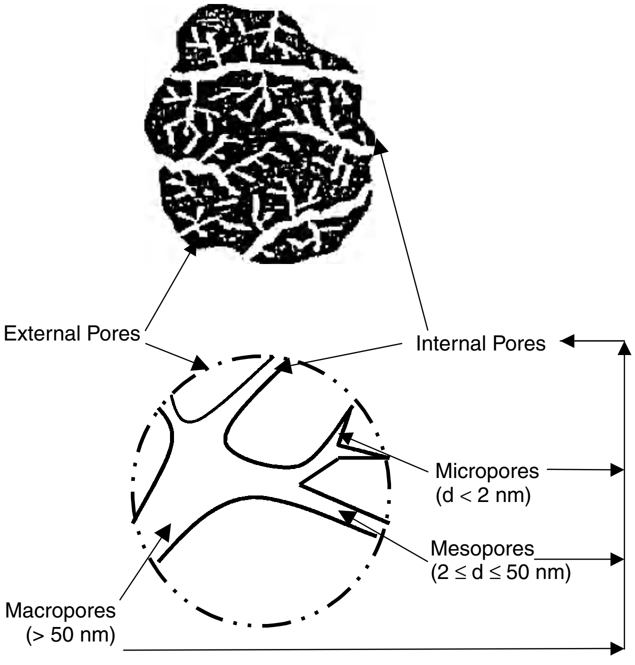
Micropores. These pores have diameter less than 2 nm (Fig. 2). Their size generally corresponds to that of molecules. The value of these pores ranges from 0.15 to 0.5 cm^3/g and surface area lies between 100 and 1000 m^2/g. They constitute about 95% of the total surface area. These pores are of great significance as far as adsorption studies are concerned.

Besides these, two different types of pores are exist in some of the carbons.

Ultramicropores. These pores have diameter <0.7 nm.

Supermicropores. These pores have diameter between 0.7 and 2 nm.

In practice, total pore volume is calculated by measuring three distinct volumes associated with one gram of the material at a constant temperature. These three distinct volumes are:



Where d represents diameter

Figure 2. Schematic activated carbon structure.

(a) the volume of its purely solid structure
(b) the external geometrical volume of the solid
(c) the volume of a given fluid that it can displace

Thus, the total pore volume can be given by the difference between (b) and (a).

Iodine Number. It is defined as the number of milligrams of iodine adsorbed by one gram of activated carbon when the iodine concentration of the residual filtrate is 0.02N.

The iodine number provides an indication of the amount of small pores in carbon. It is correlated with the surface area in pores with diameters less than 10 Å. As iodine is a small molecule, it provides an indication of a particular carbon's capacity to adsorb smaller molecules.

Molasses Number. The molasses number represents the amount of large pores in carbon. It is calculated from the ratio of the optical densities of the filtrate of a molasses solution treated with a standard activated carbon and one in question. The molasses number can be correlated with the surface area in pores with diameters greater than 10 Å.

Both the iodine number and the molasses number decrease with time as adsorption occurs.

Methylene Blue Number. It is defined as the number of milligrams of methylene blue adsorbed by one gram of activated carbon in equilibrium with a solution of methylene blue dye having concentration 1.0 mg/L.

Phenol Number. Phenol number has been found to be a less sensitive test as it is very much effected by pH of the actual water used. It is very well documented in literature that at low pH, phenol adsorption is much greater than at neutral or alkali pH.

SURFACE CHEMISTRY OF ACTIVATED CARBON

The type of starting material and the method of activation used in producing activated carbon determines the nature of various surface functional groups. The surface chemistry of carbon has been studied extensively by several investigators from time to time. The nature of the carbon surface basically depends on the conditions and temperatures employed during the activation process. Activated carbon can be divided into two major types, namely acidic (L) and basic (H), according to Steenberg's classification (1) and can be defined as follows:

L Carbons

These carbons are prepared by heating the raw materials at about 200–400 °C in the presence of air. These carbons assume a negative charge (ionized) upon hydration and, thus, yielding acidic pH, are hydrophilic in nature and can neutralize a strong base. These carbons generally develop acidic surface oxides and lower the pH value of neutral or basic solutions. They primarily sorb bases from the solutions and exhibit a negative zeta potential. Wood-based activated carbons are usually L type in nature. The predominant surface functional groups are carboxyl, phenolic hydroxyl, carbonyl (quinone type), carboxylic acid, anhydrides, lactone, and cyclic peroxide (28,29). It has been reported that carboxylic and lactone groups tend to discourage the adsorpion of many aromatic compounds (29). Carbonyl groups in the form of quinone structures, and hydroquinone groups, however, can enhance the adsorption of aromatic compounds by the formation of an electron donor-acceptor complex between the aromatic ring and the surface carbonyl groups (30,31).

H Carbons

The activated carbons are prepared by heating the raw materials at about 800–1000 °C in the absence of air or in the presence of CO_2 followed by exposure to air at room temperature. These carbons assume a positive charge (protonated) upon introduction into water, thus yielding alkaline pH. They are hydrophobic in nature and can neutralize strong acids. These carbons generally develop basic surface oxides and increase the pH value of neutral or acidic solutions. They primarily sorb strong acids from the solutions and exhibit a positive zeta potential. Coconut shell-based and dust coal activated carbons are usually H type in nature. The predominant surface functional groups on the surface of the carbons are lactones, quinones, phenols, and carboxylates. More reports of the chromene (benzpyran) groups on the surface of the carbon exist (32). Boehm and Voll (33) suggested that basic surface oxide may be represented by pyrone-like structures.

It is interesting to note that H-type carbons can be converted into L-type carbons when they are oxides by chemical oxidants or aged in the atmosphere.

The acidic groups on activated carbons are believed to be one of the most important properties of activated carbons for metal ions adsorption (34). The L-type carbon is a stronger solid acid than the H-type carbon, therefore L-type carbon is more efficient for the adsorption of heavy metal ions. Surface area is not a primary factor for adsorption on activated carbon. High surface area does not mean high adsorption capacity, as reported by Perrich, (35), because of the following factors:

(a) In adsorption, only the wetted surface area is effective, which is never equal to the total surface area.
(b) In some adsorption processes, the material to be adsorbed is too large that it cannot enter the small pores where the bulk of the surface area exists.
(c) Data on the surface area, pore volume, and surface nature usually have not been correlated with data on the material to be adsorbed.

The physical and chemical properties of the carbons are very much dependent on the properties of raw materials, method of carbonization, and activation. The properties of some selected carbons developed from different sources are given in Table 3. These properties are collected from various sources including books, literature, and company brochures.

ADSORPTION EQUILIBRIUM

To determine the ultimate adsorption capacity, the solutes are brought in contact with a given amount of activated carbon or any other adsorbent in a closed system. If adsorption is the dominating removal mechanism, then the residual concentration will be reached that will remain unchanged with time, which is also know as equilibrium concentration. This process is known as adsorption equilibrium.

The adsorption process is essentially an attraction of gaseous or liquid adsorbate molecules onto a porous adsorbent surface. In gaseous separations, activated carbon is often used to remove odors and impurities from industrial gases, to recover valuable solvent vapor, and to dehumidify air and other gases. In liquid separations, activated carbon can be applied for removing the taste and odor from water, decolorizing, and treating industrial wastewater containing organics, dyes, and heavy metal ions.

There are two types of adsorption processes.

Physical Adsorption

Physical adsorption is a reversible phenomenon. It results from the action of van der Waals forces, comprised of London dispersion forces and classic electrostatic forces of attraction between molecules of the carbon and the substance adsorbed (adsorbate). Physical adsorption is usually dominant at low temperatures. This type of adsorption is usually multilayered; i.e., each molecular layer forms on top of the previous layer, with the number of layers being proportional to the contaminant concentration.

Chemisorption

It is the result of chemical interaction between the carbon surface and the adsorbed substance. It usually involves strong bonds, and is therefore irreversible.

A number of factors exist that affect adsorption, including chemical properties of adsorbate and activated carbon, pH, and temperature of the adsorbate. Chemical adsorption is usually dominant at high temperatures because chemical reactions proceed more rapidly at elevated temperatures than at low temperatures.

The following factors affect the sorption of organics on activated carbons:

Hydrocarbon Saturation: Double- or triple-carbon bond (unsaturation) organics are adsorbed more easily than single-carbon bond (saturated) organics.

Molecular Structure: Branch-chain organics are adsorbed more easily than straight-chain organics.

Molecular Weight: Larger molecules are generally adsorbed more easily than smaller molecules.

Polarity: Less polar (or weakly ionized) organics are adsorbed more easily than polar (or strongly ionized) organics.

Solubility: Less soluble compounds are adsorbed more easily than more soluble compounds.

ADSORPTION *ISOTHERMS*

An adsorption isotherm is the relationship between the amount of a substance adsorbed on the activated carbon surface and the equilibrium concentration of dissolved adsorbate at a constant temperature and other conditions. An adsorption isotherm is an expression of the principle of microscopic reversibility, although adsorption can be irreversible. The most common method for gathering isotherm data is the bottle point experiment. These equilibrium data are formulated into an adsorption isotherm model. Brunauer et al. (36) pointed out that although the isotherms are different for all sorbents and sorbates, more or less common shapes of isotherms are observed. Six different types of isotherms (37) exist, which are named as type 1, type II, type III, type IV, type V, and type VI. The pictorial representation of the isotherms are given in Fig. 3.

Type 1

This type of isotherm is obtained from carbons having micropores only, which corresponds to monolayer adsorption as postulated by Langmuir. The volume of the gas adsorbed approaches a limiting value, just enough to complete a monomolecular layer even when the gas pressure is rather low. Further increases in pressure hardly produces any further increase in the amount of adsorption. These types of isotherms are typical of a microporous solid where only monolayer adsorption occurs. Examples include the

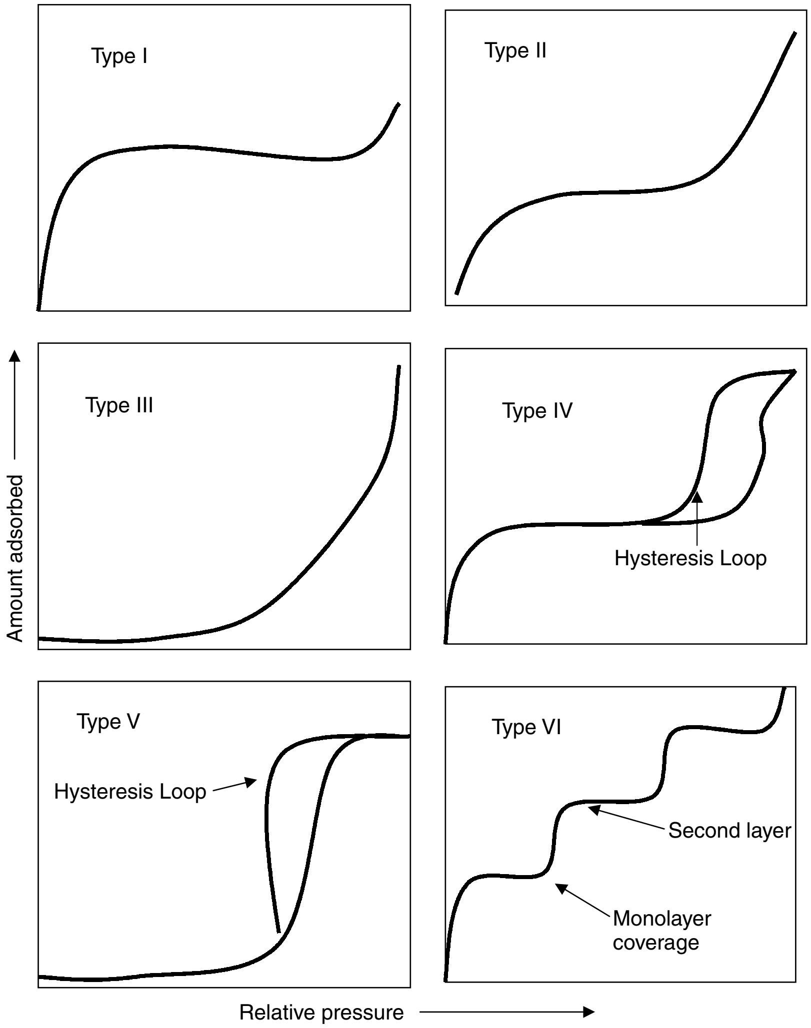


Figure 3. Type of isotherms.

adsorption of nitrogen or hydrogen on microporous carbon at temperatures close to −180 °C.

Type II

This type of isotherm describes the physical adsorption of gases by nonporous solids, and monolayer coverage is succeeded by multilayer adsorption at higher pressure. Examples include the adsorption of nitrogen on iron catalyst at −195 °C.

Type III

This type of isotherm is obtained from carbon having both micropores and mesopores. These types of isotherms show large deviations from the Langmuir model. The amount of adsorption keeps increasing in each case with an increase in pressure, which is attributed to the formation of additional layers of physically adsorbed gas molecules. It is considered that the gas molecules adsorbed in the first layer may hold by van der Waals forces a second layer of gas molecules, which, in turn, may hold a third layer and so on. The examples of type III isotherms include the adsorption of bromine on silica or alumina gel at 80 °C.

Type IV

This type of isotherm is obtained from both nonporous and mesoporous solids.

These are observed in the cases where a possibility of condensation of gases exists within the narrow capillary pores of the adsorbent. This phenomenon is also known as capillary condensation. Examples of type IV include adsorption of benzene on silica gel at 50 °C and that of water vapor on activated carbon at 100 °C.

Type V

This type of isotherm originates from microporous and mesoporous solids. Type V isotherms are basically related to type III isotherms and are very uncommon.

Type VI

This type of isotherm is obtained from uniform nonporous surfaces and represents stepwise multilayer adsorption. The sharpness of the steps depends on the system and the temperature. The step height represents the monolayer capacity for each adsorbed layer, and in the simplest case, it remains nearly constant for two or three adsorbed layers. Examples include the isotherms obtained with argon or krypton on graphitized carbon black at liquid nitrogen temperature.

APPLICATIONS OF ACTIVATED CARBONS

Activated carbons are produced in granular, powdered, and palletized forms and have a wide range of applications. The applications of activated carbon uses can broadly be divided into two categories.

Liquid-Phase Applications

Liquid-phase granular activated carbon adsorption (GACA) is an efficient, easy, and reliable treatment technology. It is very much different from gas-phase carbon as liquid-phase carbons have significantly more pore volume in the macropore range, which permits adsorbates to diffuse more rapidly into the micropores and mesopores. It is considered to be a best available control technology (BACT) by the U.S. Environmental Protection Agency (USEPA) and is a benchmark for other remediation technologies. In order for carbon adsorption to work well, it is important that the final design incorporate both the physical and adsorption process. In liquid-phase granular activated adsorption, activated carbon can be used either in powder, granular, or palletized forms. The average size of powder activated carbon ranges between 15 and 25 μm and are most frequently used in batch applications. On the other hand, the granular activated carbon particle size is normally 0.3–3.0 mm, and these are mostly used in continuous flow systems (fixed and moving bed). In this article, most of the discussion has been restricted to the liquid adsorption only.

Batch Systems. Generally, powdered activated carbons are used in batch systems. Batch system consists of contacting a whole volume of feed solution with a definite quantity of activated carbon in batch stirred vessels. The mixture is stirred or agitated to facilitate mass transfer. The important process design parameters can be calculated from laboratory batch adsorption isotherms, which precisely model the full-scale batch process. The batch adsorption processes are seldom used except in laboratories because they are highly inefficient compared with column adsorption processes and are therefore capital intensive and expensive to operate.

Various theoretical and empirical models have been proposed to describe the different types of adsorption isotherms in batch systems. The most commonly used models include Freundlich (38), Langmuir (39), and BET isotherms.

Freundlich Isotherm. The Freundlich adsorption isotherm model was given by Freundlich (38). This isotherm describes the equilibrium on heterogeneous surfaces and, hence, does not assume monolayer capacity

The Freundlich equation may be written as

$$q_e = K_F {C_e}^{1/n} \qquad \text{(Nonlinear form)}$$

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \qquad \text{(Linear form)}$$

where q_e is the amount of solute adsorbed per unit weight of activated carbon (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and 1/n is the constant indicative of the intensity of the adsorption.

Langmuir Isotherm. The Langmuir adsorption isotherm describes the surface to be homogeneous. The Langmuir adsorption isotherm assumed that all the adsorption sites have equal affinity for the molecules and that the adsorption at one site does not affect adsorption at an adjacent site (39,40).

The Langmuir equation may be written as

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \qquad \text{(Nonlinear form)}$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) \cdot C_e \qquad \text{(Linear form)}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q^0 is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption. It is the value reciprocal of concentration at which half the saturation of the adsorbent is reached.

BET Isotherm. The Brunauer, Emmett, Teller (BET) isotherm assumes the pertaining of a compound between liquid and solid compartments or phases. This isotherm assumes the multilayers adsorption of solute on activated carbon (36,40)

$$q_e = \frac{BCQ^0}{(C_s - C)[1 + (B-1)(C/C_s)]} \qquad \text{Nonlinear Form}$$

$$q_e = \frac{C}{(C_s - C)q_e} = \frac{1}{BQ^0} + \frac{B-1}{BQ^0}\frac{C}{C_s} \qquad \text{Liner form}$$

where q_e is the amount of adsorbate adsorbed per unit weight of activated carbon, B is the constant related to the energy of interaction with the surface, C is the equilibrium concentration of adsorbate in solution (mg/L or mol/L), Q^0 is the number of moles of adsorbate per unit weight of carbon to form a complete monolayer, and C_s is the saturation concentration of the adsorbate.

The limitations of the adsorption isotherms are as follows:

1. Isotherms are equilibrium tests, and therefore, the time restrictions are not considered.
2. Isotherms are based on carbon exhaustion—granular systems do not totally exhaust—and the entire bed contents.
3. Long-term chemical and biological effects are not evident.

Thus, batch equilibrium adsorption isotherm tests cannot simulate or predict dynamic performance directly.

Continuous Systems. In continuous systems, mostly granular activated carbons (GAC) are used. The fixed bed adsorber systems are most widely used for conducting adsorption operations where the adsorbate to be treated is passed through a fixed bed. In the fixed bed adsorber operation, a degree of separation and removal is achieved that would require many steps in a batch system. The parameters, which are required to establish a fixed bed reactor, include the type of carbon, physical and chemical characteristics of the carbon, column diameter, water/wastewater/effluents flow rate, pH of the effluent, carbon bed depth, weight of carbon, contact time, concentration of the influent, concentration of the effluent, and desired effluent concentration

When contaminated solute (warer/wastewater/effluents) is passed through a bed of granular activated carbon, a wave front or a mass transfer zone (MTZ) is formed by continuous adsorption of solute in the carbon bed. Figure 4 shows the change in concentration of adsorbed species on the surface of activated carbon with time. The solute is rapidly adsorbed on the top layers of the bed until the amount adsorbed is in equilibrium with influent solute concentration. At this particular time, that portion of the bed is exhausted. Below this zone is a second zone where dynamic adsorption is taking place. The solute is being transferred from the liquid to the adsorbed phase. This zone is known as mass transfer zone, and the depth of the zone is controlled by many fcators depending on the solute concentration being adsorbed, characteristics of activated carbon, and hydraulic factors.

A plot between the concentration of the adsorbate exhibits an S-shaped curve in the adsorption zone with ends asymptotically approaching zero and the influent concentration C_0. This curve is known as a *break through curve*. An ideal break through plot obtained for a fixed bed adsorber is depicted in Fig. 4. The solute or impurity is adsorbed very rapidly by the few initial upper layers of the fresh granular carbon during the initial stages of operation, as shown in Fig. 4. These upper layers are in contact with the sorbate/impurity at its highest concentration level, C_0. The small amounts of solute/impurity that escape adsorption in initial stages are adsorbed in the lower stages, and no solute escapes from the fixed bed adsorber initially ($C_1 = 0$).

FIXED BED ADSORBER

An adsorption process in which liquid being treated is allowed to pass through a carbon column in that carbon becomes exhausted and the unit is removed from service and completely recharged with fresh carbon. The carbon remains fixed in the position during the whole adsorption process.

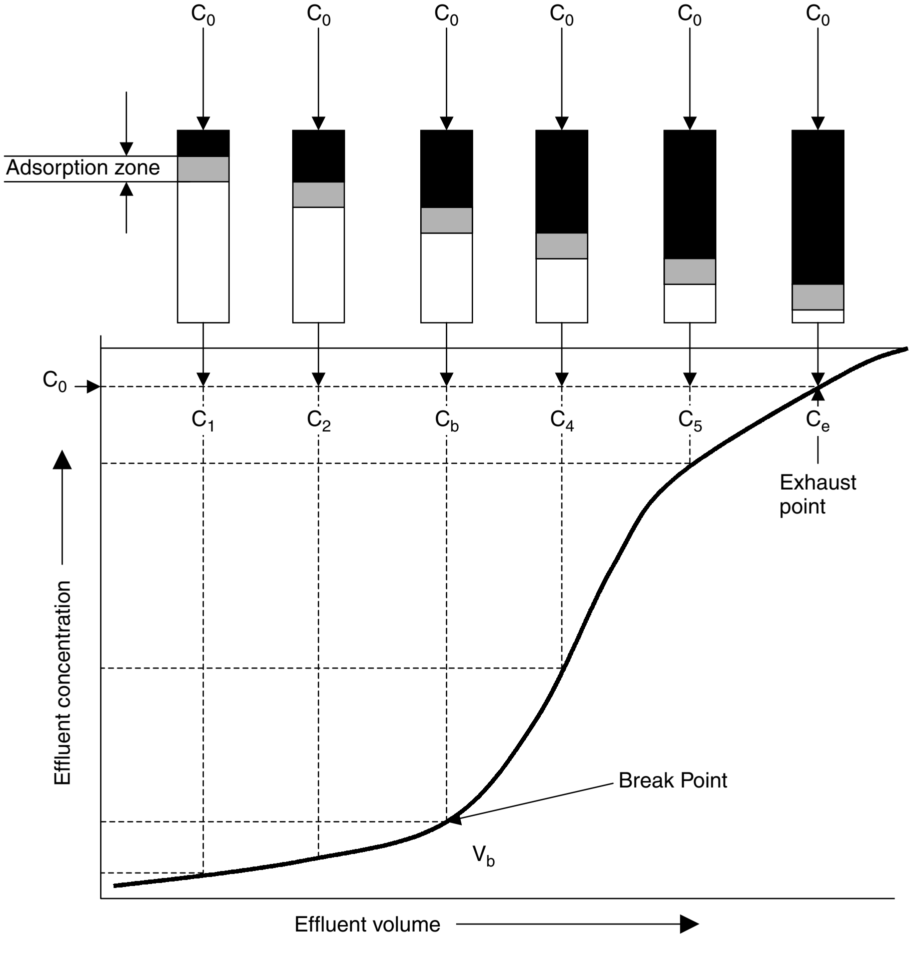


Figure 4. Typical adsorption zone movement in a fixed bed adsorber.

To construct a fixed bed adsorber, the following design parameters are used:

Volumetric Flow Rate (Q)

It is the quantity of solute fed per unit time. Flow rate influences the adsorption capacity of carbon in a dynamic system. If a 1-inch column is to be used, 20.6 ml/min flow rate, which is equal to 1 g/min/ft^2, is to be used.

The following values may further be considered for designing fixed bed reactors:

Column Diameter (cm)	Volumetric Flow Rate (cc/min)
2.56	41.6
5.08	165.2
7.62	374.0
10.16	661.6

Carbon Bed Volume (V_b)

This is the total volume of GAC packed bed, which accounts for both the activated carbon grains and the void volume.

Cross-Sectional Area (A_b)

It is simply the cross-sectional area.

Void Volume (α)

The volume between the carbon particles in a packed bed or column expressed as a percentage of the total bed volume, which corresponds to the part of the fixed bed volume that is not occupied by activated carbon particles

Filter or Linear Velocity (v_F)

It is also know as superficial linear velocity and surface loading rate, which is the velocity in an empty bed with the filter cross-sectional area.

It can be calculated from the following equation:

$$v_F = \frac{Q}{A_b}$$

Effective Contact Time, Resident Time, or Retention Time (t)

It is defined as the time within the GAC bed that is available for the mass transfer of the organic substances from bulk solution to the GAC particle. It is also defined as the theoretical length of time for a liquid to pass through a column assuming all the liquid moves through with the same uniform velocity. It is equal to the volume of liquid in the column divided by the rate of flow. The volume of liquid in a carbon column is simply the total volume of the column times the void fraction. It can be calculated by using the following equation:

$$t = \frac{V_F \alpha}{Q}$$

Empty Bed Contact Time (EBCT)

The time required for the liquid to pass through a carbon column assuming that all the liquid passes through at the same velocity. It is equal to the volume of the empty bed divided by the flow rate. Conventional water treatment plant adsorbers have EBCTs in the range of 7–10 min.

It can be calculated by using the equation

$$\text{EBCT} = \frac{V_b}{Q} = \frac{A_b L}{V_F A_b} = \frac{L}{v_F} = \frac{t}{\alpha}$$

where V_b is the volume of GAC in contactor (m^3); Q is the volumetric flow rate (m^3/h); A_b is the cross-sectional area of GAC, m^2; L is the length of the GAC in contactor (m); V_F is the linear velocity or filter velocity (m/h); t is the retention time (h); and α is the Void volume (m^3).

Filter Operation Time (t_F)

It is the time period that a GAC bed has been in operation.

Throughput Volume (V_L)

It is the volume of solute that has passed through the filter at a time.

It is calculated by using the equation

$$V_L = t_F \times Q$$

Filter Density (ρ_{GAC})

It is calculated using the following equation in g/L:

$$\rho_{\text{GAC}} = \frac{m_{\text{GAC}}}{V_b}$$

where m_{GAC} is the mass of GAC (g) and V_{b} is the volume (L).

Specific Throughput Volume (V_{sp})

As the throughput volume depends on the filter size, it does not allow a direct comparison of different size of plants. If throughput volume is divided by the mass of activated carbon in the bed, the specific throughput volume is obtained. The mass of GAC is determined by multiplying filter density and bed volume.

It is calculated by using the equation

$$V_{sp} = \frac{V_L}{V_b \times \rho_{\text{GAC}}} = \frac{Q \times t}{m_{\text{GAC}}} = \frac{V_b \times t}{\text{EBCT} \times m_{\text{GAC}}}$$
$$= \frac{V_b \times t}{\text{EBCT} \times (\rho_{\text{GAC}} \times V_b)} = \frac{t}{\text{EBCT} \times \rho_{\text{GAC}}}$$

Throughput Bed Volume (BV)

It is an another parameter used for the comparison of the removal efficiencies regardless of the bed size. It is the ratio of throughput volume and bed volume

$$\text{BV} = \frac{V_L}{V_b} = \frac{t_F}{\text{EBCT}}$$

Carbon Usage Rate (CUR)

It is expressed by the following expression:

$$\text{CUR}, g/m^3 = \frac{m_{\text{GAC}}}{Q \times t}$$

Bed Life

The volume of the water treated for a given EBCT, expressed in liters, and can be calculated as:

$$\text{Volume} = \frac{\text{mass} \cdot \text{of} \cdot \text{GAC} \cdot \text{for} \cdot \text{given} \cdot \text{EBCT}}{\text{GAC} \cdot \text{usage} \cdot \text{rate}}$$

and therefore, the bed life can be calculated as

$$\text{Bed} \cdot \text{Life} = \frac{\begin{array}{c}\text{volume} \cdot \text{of} \cdot \text{water} \cdot \text{treated} \\ \cdot\text{for} \cdot \text{given} \cdot \text{EBCT}\end{array}}{Q}$$

The typical values of the various important parameters as discussed above with their units presented in Table 5.

Carbon Dose

The amount of GAC required to fill each column is calculated by the expression:

$$\text{Weight of carbon} = \text{volume of column} \times \text{A.D} \times 0.85$$

where A.D is the apparent density and 0.85 is the factor to allow backwashed density.

This amount should be degassed and wetted prior to installation in the column. The degassing can be done by boiling the carbon in organic-free water for 2 h or soaking at room temperature for 24 h. The degassed carbon should be charged into the column in small increments as a slurry keeping a layer of organic-free water above the GAC during charging, which is best accomplished by filling the column one-third of organic-free water prior to charging the degassed-free water into the column. It is also noted that all connecting tube and other void space must be filled with liquid in order to avoid the formation of gas pockets in carbon bed.

For designing of fixed bed reactors, a number of theories have been proposed by various researchers. These theories include:

1. Length of unused bed (LUB) approach
2. Bed-depth-service time (BDST) approach
3. Empty bed residence time (EMRT) approach

Table 5

Parameter	Symbol	Units	Typical Values
Volumetric flow rate	Q	m^3/h	50–400
Bed volume	V_b	m^3	10–50
Cross-sectional area	A_b	m^2	5–30
Length	L	m	1.8–4.0
Void fraction	α	m^3/m^3	0.38–0.42
GAC density	ρ	kg/m^3	350–550
Filter velocity	v_F	m/h	5–15
Effective contact time	t	min	2–10
Empty bed contact time	EBCT	min	5–30
Operational time	t_F	days	100–600
Throughput volume	V_L	m3	10^4–10^5
Specific throughput	V_{sp}	m3/kg	50–200
Bed volume	BV	m3/m3	2,000–20,000

PULSED BED

In this type of bed, carbon is removed at intervals from the bottom of the column and replaced at top by fresh adsorbent.

MOVING BED SYSTEM

The most recent development of granular activated carbon has been the use of moving bed. In this system, the direction of the liquid flow is upward, whereas the carbon moves in a downward direction. The basic principle behind this technique is to have one column (or multiple columns running in parallel) packed completely with a carbon bed of sufficient height to have the adsorption–wave front and to provide some operating time with the effluent flow being within specification. As the adsorption wave front moves up the column, it is periodically displaced downward by the removal of a quantity of saturated carbon from the base of the column and the replacement of the same quantity with fresh or regenerated carbon at the top of the column. Although the principle of the moving bed can be applied in smaller units, it is most frequently used in larger units where the lower capital investment is important.

GAS-PHASE APPLICATIONS

Gas-phase applications of activated carbons include separation, gas storage, and catalysis. It is well documented in literature that only 20% of produced activated carbons are used for gas-phase applications. The carbons applied for gas-phase applications are mostly granular in shape.

REGENERATION

Once the granular activated carbons become saturated, it is necessary to change the carbon or to regenerate the fixed bed adsorber. Regeneration is the process of removing adsorbed compounds from the granular activated carbon surface. Here, the carbon surface includes external macropores and micropores.

Carbon regeneration frequently is a major part of total operating cost associated with granular activated carbon (GAC) adsorption systems. Following are the important and potential regeneration methods:

1. Thermal regeneration
2. Biological regeneration
3. Infrared regeneration
4. Supercritical fluids

Spent GAC used in water/wastewater, and other liquid-phase applications, is generally reactivated using a high-temperature thermal process where the GAC is heated to about 815 °C (1500 °F), allowing drying, baking, and gasification to occur. Various types of furnaces used for the regeneration purpose include multiple hearth furnace (MHF) or rotary kilns (RK), electric belt furnaces (EBF), and fluidized bed regenerators (FBR). Details about these furnaces and their operation are well documented in literature (41). The two major criteria involved in the regeneration of the granular activated carbon are (a) characteristic of the spent carbon and (b) choice of the furnace for that particular application. The spent carbon characteristics include the potential for char formation, corrosion, and slagging, whereas the furnace characteristics are assessed by determining the mass transfer efficiency, particle residence time, and temperature control. After reviewing the properties of furnaces and activated carbons, one can select the best possible option.

In thermal regeneration, 5–10% of granular activated carbon is lost as a result of oxidation and attrition, and by the cost of energy in heating, the carbon around 800–850 °C (42). An alternative technique is that of chemical regeneration in which chemical reagents are applied to the exhausted granular activated carbon. The chemical regeneration of exhausted GAC can be achieved by two main categories of substances: inorganic chemical regenerates with oxidizing powers and organic chemical regenerates with solubilizing powers. The efficiency of any regenerate is judged on the extent that it effects the recovery of the adsorptive powers of the granular activated carbons. The regeneration efficiency can be calculated as

$$\text{Regeneration efficiency (RE\%)} = (A_r/A_0) \times 100$$

where A_0 is the original capacity of GAC for a particular adsorbate and A_r is the capacity of regenerated carbon.

APPLICATIONS AND COMMON USES (BOTH LIQUID PHASE AND GAS PHASE)

Activated carbon has wide applications in both liquid and gas/solvent phase systems (43).

Groundwater Remediation

Granular activated carbon is the most common technology employed to pump and treat groundwater remediation systems. It is highly suited to this application and is often used as a single treatment step to remove compounds such as chlorinated hydrocarbons and aromatic compounds, including benzene, toluene, ethylbenzene, and xylene (BTEX). For more highly contaminated groundwater, two or more carbon units may be placed in series or carbon may be used in combination with other treatment technologies such as air stripping or advanced oxidation processes.

Soil Vapor Extraction and Air Sparring

Activated carbon can also be used for the removal of Volatile Organic Compounds (VOCs) from air streams resulting from *in situ* removal techniques such as soil vapor extraction.

Chemical and Pharmaceutical Industries

Chemicals. Activated carbon is suitable for the decolorization and purification of a wide range of organic and inorganic compounds, including amines, hydrochloric and other mineral acids, amino acids, glycols, and hydrocarbons.

Pharmaceuticals. Activated carbon is used to purify a wide range of pharmaceuticals and intermediates.

Granular activated carbon is installed to purify the recirculating amine to remove degradation products and dissolved hydrocarbons.

Military Use

Most of the world's armed forces are using activated carbons to protect against attack by toxic gases such as mustard gas. This is also used in military suiting where combat uniforms are coated by a layer of impregnated carbon under the outer cover.

Nuclear Reactors

Most of the nuclear reactors, especially in the western world, have activated carbon ventilators to protect against radioactive iodine leaks from the core or heat exchanger systems, if any. Special activated carbons impregnated with potassium iodide or potassium tri-iodide are commonly used for this purpose. Another application in nuclear technology is as a filter in emergency ventilation system for the reactor building, which is switched on automatically in case of breakdowns.

Landfill Leachate Treatment

Granular activated carbon in combination with biological pretreatment is the leading technology for the treatment of landfill leachate for the removal of Chemical Oxygen Demand (COD), Adsorbable Organic Halogens (AOX), and other toxic substances. Granular activated carbon is now used at over 50 sites in Europe for this application.

Catalysis

Many chemical reactions require a catalyst to improve efficiency, accordingly; in many cases, activated carbons provide large surface area, thus, further improving the efficiency.

Medicinal Activated Carbon

The activated carbon has been applied in medicine for a long time. The carbons originally used were prepared from waste materials of animal origin, especially blood (animal charcoal-carbo animalis). In *catarrhal* infections of the digestive system, the use of activated carbon serves primarily to remove bacterial toxins, which, being high-molecular-weight substances, are easily adsorbed on active carbon. Activated carbons are also prescribed in large doses in all the cases of acute gastritis and enteritis. It is also a very effective antidote in all the cases of poisoning.

Domestic Use

Activated carbons are used in various home appliances, including fridge deodorizers, air purifiers, and cooker hoods. The activated carbons are used in the removal of caffeine from coffee. Cigarettes are made that, in addition to an antismoke filter, contain finely granulated activated carbon.

Also, activated carbons are used in the coating and printing industries, degreasing and cleaning, solvent recovery, tank venting, ventilation, and air conditioning

The other uses are systems annihilation, condensate de-oiling, and gold recovery.

BIBLIOGRAPHY

1. Mattson, J.S. and Mark, H.B., Jr. (1971). *Activated Carbon*. Marcel Dekker, New York.
2. Hamerlinck, Y. and Mertens, D.H. (1994). *Activated Carbon Principles in Separation Technology*, E.F. Vansant (Ed.). Elsevier, New York.
3. Bansal, R.P., Donnet, J.-P., and Stoeckli, F. (1988). *Active Carbon*. Marcel Dekker, New York.
4. Pollard, S.J.T., Fowler, G.D., Sollars, C.J., and Perry, R. (1992). Low cost adsorbents for waste and wastewater treatment: A review. *The Science Total Environ.* **116**: 31–52.
5. Gupta, V.K. and Ali, I. (2002). Adsorbents for water treatment: low cost alternatives to carbon. In: *Encyclopedia of Surface and Colloid Science*. Marcel Dekker, New York, pp. 136–166.
6. Allen, S.J., Whitten, L., and Mckay, G. (1998). The production and characterization of activated carbons: A review. *Dev. Chem. Eng. Mineral Process* **6**(5): 231–261.
7. Arulanantham, A., Balasubramanian, N., and Ramakrishna, T.V. (1989). Coconut shell carbon for treatment of cadmium and lead containing wastewater. *Metal Finish* 51–55.
8. Ferro-Garcia, M.A., Rivera-Ultrilla, J., Ropdriquez-Gordillio, J., and Bautista-Tolego, I. (1988). Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. *Carbon* **26**(3): 363–373.
9. Manju, G.N., Raji, C., and Anirudhan, T.S. (1998). Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res.* **32**(10): 3062–3070.
10. Srivastava et al. (1987).
11. Renouprez, A. and Avom, J. (1988). Characterization of active carbons from palm tree fibres using nitrogen adsorption and small angle X-ray scattering. In: *Characterization of Porous Solids*. K.K. Unger, J. Rouquerol, and K.S.W. Sing (Eds.). Elsevier Science, Amsterdam, the Netherlands, pp. 49–54.
12. Laine, J., Calafat, A., and Labady, M. (1989). Preparation and characterization of activated carbons from coconut shell impregnated with phosphoric acid. *Carbon* **27**(2): 191–195.
13. Korczak, M. and Kuribiel, J. (1989). New mineral-carbon sorbent: mechanism and effectiveness of sorption. *Water Res.* **23**(8): 937–946.
14. Ehrburger, P., Addoun, A., Addoun, F., and Donnet, J.-P. (1986). Carbonization of coals in the presence of alkaline hydroxides and carbonates: Formation of activated carbons. *Fuel* **65**(10): 1447–1449.
15. Alvim-Ferraz, M.C. (1988). Preparation of activated carbon for air pollution control. *Fuel* **67**(9): 1237–1241.
16. Toles, C.A., Marshall, W.E., and Johns, M.M. (1997). Granular activated carbons from nutshells for the uptake of metals and organic compounds. *Carbon* **35**(9): 1407–1414.
17. Tancredi, N., Cordero, T., Rodriguez-Mirasol, J., and Rodriguez, J.J. (1997). Activated carbons from eucalyptus wood. Influence of the carbonization temperature. *Sep. Sci. Technol.* **32**(6): 1115–1126.
18. Teng, H. and Yeh, T.-S. (1998). Preparation of activated carbons from bituminous coals with zinc chloride activation. *Ind. Eng. Chem. Res.* **37**(1): 58–65.
19. Hall, R.C. and Holmes, R.J. (1992). The preparation and properties of some activated carbons modified by treatment with phosgene or chlorine. *Carbon* **30**(2): 173–176.
20. Otowa, T., Nojima, Y., and Miyazaki, T. (1997). Development of KOH activated high surface area carbon and its application to drinking water purification. *Carbon* **35**(9): 1315–1319.
21. Duggan, O. and Allen, S.J. (1997). Study of the physical and chemical characterstics of a range of chemical treated lignite based carbons. *Wat. Sci. Tech.* **35**: 21–27.
22. Periasamy, K. and Namasivayam, C. (1995). Adsorption of Pb(II) by peanut hull carbon from aqueous solution. *Sep. Sci. Technol.* **30**(10): 2223–2237.
23. Mohan, D., Singh, K.P., Sinha, S., and Gosh, D. (2004). Removal of pyridine from aqueous solution using low cost activated carbon derived from agricultural waste materials. *Carbon* **42**: 2409–2421.
24. Rodriguez-Reinoso, R.F. and Solano, A.L. (1989). Microporous structure of activated carbons as revealed by adsorption methods. In: *Chemistry and Physics of Carbon*, Vol. 12, P.A. Thrower (Ed.). Marcel Dekker, New York.
25. Hassler, J.W. (1963). *Active Carbon*. Chemical Publishing Company, New York.
26. Hu et al. (1996).
27. Gregg, S.J. and Sing, K.S.W. (1982). *Adsorption, Surface Area and Porosity*. Academic Press, London.
28. Snoeyink, V.L. and Weber, W.J., Jr. (1967). The surface chemistry of active carbon;discussion of structure and surface functional groups. *Environ. Sci. Technol.* **1**(3): 228.
29. Cookson, J.T., Jr. (1975). The adsorption chemistry of organics from waters on activated carbon AIChE Synposium Series. *Water* **71**(151): 376.
30. Epstein, B.D.E., Dalle-Molle, J.S., and Mattson, J.S. (1971). Electrochemical investigation of durface functional groups of isotropic pyrolytic carbon. *Carbon* **9**: 609.
31. Mattson, J.S., Mark, Jr., H.B., Malbin, M.P., Weber, W.J., Jr., and Crittenden, J.C. (1969). Surface chemistry of active carbon:specific adsorption of phenols. *J. Colloid Interface Sci.* **31**(1): 116–130.
32. Garten, V.A. and Weiss, D.E. (1957). A new interpretation of the acidic and basic structures in carbon II: The chromene-carbonium ion couple in carbon. *Aust. J. Chem.* **10**: 309.
33. Boehm, H.P. and Voil, M. (1970). Basische Oberflachernoxide an Kohlenstoff-I: Adsorption von Sauren. *Carbon* **8**: 227.
34. Corapcioglu and Huang (1987).
35. Perrich, J.R. (1981). *Activated Carbon Adsorption for Wastewater Treatment*. CRC Press, Boca Raton, FL.
36. Brunauner, S., Emmett, S.P.H., and Teller, E. (1972). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**: 309–319.
37. Sing et al. (1985). Physisorption data for gas/solid systems. *Pure Appl. Chem.* **57**: 603–619.
38. Freundlich, H. (1906). Uber die adsorption n losungen *Z. Phys. Chem.* **57**: 385–470.
39. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40**: 1361–1367.
40. Weber, Jr., W.J. (1972). *Physicochemical Processes for Water Quality Control*. Wiley Interscience, New York.
41. Liu, P.K.T. and Wagner, N.J. (1985). Thermal regeneration of granular active carbon. *Environmental Progress* **4**(2): 136–140.
42. Gaymont, F.J. (1980). The effect of capital and operating costs on GAC adsorption system design. In: *Activated Carbon*

Adsorption of Organics from the Aqueous Phase, Vol. 2, M.J. McGuire and I.H. Suffet (Eds.). Cap 23. Ann Arbor Science, Ann Arbor, MI, pp. 531–538.

43. Mckay, G. (1995). *Use of Adsorbents for the Removal of Pollutants from Wastewaters*. CRC Press, Boca Raton, FL.

READING LIST

Mohan, D. and Chander, S. (2001). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste material. *Colloids and Surfaces A* **177**: 169–181.

COMPETITIVE ADSORPTION OF SEVERAL ORGANICS AND HEAVY METALS ON ACTIVATED CARBON IN WATER

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In practice, the water/wastewater/effluents to be treated are multicomponent mixtures. Therefore, other organic or inorganic substances influence the efficacy of activated carbons. In the recent past, most of the research work has been focused on the removal of single solute from its pure solution or a particular solute from a solution having ill-defined chemical character. The other reports available are addressed to the removal of gross organic/inorganic substances, which are measured in terms of BOD or COD from water/wastewater. In actual practice, the treatment of wastewater by activated carbon normally involves a variety of adsorbates competing for adsorption sites on the carbon surface. Thus, a thorough understanding of the competitive effect on various organic/inorganic compounds on carbon adsorption is a must. Unfortunately, very few reports/papers about the competitive adsorption on activated carbon in aqueous solution are available. Thus, a need exists to explore the current status of the competitive adsorption of various organic/inorganic substances from water/wastewater on activated carbons. Multiion systems received less attention than single ion systems.

The adsorption in multicomponent systems is complicated because of the solute–solute competition and the solute-surface interaction involved. Multicomponent interactions take place at the active adsorption sites where the solid-liquid phase equilibrium will emerge showing a different capacity of single solute with a new set of isotherm systems. The interpretation of the multicomponent systems has proved to be complex and may be the function of one or all of the following parameters: ionic radii, electronegativity, system pH, and the availability of the active sites on the adsorbent.

The adsorption capacity or the degree of removal of various organic and inorganic substances from water/wastewater on activated carbon (GAC) very much depends on the multicomponent competitive interactions of organic chemicals that are present in the system. In order to design a cost-effective system, it is necessary to know the adsorption capacity of a solute in the presence of others (1–4). To determine the effects of competing adsorption, mathematical models/equations must be developed to describe the adsorption equilibrium in multicomponent system. Several models are available in literature, but most of them suffer from one limitation or an other. In the paragraphs below, several models are discussed with a view that these are mostly used in multicomponent modeling in aqueous systems. Butler and Ockrent (5), in 1930, developed the first model for binary systems. Since then, a number of models have been developed that are shown to be valid for certain mixtures and conditions by comparing them to the experimental data.

MULTICOMPONENT ADSORPTION MODELS

Prediction of multicomponent adsorption is still a very challenging problem in the adsorption. Many models have been proposed and employed from time to time to obtain the multisolutes isotherms using single-component equilibrium data. However, most of the models are based on either unrealistic assumptions or an empirical equations with no apparent definitions (6,7). Some of the important and widely used models are discussed below to understand the multicomponent sorption of oraganic and inorganic substances on activated carbon.

Butler and Ockrent Model

This model was presented by Butler and Ockrent in 1930 (5). Basically, this model is an extended form of Langmuir model. According to this model, if two solutes are present in an adsorption system, the Langmuir model for the competitive adsorption can be given by Equations 1 and 2 as follows:

$$q_1 = \frac{Q_1^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \tag{1}$$

$$q_2 = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \tag{2}$$

where Q_1^0, b_1 and Q_2^0, b_2 are the Langmuir constants determined from single-solute system with solutes 1 and 2, respectively, and C_1 and C_2 are the equilibrium concentrations of the solutes 1 and 2, respectively, in the mixture.

This model is valid only if the surface area available for adsorption is identical for both the solutes and Q_1^0 and Q_2^0 reflect the size difference for a mono-layer surface coverage of solutes. Further, the free energy change for adsorption is assumed to be independent of surface coverage.

For simultaneous adsorption of N components from a solution, the multicomponent Langmuir equation can be given as

$$q_i = \frac{Q_i^0 b_i C_i}{1 + \sum_{j=1}^{N} b_j C_j} \tag{3}$$

In spite of the limitations, this model was used by various researchers (8,9) to describe their multicomponent sorption on activated carbons.

Jain and Snoeyink Model

The model given by Butler and Ockrent (5) was modified by Jain and Snoeyink (10). Earlier models used for multicomponent systems are not able to explain the fact that in a bi-solute system, a portion of the adsorption often takes place without competition. To overcome this difficulty, Jain and Snoeyink proposed a model for binary systems, which takes into account the noncompetitive adsorption on activated carbon/adsorbent.

Based on this hypothesis, adsorption without competition occurs when $Q_1^0 \neq Q_2^0$ and the number of adsorption sites not being subjected to the competition is equal to the quantity of $(Q_1^0 - Q_2^0)$ where $Q_1^0 > Q_2^0$. Equations 4 and 5 are as follows:

$$q_1 = \frac{({Q_1}^0 - {Q_2}^0) b_1 C_1}{1 + b_1 C_1} + \frac{Q_2^0 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \tag{4}$$

$$q_2 = \frac{Q_2^0 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \tag{5}$$

where q_1 and q_2 are the amounts of solute 1 and 2, respectively, adsorbed per unit weight of activated carbon/adsorbent at equilibrium concentrations of C_1 and C_2, respectively. Q_1^0 and Q_2^0 are the maximum value of adsorption for solute 1 and 2, respectively, determined from the respective single-solute systems, whereas b_1 and b_2 are the constants related to the energy of adsorption from solute 1 and 2, respectively, in their pure solution systems.

This model also has some limitations. It is only appropriate to describe the competitive adsorption between the molecules having very different single-solute adsorption capacity. In spite of its limitations, a number of workers have applied this model in their multicomponent adsorption studies. In one of the studies, Huang and Steffens (11) applied this model to determine the competitive adsorption of organic materials by activated carbons. It was concluded that mutual suppression of equilibrium adsorption because of competition between acetic and butyric acids has shown that the observed data are somewhat closer to the values predicted by Jain and Snoeyink's model than by the original Langmuir equation. However, the actual degree of suppression is greater than the prediction for acetic acid and smaller for butyric acid.

Multicomponent Isotherm of Mathews and Weber

Mathew (12) proposed this model in 1975. This model is a modified and extended form of the Redlich–Peterson model (13), which can be given by the expressions below, which is basically three parameter, single-solute adsorption isotherm model

$$q_e = \frac{K C_e}{1 + a_R C^b{}_e} \tag{6}$$

where K, a_R, and b are the Redlich–Peterson constants.

For the N solute mixtures, this equation can be written as

$$q_i = \frac{K_j C_i}{1 + \sum_{j=1}^{N} a_j {C_j}^{b_j}} \tag{7}$$

The parameters K_j, a_j, and C_j can be determined from single-solute isotherm data. A new constant, η_i, has been introduced in this model, which has to be determined from adsorption data in the mixtures. With the addition of this constant, the equation may be written as

$$q_i = \frac{k_j \left[\dfrac{C_i}{\eta_i}\right]}{1 + \sum_{j=1}^{N} a_j \left[\dfrac{C_j}{\eta_i}\right]^{b_j}} \tag{8}$$

where η_I is the interaction parameter, which is constant. In practice, this parameter varies from different equilibrium compositions. Therefore, this model is not very successful in explaining the multicomponent systems.

Fritz and Schlunder Multicomponent Model

This model was given by Fritz and Schlunder in 1974 (14,15). For modeling multicomponent systems comprising species whose single-solute isotherms follow the Freundlich isotherm, a multicomponent Freundlich equation may be used. The first model of this type, as proposed by Fritz and Schlunder (14), can be expressed by Equations 9–12:

$$q_1 = \frac{K_1 {C_1}^{n_1 + \beta_{11}}}{C_1^{\beta_{11}} + \alpha_{12} {C_2}^{\beta_{21}}} \tag{9}$$

$$q_2 = \frac{K_2 {C_2}^{n_2 + \beta_{22}}}{C_2^{\beta_{22}} + \alpha_{21} C_1^{\beta_{21}}} \tag{10}$$

$$\alpha_{1,2} = \frac{\alpha_{1,2}}{\alpha_{1,1}} \tag{11}$$

$$\alpha_{2,1} = \frac{\alpha_{2,1}}{\alpha_{22}} \tag{12}$$

where q_1 and C_1 are the concentrations of solute 1 in the solid and liquid phase, respectively; q_2 and C_2 are the concentrations of the solute 2 in solid and liquid phase, respectively; and K_1, n_1, and K_2, n_2 are the Freundlich constants in single-solute 1 and solute 2 systems.

Equations 9 and 10 consist of ten adjustable variables; however, K_1 and K_2, n_1 and n_2 can be determined from single-solute isotherms using Freundlich model for single-solute systems.

Dastgheib and Rockstraw Model

Very recently Dastgheib and Rockstraw (16) proposed a multicomponent Freundlich equation for binary systems, as given by Equations 13–15:

$$q_1 = \left[\frac{K_1 {C_1}^{n_1}}{K_1 {C_1}^{n_1} + \alpha_{12} K_2 {C_2}^{n_2} + b_{12} {C_2}^{n_{12}}}\right] K_1 {C_1}^{n_1} \tag{13}$$

$$q_2 = \left[\frac{K_2 {C_2}^{n_2}}{K_2 {C_2}^{n_2} + \alpha_{21} K_1 {C_1}^{n_1} + b_{21} {C_1}^{n_{21}}}\right] K_2 {C_2}^{n_2} \tag{14}$$

where q_1 and C_1 are the concentrations of solute 1 in the solid and liquid phase, respectively; q_2 and C_2 are the concentrations of solute 2 in the solid and liquid phase, respectively; K_1, n_1, K_2, and n_2 are the Freundlich constants in single-solute system; and α_{12}, α_{21}, b_{12}, b_{21}, n_{12}, and n_{21} are the interaction constants obtained from a least-squares analysis of the binary data. The term in brackets on the right-hand side represents the overall competition and interaction factor and has a value of less than or equal to unity (where C_2 tends to zero, it is equal to 1). The terms $\alpha_{12}K_2$ and $\alpha_{21}K_1$ can be condensed to single terms and are considered as constants.

For the ith component systems, the general equation model can be written as

$$q_i = \frac{(K_i C_i^{n_i})^2}{K_i C_i^{n_i} + \sum_{j=1}^{N}(\alpha_{ij} K_j C_j^{n_j} + b_{ij} C_j^{n_{ij}})} \tag{15}$$

where q_i and C_1 are the concentrations of solute I in the solid and liquid phase, respectively; C_j is the concentration of other solutes in liquid phase; K_i and n_i, K_j and n_j are the single component Freundlich constants; α_{IJ}, b_{ij}, and n_{ij} are the binary interaction constants obtained from a least-squares analysis of the multicomponent data having $\alpha_{ii} = b_{ii} = 0$; and N is the number of solute. This model is different from the Fritz and Schlunder model in the sense that this demonstrates equal or stronger performance.

Sheindorf et al. Model

This model was given by Sheindorf et al. (17,18) for the multicomponent systems comprised of species whose single-solute isotherm obeys the Freundlich isotherm. This equation was based on the following assumptions:

1. each component in single system obeys the Freundlich model
2. each component in multicomponent system and the adsorption energies of different sites are disturbed exponentially, with the distribution function being identical to that for single-component systems.

The model equations can be given by Equations 16 and 17:

$$q_1 = K_1 C_1 (C_1 + \eta_{12} C_2)^{n_1 - 1} \tag{16}$$

$$q_2 = K_2 C_2 (C_2 + \eta_{21} C_1)^{n_2 - 1} \tag{17}$$

where q_1 and C_1 are the concentrations of solute 1 in the solid and liquid phase, respectively; q_2 and C_2 are the concentrations of solute 2 in the solid and liquid phase, respectively; K_1, n_1, K_2, and n_2 are the Freundlich constants in single-solute system; and η_{12} and η_{21} are the interaction constants.

Ideal Adsorbed Solution Theory (IAST)

The ideal adsorbed solution theory is based on the thermodynamics of adsorption, which is analogous to Roul's law in a liquid-gas system. The only difference is that it is applied to a solid-liqid system. Initially, this model was used to calculate multicomponent adsorption of gaseous mixtures (19) using the parameters calculated from single-solute systems. This model was later modified and applied to calculate various multicomponent adsorption parameters by Radke and Praunitz (20). In the IAST model, the following five basic equations (18–22) are used to predict multicomponent behavior from single-solute adsorption isotherms (21).

The total surface loading can be defined by Equation 18:

$$q_T = \sum_{i=1}^{N} q_i \tag{18}$$

where q_I is the single-solute solid phase concentration for component i, which is evaluated at spreading pressure of the mixture, and N is the number of components.

The mole fraction on the carbon surface for component i can be calculated by Equation 19:

$$Z_i = \frac{q_i}{q_T} \quad \text{and} \quad I = 1 \text{ to } N \tag{19}$$

$$C_i = Z_i C_i^0 \quad \text{and} \quad I = 1 \text{ to } N \tag{20}$$

where C_I is the single-solute liquid phase concentration for component i, which is evaluated at the spreading pressure of the mixture.

The single-solute liquid phase concentration in equilibrium with q_i^0 is

$$\frac{1}{q_T} = \sum_{i=1}^{N} Z_i / q_i^0 \tag{21}$$

$$\frac{\pi_m}{RT} = \int_0^{q_i^0} \frac{d \ln C_i^0}{d \ln q_1^0} dq_1^0 = \frac{\pi_1^0 A}{RT}$$

$$= \int_0^{q_j^0} \frac{d \ln C_j^0}{d \ln q_j^0} dq_j^0 = \frac{\pi_j^0 A}{RT} = \text{for} \cdot j = 2 \cdot \text{to} \cdot N \tag{22}$$

where A is the surface area of carbon per unit mass of adsorbent, R is the gas constant, T is the absolute temperature, π_i is the spreading pressure of the single solute i, and π_m is the spreading pressure of the mixture.

LeVan and Vermeulen Model

LeVan and Vermeulen (22) have modified the competitive Langmuir-like model. IAS theory was considered in modifying the model. This model predicts the equilibrium relationships of solute mixture only from the data derived from single adsorption isotherms. It is the simplest isotherms derived from the IAS model.

Statistical Design for Competitive Adsorption

2^4 factorial experimental design was used to study the competitive adsorption of Fe(II), Mn(II), Ca(II), and Zn(II) on selected activated carbons B3, W2, W3, and lignite by Mohan and Chander (23).

These designs are important for the following reasons:

1. They require relatively few runs per factor studied; and although they are unable to explore fully a

wide region in the factor space, they can indicate major trends and therefore determine a promising direction for further experimentation.

2. When a more thorough local exploration is needed, they can be suitably augmented to form composite designs.
3. These fractional designs are often of great value at an early stage of an investigation, when it is frequently good practice to use the preliminary experimental efforts to look at a large number of factors superficially rather than a small number.
4. These designs and the corresponding fractional designs may be used as building blocks so that the degree of complexity of the family-constructed design can match the sophistication of the problem.
5. The interpretation of the observations produced by the designs can proceed largely by using common sense and elementary arithmetic.

The authors have used a total run of $2^4 = 16$. The variables were the concentration levels of various metal ions, with high level (+) 100 ppm and low level (−) 0 ppm. The experiments were conducted at pH 3.5. The experiments were arranged as the design matrix.

General Factorial Design

To perform a general factorial design, a fixed number of "levels" or (versions) for each of the variables (factors) can be selected, and then experiment is run with all possible combinations. If l_1 levels exist for the first variable, l_2 for the second, ..., and l_k for the kth, the complete arrangement of $l_1 \times l_2 \times l_3 \times \ldots l_k$ experimental runs is called an $l_1 \times l_2 \times l_3 \times \ldots l_k$ factorial design, e.g., a $2 \times 3 \times 5$ factorial design requires $2 \times 3 \times 5 = 30$ runs and a $2 \times 2 \times 2 = 2^3$ factorial design.

COMPETITIVE SORPTION OF INORGANICS ON ACTIVATED CARBON

The adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} from aqueous solutions by three activated carbons in single and multicomponent systems were studied by Budinova et al. (24). These three activated carbons were obtained from apricot stones (A), coconut shells (C), and lignite coal (L). The results of the individual metal ions from an aqueous solution containing all four metal ions together in equal concentration are presented in Table 1.

It is clear from Table 1 that the presence of foreign ions diminishes the adsorption of each of the ions. The effect is greatest for the lead ions and smallest for the copper ions. The authors did not mention any mechanism for the multicomponent sorption of these ions. The only reason given was that, apart from the properties of the cations, the chemical nature of the metal ions is of great importance for the adsorption process. They also concluded that a selective adsorption of the metals is observed; the ones preferentially adsorbed do not completely prevent the adsorption of other ions.

Johns et al. (25) reported the sorption of cadmium, copper, lead, nickel, and zinc in single and multicomponent systems on various granular activated carbon developed from agricultural waste materials. A study on the competitive effect of metal ions was carried out from a solution having 2.5 mM of each metal at pH 5.0 and was also unbuffered to reduce solution species complexation. The uptake of various metals from a mixed solution is presented in Table 2.

Bansode et al. (26) evaluated the adsorption effectiveness of pecan shell-based granular activated carbons (GACs) in removing metal ions Cu(II), Pb(II), and Zn(II) commonly found in municipal and industrial wastewater. Pecan shells were activated by phosphoric acid, steam, or carbon dioxide activation methods. Metal ion adsorption

Table 1

	Adsorption from Solution Containing All the Four Ions (mol g^{-1})				Decrease of Ion Adsorption in the Presence of the ion (%)			
Carbon	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}
A	434.4	355.4	410.0	385.0	11.6	28.3	11.0	19.9
C	430.7	354.0	390.0	360.0	11.6	28.1	17.2	19.4
L	403.5	328.7	390.0	360.3	15.4	32.1	17.0	21.0
OA	398.5	1550.4	73.6	47.6	12.1	37.3	27.1	32.2

Table 2

	BET Surface Area	μ Moles of Metals Adsorbed per Gram of GAC					
GAC	(m^2g^{-1})	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)	Total
Calgon GAC	783	0	97	0	30	113	240
Norit RO3515	827	0	117	0	11	67	195
Norit vapure	876	0	98	0	4	66	168
Soybean hulls	479	14	127	29	36	190	396
Peanut shells	275	9	195	31	39	236	510
Sugar cane bagasse	162	7	132	21	29	206	395
Rice straw	460	2	144	24	32	174	376

of shell-based GACs was compared with the metal ion adsorption of a commercial carbon, namely Calgon's Filtrasorb 200. Adsorption experiments were conducted using solutions containing all three metal ions in order to investigate the competitive effects of the metal ions as would occur in contaminated wastewater. The results obtained from this study showed that acid-activated pecan shell carbon adsorbed more lead ion and zinc ion than any of the other carbons, especially at carbon doses of 0.2–1.0%. However, steam-activated pecan shell carbon adsorbed more copper ion than the other carbons, particularly using carbon doses above 0.2%. In general, Filtrasorb 200 and carbon dioxide-activated pecan shell carbons were poor metal ion adsorbents. The results indicate that acid- and steam-activated pecan shell-based GACs are effective metal ion adsorbents and can potentially replace typical coal-based GACs in treatment of metal contaminated wastewater. The surface complex formation model was used successfully to describe the surface change density, as well as the single and multispecies metal adsorption equilibrium by Chen and Lin (27).

Choi and Kim (28) studied the adsorption characteristics of zinc and cadmium ion on granular activated carbon in singular and binary systems. Features of binary adsorption were discussed for several influential parameters, and experimental observations for both ions were correlated with a predicted adsorption isotherm based on a Langmuir multicomponent model.

Yu and Kaewsarn (29) used the multicomponent model on the sorption of heavy metals on low-cost adsorbents. An equilibrium isotherm was predicted by the extended Langmuir model using Langmuir parameters as determined from a single component system. Copper ions were found to have adsorption affinity, and the separation factor $\alpha_{Cu/Cd}$ was determined as 3.05. Trujullo et al. (30) reported the competitive adsorption of six metal ions from a single solution, which led to a model applicable to their batch and semicontinuous packed beds. Binding capacity was highest for copper, independent of the other ions, and copper also exerted the largest competing effect.

Bunzle et al. (31) carried out the studies in the pH range of 3.5–4.5, and the order was found to be $Pb^{2+} > Cu^{2+} > Cd^{2+} \approx Zn^{2+} > Ca^{2+}$, whereas Masslenilov and Kiselva (32) reported the adsorption capacity order as $Cu^{2+} > Zn^{2+} > Fe^{3+} > Ca^{2}$.

Ho et al. (33) reported that competitive effect affected the sorption of three metals in the order $Ni^{2+} > Pb^{2+} > Cu^{2+}$. It was concluded that all the metals are not necessarily adsorbed by exactly similar mechanisms for all the biosorbents, and that each needs to be tested to determine its characteristics. Adsorption of lead is usually greater than of copper, although copper is a more aggressive competitor and the adsorption of nickel is usually weaker than that of others.

The influence of a range of commercially available, water-soluble surfactants on the uptake of heavy metal ions (Cu, Zn, Cd, and Pb) by three types of clay (kaolinite, illite, and a montmorillonite) was reported by Beveridge and Fickering (34). The adsorption of Cu, Pb, Cd, and Zn was significantly reduced in the presence of small amounts of cationic surfactants, particularly with montmorillonite suspensions. The addition of anionic surfactants led to increase metal loss from the solution. Studying multicomponent adsorption system equilibria must commence with an accurate description of each component in its single (or pure) component equilibrium state.

Allen and Brown (35) studied the single component and multicomponent metal sorption onto lignite. A comparison was made between the single component saturation uptake and multicomponent uptakes The multicomponent systems were equimolar binary solutions solutions Cu-Cd, Cu-Zn, and Cd-Zn and a ternary mixture of equimolar Cu-Cd-Zn. In single component systems, the adsorption capacity followed the order Cu > Zn > Cd. These capacities were reported on a molar basis. Despite the competition, the total sorption capacity was found to increase even though the adsorption capacity of a single ion may be less than if it were to present alone. It has been pointed out that a substantial effect of multicomponent mixtures was observed on the capacity of lignite for cadmium and zinc. There appears to be slight increases in capacity in binary Cu-Cd, Cd-Zn, and ternary mixtures and a decrease in the capacity of Cu-Zn mixture compared with single component data. The order of sorption of metals in multicomponent systems is as follows: Cu > Cd > Zn. The preference of the sorbents for metals uptake is related to the electronegativity of the ions. Copper possessing the greatest ionic potential has the strongest attraction to the adsorbent, followed by cadmium then closely by zinc. The sorption capacities for single as well as multicomponent systems as reported by Allen and Brown are presented in Table 3.

Tan et al. (36) reported the uptake of metal ions in single and multicomponent systems by chemically treated human hairs. Various suppressors and promoters were identified and given in Table 4.

Beveridge and Pickering (34) reported the effect of various water-soluble surfactants on the uptake of Cu, Zn, Cd, and Pb ions by three types of clays, kaolinite, illite, and montmorillonite, over the pH range 3–10. Adsorption of Cu(II), Pb(II), Cd(II), and Zn(II) was significantly reduced in the presence of small amounts of cationic surfactants, particularly with montmorillonite suspensions. No multicomponent sorption modeling was reported.

The effect of Cu(II), Hg(II), and Pb(II) on the uptake of Cd(II) by activated carbon was investigated by Krishnan

Table 3

Metal Systems	μmol/gram
Copper alone	440
Cu in Cu-Cd	350
Cu in Cu-Zn	370
Cu in Cu-Cd-Zn	360
Cadmium alone	360
Cadmium in Cu-Cd	90
Cadmium in Cd-Zn	250
Cadmium in Cu-Cd-Zn	85
Zinc alone	375
Zinc in Cu-Zn	50
Zinc in Cd-Zn	130
Zinc in Cu-Cd-Zn	70

Table 4

Metal Ions	Promoters	Suppressor
Hg(II)	Ag(I)>Pb(II)	Cu(II)
Ag(I)	Cd(II)>Cu(II)	Hg(II)
Pb(II)	Cd(II)>Cu(II)	Hg(II)>Cu(II)
Cd(II)	–	Cu(II)>Ag(I)>Ni(II)
Cu(II)	Ni(II)~Cd(II)	Ag(I)>Hg(II)>Cr(VI)>Pb(II)
Cr(VI)	Cu(II)	–
Ni(II)	–	Ch(II)>Cd(II)

and Anirudhan (37). The removal of Cd(II) was reported to be 98.8% in absence of any co-ions. The same decreases to 83.3%, 79.1%, and 72.1%, respectively, when Cu(II), Hg(II), and Pb(II) ions are present in a 1:1 ratio. The results further showed that a 72.2%, 70.5%, and 60.6% reduction in Cd(II) removal was observed when Cu(II), Hg(II), Pb(II) ions were present at a molar ratio of 1:2. The reduction may be because of the competitive ion effect between Cd(II) and co-ions for the adsorption sites available on the carbon surface. Based on these results, it was concluded that Pb(II) ions may be stronger competitive ions than Hg(II) and Cu(II) removal by SA-S-C. The results can also be explained by the selectivity sequence of the most common cations on the adsorbent surface. It was also observed that, among the cations used, interference of Pb(II) ion is highest, followed by Hg(II) and Cu(II). The observed order of interference was the same as that of their increasing ionic radii, i.e., their decreasing hydrated ionic radii. The smaller the hydrated ionic radii, the greater its efficiency to active groups of the adsorbent, which suggests that the energy required in the dehydration of the metal ions, in order that they could occupy a site in the adsorbent, plays an important role in determining the selectivity series for the metal ions.

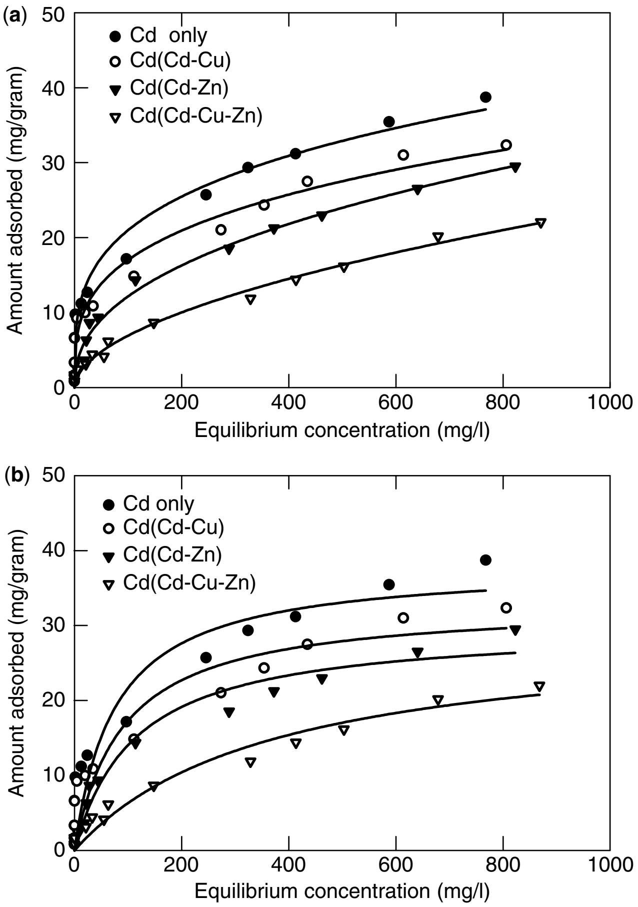

Figure 1. Multicomponent adsorption of Cd(II) on activated carbon developed from bagasse. Solid lines represent the fitting of data by (**a**) Freundlich and (**b**) Langmuir isotherms.

Recently, Mohan and Singh (38) reported the batch sorption isotherm studies to obtain the data required in the design and operation of column reactors for treatment of cadmium- and zinc-bearing wastewater both in single and multicomponent systems. The metals chosen for the investigation in single component studies were Cd (II) and Zn(II). In multicomponent system investigations, four binary systems, Cd(Cd-Cu), Cd(Cd-Zn), Zn(Zn-Cu), and Zn(Zn-Cd), and two ternary systems, Cd(Cd-Cu-Zn) and Zn(Zn-Cu-Cd), were selected. The adsorption isotherms for binary, ternary, and multicomponent systems were obtained at pH 4.5. A 1:1 ratio was used to determine the effect of other metal ions on the adsorption of Cd(II) and Zn(II) on the prepared carbon. The Freundlich and Langmuir adsorption isotherms for Cd(II) and Zn(II) in binary and ternary systems are presented in (Figs. 1 and 2), respectively (38). The results clearly revealed that the presence of other metal ions compete with Cd(II) and Zn(II) ions. It was observed that Cu(II) had the least interfering capacity among Cd(II), Zn(II), and Cu(II) ions in binary systems. Both Langmuir and Freundlich isotherms adequately described the data over the entire range of concentration, and corresponding parameters are presented in Table 5. The effect of ionic interaction (36,39) on the sorption process may also be represented by the ratio of the sorption capacity for one metal ion in the presence of the other metal ions, Q^{mix}, to the sorption capacity for the same metal when it is present alone in the solution, Q^0, such that when:

$$\frac{Q^{\mathrm{mix}}}{Q^0} > 1, \text{ the sorption is promoted by the presence of other metal ions}$$

$$\frac{Q^{\mathrm{mix}}}{Q^0} = 1, \text{ no observable net interaction exists}$$

$$\frac{Q^{\mathrm{mix}}}{Q^0} < 1, \text{ sorption is suppressed by the presence of other metal ions}$$

The values of $\frac{Q^{\mathrm{mix}}}{Q^0}$ were found to be less than 1, as presented in Table 5. The prepared activated carbon followed the same trend, that is, Q^{mix} decreased in the following order for the adsorption of Cd(II) and Zn(II) in multicomponent systems:

Cd(II) $<$ Cd-Cu $<$ Cd-Zn $<$ Cd-Cu-Zn for Cd(II)

Zn(II) $<$ Zn-Cu $<$ Zn-Cd $<$ Cd-Cu-Zn for Zn(II)

Table 5. Freundlich and Langmuir Isotherm Constants for Singe and Multicomponent Adsorption of Cd(II) and Zn(II) on Activated Carbon Developed from Bagasse Carbon

Metal Ions	System	Freundlich Constants				Langmuir Constants			
		K_F	1/n	R^2	K_F^{mix}/K_F	Q^0	$b \times 10^{-3}$	R^2	Q^{mix}/Q^0
Cd	Cd alone	5.78	0.28	0.9760	–	38.03	13.2	0.8886	–
Cd	Cd + Cu	4.30	0.29	0.9706	0.74	33.11	11.0	0.8829	0.87
Cd	Cd + Zn	1.74	0.02	0.9864	0.30	30.02	8.8	0.9678	0.79
Cd	Cd + Cu + Zn	0.59	0.03	0.9864	0.10	29.77	2.7	0.9583	0.78
Zn	Zn alone	5.62	0.25	0.9659	–	31.11	14.2	0.8683	–
Zn	Zn + Cu	3.96	0.27	0.9674	0.70	26.00	13.5	0.8723	0.84
Zn	Zn + Cd	1.42	0.41	0.9868	0.25	23.09	8.00	0.9794	0.74
Zn	Zn + Cu + Cd	0.79	0.45	0.9792	0.14	19.02	5.4	0.9804	0.61

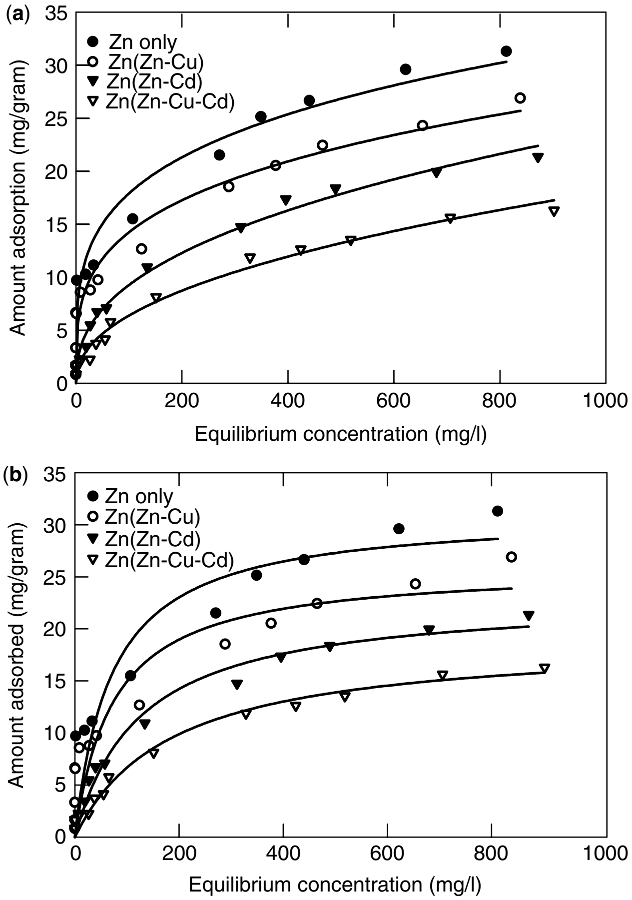

Figure 2. Multicomponent adsorption of Zn(II) on activated carbon developed from bagasse. Solid lines represent the fitting of data by (**a**) Freundlich and (**b**) Langmuir isotherms.

Overall, it was concluded that the adsorption capacity of activated carbon for Cd(II) and Zn(II) decreased more in ternary systems as compared with binary systems.

In acid mine wastewater, some other metal ions are always present besides iron and manganese; therefore, it is desirable to see the effect of other metal ions on the adsorption capacity of different activated carbons. A very important study in this regard was carried out by Mohan and Chander (39) where the adsorption of four metal ions, i.e., Mn(II), Fe(II), Zn(II), and Ca(II), were conducted in binary, ternary, and multicomponent systems on different types of activated carbons. The adsorption isotherms for binary, ternary, and multicomponent systems were obtained at pH 3.5 and 25 °C. The concentration range of 5.0×10^{-5} to 9.0×10^{-3} M was investigated, and a 1:1 ratio was used to determine the effect of Mn(II), Ca(II), and Zn(II) on the adsorption of Fe(II) on carbons. The Freundlich and Langmuir adsorption isotherms for Fe(II) in the absence and presence of interfering metal ions were determined.

Both Langmuir and Freundlich adsorption isotherms were found to adequately describe the data over the entire range of concentration, and the Langmuir and Freundlich isotherm parameters are presented in Tables 6 and 7, respectively. The detailed analysis of the regression coefficients showed that the data was slightly better fitted by Freundlich adsorption isotherm for multicomponent systems. The adsorption isotherms for different carbons revealed that, when Ca(II), Mn(II), and Zn(II) were present in the system with Fe(II), the interference did not change the adsorption of Fe(II) in the low concentration range, whereas a competitive uptake, with Fe(II) being preferentially adsorbed by carbons, took place at the higher concentrations. Carbon B0, which showed abnormal behavior and adsorption, was found to increase in the presence of other metal ions.

It was further concluded that the presence of manganese and/or zinc had limited effect on the capacity of carbons for Fe(II) in comparison with calcium. Thus, overall it was found that Ca(II) had the highest interfering capacity. The adsorption capacity of various activated carbons for Fe(II) in the presence and absence of Mn(II), Zn(II), and Ca(II) are presented in Table 6, whereas the Freundlich constants are presented in Table 7. Thus, when two or more metal ions are present in the solution, they seem to compete for the adsorption sites as the metal ions are adsorbed on the same sides.

The values of $\frac{Q^{\text{mix}}}{Q^0}$ are found to be less than 1, as presented in Table 6, except for carbon B0, thereby confirming the suppression in the adsorption of Fe(II) by the presence of other metal ions. These results are consistent with the adsorption isotherms obtained for Fe(II) in the absence and presence of various metal ions. It is clear from Table 6 that carbons can be divided into two different categories, i.e., wood-based activated

Table 6. Langmuir Isotherm Constants for Multicomponent Metal Ion Adsorption on Different Types of Activated Carbons

Activated Carbons	Parameters	Fe(II)	Fe(Fe-Ca)	Fe(Fe-Mn)	Fe(Fe-Zn)	Fe(Fe-Mn-Zn)	Fe(Fe-Mn-Zn-Ca)
W1	Q^0	22.27	15.35	17.65	16.26	13.79	12.36
	$b \times 10^{-3}$	38.63	42.14	38.67	53.86	30.36	44.75
	R^2	0.9606	0.8615	0.7013	0.7223	0.9609	0.7581
	Q^{mix}/Q^0	–	0.69	0.79	0.73	0.62	0.56
W2	Q^0	25.60	18.16	19.73	18.78	17.16	13.26
	$b \times 10^{-3}$	70.74	37.59	117.37	90.70	34.22	81.73
	R^2	0.9409	0.7529	0.7474	0.7643	0.9491	0.7516
	Q^{mix}/Q^0	–	0.71	0.77	0.73	0.67	0.52
W3	Q^0	21.67	14.58	16.86	16.10	13.64	13.06
	$b \times 10^{-3}$	53.97	82.39	78.06	86.71	34.91	21.71
	R^2	0.9302	0.8054	0.6983	0.7206	0.9735	0.6746
	Q^{mix}/Q^0	–	0.67	0.78	0.74	0.63	0.60
B0	Q^0	14.59	15.2	22.98	22.02	18.78	14.44
	$b \times 10^{-3}$	2.643	21.485	33.22	32.558	75.111	32.318
	R^2	0.8334	0.8525	0.6847	0.6700	0.8929	0.7157
	Q^{mix}/Q^0	–	1.0418	1.57505	1.509253	1.287183	0.989719
B4	Q^0	28.78	16.58	22.32	20.84	18.21	15.3184
	$b \times 10^{-3}$	27.560	14.609	35.662	34.002	23.964	18.943
	R^2	0.8773	0.8722	0.8257	0.7682	0.9549	0.7780
	Q^{mix}/Q^0	–	0.58	0.7241	0.7755	0.63	0.53
B3	Q^0	25.61	12.05	16.90	15.80	16.47	9.74
	$b \times 10^{-3}$	2.28	1.69	3.73	4.46	1.80	2.98
	R^2	0.9287	0.9809	0.9498	0.9672	0.9858	0.9728
	Q^{mix}/Q^0	–	0.47	0.66	0.61	0.64	0.38
C1	Q^0	46.35	21.77	27.40	26.05	23.85	18.31
	$b \times 10^{-3}$	36.85	34.77	77.15	31.73	23.72	43.12
	R^2	0.92668	0.619730	0.60214	0.5852	0.6432	0.7003
	Q^{mix}/Q^0	–	0.47	0.59	0.56	0.51	0.40
Lignite	Q^0	34.22	19.59	20.88	19.96	12.39	11.23
	$b \times 10^{-3}$	28.98	32.87	68.67	33.50	55.21	53.12
	R^2	0.8768	0.8912	0.8714	0.8986	0.9662	0.9238
	Q^{mix}/Q^0	–	0.5725	0.6101	0.5832	0.3621	0.3282

Table 7. Freundlich Isotherm Constants for Multicomponent Metal Ion Adsorption on Different Types of Activated Carbons

Activated carbons	Parameters	Fe(II)	Fe(Fe-Ca)	Fe(Fe-Mn)	Fe(Fe-Zn)	Fe(Fe-Mn-Zn)	Fe(Fe-Mn-Zn-Ca)
W1	K_F	90.70	36.90	34.78	27.00	44.30	34.12
	$1/n$	0.21	0.13	0.10	0.10	0.17	0.14
	R^2	0.9299	0.8715	0.7857	0.7957	0.9173	0.7240
W2	K_F	90.34	33.67	38.77	39.91	57.00	39.37
	$1/n$	0.18	0.09	0.09	0.10	0.18	0.52
	R^2	0.9452	0.8170	0.8235	0.8343	0.8712	0.7423
W3	K_F	80.67	29.37	28.80	25.42	51.54	27.83
	$1/n$	0.19	0.10	0.08	0.07	0.19	0.12
	R^2	0.9163	0.8653	0.7800	0.7953	0.8671	0.7989
B0	K_F	57.16	29.04	67.88	57.86	63.04	27.60
	$1/n$	0.25	0.10	0.15	0.14	0.16	0.097
	R^2	0.8257	0.84426	0.9054	0.9787	0.9938	0.7268
B4	K_F	281.88	123.33	112.86	109.11	265.72	100.18
	$1/n$	0.41	0.42	0.32	0.32	0.47	0.39
	R^2	0.9447	0.9667	0.9726	0.9725	0.9656	0.9614
B3	K_F	1.87	41.94	70.03	53.18	101.13	44.18
	$1/n$	0.87	0.14	0.16	0.13	0.24	0.16
	R^2	0.3759	0.8618	0.8376	0.8419	0.9675	0.7561
C1	K_F	444.84	37.36	–	–	–	38.1925
	$1/n$	0.28	0.08	–	–	–	0.11
	R^2	0.9325	0.6869	–	–	–	0.7738
Lignite	K_F	214.24	66.190	69.79	60.358	8.345	9.5887
	$1/n$	0.2455	0.1732	0.1618	0.1580	0.1367	0.1396
	R^2	0.9215	0.9061	0.9030	0.8971	0.9070	0.9067

carbons follow the same trend (Fe-Mn<Fe-Zn<Fe-Ca<Fe-Mn-Zn<Fe-Mn-Zn-Ca) whereas the other carbons behave in a similar fashion (Fe-Mn<Fe-Zn< Fe-Mn-Zn<Fe-Ca < Fe-Mn-Zn-Ca). Also, the effect of other interfering metal ions on the adsorption of Fe(II) was found to be less on coconut-based activated carbon followed by coal-based and wood-based activated carbon, respectively. Overall, it was concluded that the adsorption capacity of different carbons decreased more in ternary and quaternary systems as compared with binary systems.

Fixed bed studies were also conducted on solution containing a mixture of several metal ions. For these studies, a bed filled with activated carbon was treated with a solution containing 60 mg/L Fe (II) and 50 mg/L each of Mn (II), Zn (II), and Ca (II). The hydraulic flow rate was 1.7 mL/min. The breakthrough curves are presented in (Figs. 3 and 4). The results are plotted as dimensionless concentration (C_e/C_0) vs. effluent volume. Initially, all the metal ions were adsorbed nonselectively and a metal ion-free effluent was produced. With continued treatment, manganese began to escape the column, followed by zinc and then iron. One can see that manganese and zinc, which initially adsorbed nonselectively, are released with continued passage of iron-bearing solutions. Iron could be adsorbed selectively during the period of testing. Similar results were obtained with other carbons. These results demonstrate that metal ions can be separated and possibly recovered in useful form by treating metal-bearing wastewaters with activated carbons. The studies were also performed in the single column as well as when columns were connected in series. The difference in various parameters obtained are presented in Table 8.

The uptake of Pb(II), Hg(II), and Cr(VI) in a multicomponent system was studied by Srivastava et al. (40) on the activated carbon developed from fertilizer waste material. The sorption efficiency of the adsorbent was found to decrease by 15% and 7%, respectively, for lead and mercury in the presence of each other. No decrease, however, was reported for chromium in the presence of mercury, but the uptake of mercury reduced by 8–10% in the presence of chromium. The reduction in the sorption of metal ions from the mixtures was observed to be almost the same for different levels of interference. Competitive adsorption of various metal ions in the presence of each other is presented (40,41) in Tables 9–12.

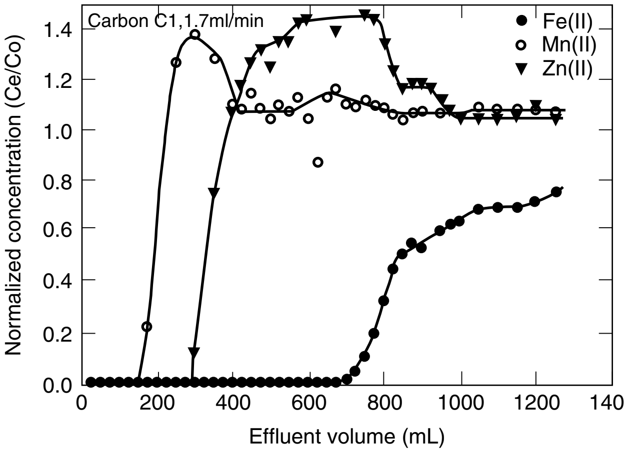

Figure 3. Breakthrough curves showing the multicomponent adsorption on carbon UU at pH 3.5 and hydraulic flow rate of 1.7 ml/min. Metal concentration = Fe(II):Mn(II):Zn(II):Ca(II):: 60:50:50:50 ppm.

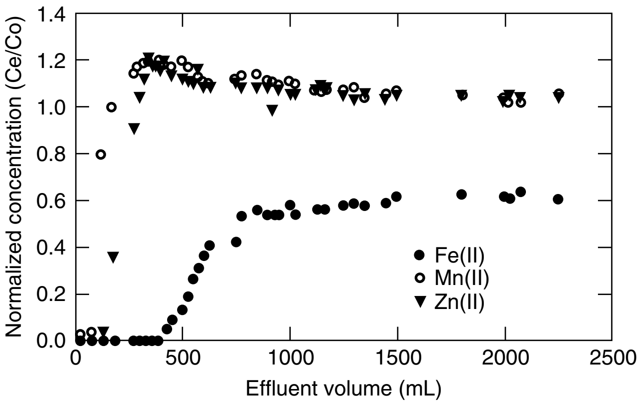

Figure 4. Breakthrough curves showing the multicomponent adsorption on carbon B3 at pH 3.5 and hydraulic flow rate of 1.7 ml/min. Metal concentration = Fe(II):Mn(II):Zn(II):Ca(II):: 60:50:50:50 ppm.

Table 8. Comparison Between Single- and Three-Column System for Fe(II) Adsorption

Types of Column	Number of Bed Volume	EBCT* (min)	$Q^\dagger$ (ml/min)	V_b	BV_b	Column Capacity (mg/g)
Single column	22	9	2.7	85 ml	4	3.4
Three column system	235	24	10	15 liter	63	18.7

*Empty bed contact time or residence time.
†Volumetric flow rate.
V_b = Breakthrough volume.
BV_b = Bed volumes at breakthrough.
[Concentration of metal ions in the inlet: 60 ppm for Fe(II); 50 ppm each for Mn(II), Zn(II), and Ca(II).]

Parameter	Value
Column diameter (cm)	2.5
Column bed height (cm)	16
Bed volume (ml)	78 each, i.e., 235
Flow rate (ml/min)	10
Residence time (min)	24
Particle size (mesh)	20 × 40
Amount of carbon	50 gm in each column, i.e., 150 gm
Concentration of metal ions (ppm)	Fe^{2+}: Mn^{2+}: Zn^{2+}: Ca^{2+}:: 60:50:50:50
pH of the solution	3.5

COMPETITIVE SORPTION OF ORGANICS

Yen and Singer (42) studied the adsorption of phenols and substituted phenols on activated carbon. Mixtures of phenolic compounds were taken to explore the Ideal Adsorbed Solution (IAS) theory using an improved method of calculation that had been developed to describe the multicomponent adsorption. The IAS model with the

Table 9. Competitive Adsorption of Pb(II) in Presence of Hg(II)

Pb(II) Concentration (mol/l)	Hg(II) Concentration (mol/l)	Amount of Pb(II) Adsorbed in Absence of Hg(II), (mol/g)	Amount of Pb(II) Adsorbed in Presence of Hg(II) (mol/g)
5×10^{-3}(fixed)	1×10^{-4}	4.7×10^{-3}	4.2×10^{-3}
	5×10^{-4}	4.7×10^{-3}	4.0×10^{-3}
	1×10^{-3}	4.7×10^{-3}	4.0×10^{-3}

Table 10. Competitive Adsorption of Hg(II) in Presence of Pb(II)

Hg(II) Concentration (mol/l)	Pb(II) Concentration (mol/l)	Amount of Hg(II) Adsorbed in Absence of Pb(II), (mol/g)	Amount of Hg(II) Adsorbed in Presence of Pb(II) (mol/g)
5×10^{-3}(fixed)	1×10^{-4}	4.0×10^{-3}	2.3×10^{-3}
	5×10^{-4}	2.7×10^{-3}	2.6×10^{-3}
	1×10^{-3}	2.7×10^{-3}	2.6×10^{-3}

Table 11. Competitive Adsorption of Cr(VI) in Presence of Hg(II)

Cr(VI) Concentration (mol/l)	Hg(II) Concentration (mol/l)	Amount of Cr(VI) Adsorbed in Absence of Hg(II), (mol/g)	Amount of Cr(VI) Adsorbed in Presence of Hg(II); (mol/g)
5×10^{-3}(fixed)	1×10^{-4}	4.0×10^{-3}	4.0×10^{-3}
	5×10^{-4}	4.0×10^{-3}	4.0×10^{-3}
	1×10^{-3}	4.0×10^{-3}	3.9×10^{-3}

Table 12. Competitive Adsorption of Hg(II) in Presence of Cr(VI)

Hg(II) Concentration (mol/l)	Cr(VI) Concentration (mol/l)	Amount of Hg(II) Adsorbed in Absence of Cr(VI), (mol/g)	Amount of Hg(II) Adsorbed in Presence of Cr(VI) (mol/g)
5×10^{-3}(fixed)	1×10^{-4}	3.0×10^{-3}	2.7×10^{-3}
	5×10^{-4}	2.7×10^{-3}	2.5×10^{-3}
	1×10^{-3}	2.7×10^{-3}	2.5×10^{-3}

modified calculation method was tested for its performance on ten sets of binary and ternary phenolic mixtures. The Langmuir model was also taken just to compare the results, but the IAS model was found to be successful in precisely describing the competitive adsorption behavior of phenolic mixtures.

The impact of the presence of molecular oxygen on multisolute adsorption of phenols on granular activated carbon was evaluated by Sorial et al. (43). Adsorption equilibrium for binary mixtures of phenol/O-cresol and ternary mixtures of phenol/O-cresol/3-ethylphenol was carried out at 23 °C using three different initial concentration combinations. Adsorption was carried out under oxic and anoxic conditions. The ideal adsorbed solution theory, using Myers equation for correlating the single-solute anoxic isotherms, was found to accurately describe the competitive adsorption behavior of these phenolic mixtures under anoxic conditions. When the Freundlich model was used to describe the single-solute sorption, the deviations were found to increase. It was concluded that poor model predictions for the oxic isotherms were attributed to the presence of molecular oxygen, which promotes the polymerization of solutes on the surface of granular activated carbon. In continuation of this study, the same authors (44) conducted the adsorption of these phenolic compounds in fixed bed GAC adsorbers. The adsorption breakthrough curves were obtained for a single-solute system, i.e., phenol, O-cresol, and 3-ethylphenol, as well as for multisolute systems, i.e., phenol/O-cresol and phenol/O-cresol/3-ethylphenol. The plug through homogenous surface diffusion model was evaluated as a predictor of GAS adsorber, whereas the binary and ternary solute calculations were performed using kinetic parameters determined from a single-solute system. The ideal adsorbed solution theory was implemented. The model for binary and ternary solute systems agrees well with the experimental data collected under anoxic conditions.

The adsorption of 2,4,6-trichlorophenol (TCP) and N-[2-(2,4,6-trichlorophenoxy)propyl] amine(BTS40348) in single and binary systems was carried out on four different activated carbon at pH 4.0 and 9.0 by Garner et al. (45). Competitive adsorption was observed, and at respective pH optima, reduction in adsorption efficiencies were found to be 10% for TCP and 43% for BTS40348.

The interference of catioinc, nonionic, and anionic detergents on the adsorption of phenols was studied as a function of the concentration of detergents (46). As all types of surfactants are found to interact to a varying degree with activated carbons, the effect of anionic detergent (Manoxol 1B), nonionic detergent (triton), and cationic detergent (cetylpyridinium chloride) on the uptake of 2,4,6-trinitrophenol, 4-nitrophenol, 4-chlorophenol, and 1,3-dihydroxybenzene by the activated carbons was studied. The adsorption of 2,4,6-trinitrophenol was found to decreased by 1.3–3.3% in the presence of increasing anionic detergent concentration. A decrease in adsorption efficiency by 3.0–6.0% was observed in the case of 4-nitrophenol. In the case of 4-chlorophemol, the uptake decreased by 5–7%, whereas a 2–5% decrease was observed for 1,3 dihydroxybenzene. In the case of nonionic surfactant, the removal efficiencies of activated carbon was found to decrease by 2–4%, 3–8%, 3.7–7.5%, and 3.3–6.7% for 2,4,6-trinitrophenol, 4-nitro phenol, 4-chloro phenol, and 1,3-dihydroxybenzene, respectively. In the case of cationic detergent, a decrease in the scavenging efficiency of activated carbon by 2.7–6.7% for 2,4,6-trinitrophenol and 4.0–10.0% for 1,3-dihydroxybenzene was observed. Thus, the maximum effect was found with cationic detergent and the minimum with anionic detergent. Nonionic detergent falls in between the two. Authors explained that the decrease in the scavenging efficiency of activated carbon for phenols in the presence of surfactants is consistent with the act that the particles of the carbon surface are negatively charged.

Jossens et al. (47) studied the sorption data at 20 °C for six dilute aqueous bi-solute systems in activated carbon. The six systems were phenol/p-nitrophenol, p-nitrophenol/p-chlorophenol, p-nitrophenol/benzoic acid, p-chlorophenol/phenyl acetic acid, p-nitrophenol/o-phenyl phenol, and 2,4-dichlorophenol/dodecyl-benzol sulfonic acid. A new three-parameter adsorption isotherm was presented that represents the single-solute data very well. For bi-solute systems where dissociation is negligible, the calculated individual adsorption agrees with experimental data within 2%.

The adsorption of acetaldehyde, acetone, 2-butanone, pyridine, and phenol from binary aqueous solutions on activated carbon was reported by Barton (48). The author has applied the Dubbinin–Radushkevich (DR) equation with some slight modifications. The authors explained that the displacement adsorption of 2-butanone and pyridine is driven mainly by the displacement enthalpy. As desorption of water involves an increase in motional entropy, it was therefore concluded that strong adsorbed solutes 2-butanone and pyridine produce a large compensating entropy decrease. On the other hand, more weakly adsorbed substances, such as acetone and acetaldehyde, were not able to compensate for the entropy increase associated with the desorbed water on adsorption. Single and multisolute adsorption isotherms studies of three phenolic compounds, i.e., gallic acid, *p*-hydroxybenzoic acid, and syringic acid, were investigated at 20 °C, 30 °C, and 40 °C using a bituminous coal-based activated carbon (49). The capacity of the activated carbon used to adsorb these compounds follows the order: syringic acid > *p*-hydroxybenzoic acid > gallic acid. In binary and ternary components, experimental data suggested that interactions between adsorbates improve the adsorption capacity of some of the phenolic acid compounds. On the contrary, at high organic concentrations, adsorbed gallic acid was partially removed from the activated carbon surface because of the presence of the other components. A two-component isotherm (phenol/2,6-dichlorophenol) adsorption was also studied by Mameli et al. (50) in order to test activated carbon behavior during competitive adsorption.

Kim and Lordgooei (51,52) reported the adsorption modeling of various volatile organic compounds in single and multicomponent systems. A Dubinin–Astakhov thermal equation of equilibrium adsorption (DA-TEEA) for single component and ideal/real adsorbed solution theories (IAST/RAST) for multicomponent systems were presented successfully. In an another study, Semmens et al. (53,54) studied the influence of pH and coagulation on the removal of organics by granular activated carbon. Okazaki et al. (55,56) reported the multicomponent adsorption of organics from water, whereas Ha et al. (57) developed a predictive isotherm model to evaluate the extent of bioregeneration of granular activated carbon loaded with phenol and 2,4-dichlorophenol (2,4-DCP) in single and bisolute systems. A bisolute system was taken up for assessing the competitive adsorption. The effect of byproducts, which were generated during biodegradation of substrate and measured as COD, on bioregeneration in the bisolute was also investigated. Freundlich adsorption capacity of 2,4-DCP was found to be more as compared with phenol in both single and bisolute systems. Byproducts in the bulk solution brought an adverse effect on adsorption capacity of GAC in all cases. By taking into account the byproduct effect on adsorption, the Freundlich isotherms were used to formulate a predictive model of bioregeneration.

The adsorption of benzoic acid and p-nitrophenol (PNP) at 25 °C was performed by Chern and Chien (58) in a binary system on GAC. The sorption experimental data were fitted to the extended Langmuir isotherm model successfully. The experimental data and the isotherm model parameters showed that the GAC used in this study had a higher affinity to PNP than benzoic acid. Three-column tests were performed to determine the breakthrough curves and effluent solution pH with varying feed compositions. The weakly adsorbed BA exhibited an intermediate zone of effluent concentration higher than its feed one. The authors predicted that the breakthrough curves with varying feed compositions could be predicted by the nonlinear wave propagation theory satisfactorily, only the adsorption isotherm models were required to construct the composition path diagram with which the breakthrough curves could be predicted. In an important study, Bulloch et al. (59) developed a thermodynamic model to predict adsorption equilibrium in the international space station water processor's multifiltration beds. The model was able to predict the multicomponent adsorption equilibrium behavior using single component isotherm parameters and fictitious components representing the background matrix. The fictitious components

Table 13. Competitive Adsorption of Phenols in Presence of Each Other

Adsorbate	Adsorbate Concentration mol/l	Amount Adsorbed mol/g	Amount Adsorbed in Presence of 2,4,6-Trinitrophenol (1×10^{-5} M) mol/g	Amount Adsorbed in Presence of 4-Nitrophenol (1×10^{-5} M) mol/g	Amount Adsorbed in Presence of 4-Chlorophenol (1×10^{-5} M) mol/g	Amount Adsorbed in Presence of 1,3 Dihydroxy Benzene (1×10^{-5} M) mol/g
2,4,6-trinitro phenol	1×10^{-4}	1×10^{-4}	—	—	—	X
2,4,6-trinitro phenol	1×10^{-3}	7.50×10^{-4}	—	—	—	X
4-nitrophenol	1×10^{-4}	0.9×10^{-4}	0.84×10^{-4}	—	—	X
4-nitrophenol	1×10^{-3}	5.00×10^{-4}	4.80×10^{-4}	—	—	X
4-chlorophenol	1×10^{-4}	0.73×10^{-4}	0.65×10^{-4}	0.70×10^{-4}	—	X
4-chlorophenol	1×10^{-3}	4.00×10^{-4}	3.50×10^{-4}	3.80×10^{-4}	—	X
1,3 dihydroxy benzene	1×10^{-4}	0.70×10^{-4}	0.55×10^{-4}	0.65×10^{-4}	0.70×10^{-4}	X
1,3 dihydroxy benzene	1×10^{-3}	3.00×10^{-4}	2.50×10^{-4}	2.75×10^{-4}	2.90×10^{-4}	X

were determined by fitting total organic carbon and tracer isotherms with the ideal adsorbed solution theory. Multicomponent isotherms using a wastewater with high surfactant and organic compound concentrations were used to validate the equilibrium description on a coconut-shell-based granular activated carbon (GAC), coal-based GAC, and a polymeric adsorbent.

The adsorption of three barbiturates—phenobarbital, mephobarbital, and primidone—from simulated intestinal fluid (SIF), without pancreatin, by activated carbon was studied by Wurster et al. (6). The competitive Langmuir-like model, the modified competitive Langmuir-like model, and the LeVan–Vermeulen model were each fit to the data. Excellent agreement was obtained between the experimental and predicted data using the modified competitive Langmuir-like model and the LeVan–Vermeulen model. The agreement obtained from the original competitive Langmuir-like model was less satisfactory. The results of these studies indicate that the adsorbates were found to compete for the same binding sites on the activated carbon surface. The results demonstrated that it is possible to accurately predict multicomponent adsorption isotherms using only single-solute isotherm parameters.

Rozada et al. (60) studied the adsorption of methylene blue and saphranine from single and bisolute systems using the activated carbons developed by chemical activation and pyrolysis of sewage sludges.

The effect of presence of an anionic (Manoxol 1B), nonionic (Triton), and cetyl pyridinium chloride detergent on the uptake of dinitrophenol by activated carbon developed from fertilizer waste slurry was studied by Srivastava et al. (61). The dinitrophenol adsorption showed a decreased (2–8%) w/w with increasing concentrations of anionic, nonionic, and cationic surfactants. The uptake of DNP was also observed in the presence of NaCl, $BaCl_2$, and $AlCl_3$ at a fixed adsorbent concentration. No effect of NaCl was observed on DNP uptake between pH 2 to 4, but at pH 10, adsorption increases by 66% w/w. The presence of $BaCl_2$ and $AlCl_3$ did not affect the uptake of DNP to a significant extent ($2 < 2\%$ w/w). The influence of anions (ClO_4^-, PO_4^{3-}, SO_4^{2-}, and NO_3^-) on the uptake of dinitrophenol was also reported. It was observed that anions have a negligible effect on the sorption of DNP. Various explanations were given for the competitive adsorption, some of which are listed below:

1. Interaction in solution between salts and organics to produce a change in the distribution of the organic species present, thereby influencing the rate or the extent of adsorption.
2. Interactions between salts and the adsorbed organics, resulting in the alteration of the packing, spacing, or alignment of the adsorbed molecules.
3. Interactions between salts and the adsorbate and adsorbent to perhaps create new or particularly favorable adsorption sites.

The enhanced adsorption of DNP in the presence of slats was thus attributed to the interaction between cations and organics in the solution or at a solid surface. Such interaction influences adsorption through the alteration of solubility or the degree of ionization of the organic molecule via the common ion effect, ion pairing, or complexation. The enhance in the uptake of DNP was attributed to ion pair formation

The adsorption of malachite in presence of Manoxol 1B detergent was reported by Gupta et al. (62). The removal was found to decrease by 1.5–2.0%.

Sung-Ryong and Vinitnantharat (63) studied the sorption of phenol and 2,4 dichlorophenol in single and bisolute systems. It was concluded that 2,4 DCP was a stronger adsorbate than phenol in both single and bisolute systems. On desorption of 2,4 DCP, the small fraction of sorbed compounds was reversible, but phenol has comparatively high reversibility.

The competitive adsorption of three cationic polymers, namely JR125, JR400, and JR30M, and a cationic surfactant (cetyl trimethyl ammonium bromide) onto a silica surface from a low ionic strength medium was investigated by Harrison et al. (64). It was reported that competition between polymers showed that smaller molecules were adsorbed, initially preventing the subsequently adsorption on larger polymers. Adsorption from the combined polymer and the smallest polymer (JR 125) was excluded from the surface; the intermediate molecular mass polymer (JR

400) was almost unaffected; the surfactant and the largest molecular mass polymer (JR 30M) were partially excluded from the surface.

Competitive adsorption of substituted phenols by activated carbon developed from fertilizer waste slurry was investigated by Srivastava and Tyagi (65). The uptake of 4-chlorophenol, 4-nitophenol, 2,4,6-trinitrophenol, and 1,3-dihydroxybenzene in the presence of each other provided some interesting data, which is presented in Table 13. Surprisingly, the adsorption of 2,4,6-trinitrophenol did not get at all affected by 4-nitrophenol, 4-chlorophenol, and 1,3-dihydroxybenzene. However, the uptake of 4-nitophenol went down by 6.0% in the presence of 2,4,6-trinitrophenol. No decrease, however, was observed in the presence of 4-chlorophenol and 1,3-dihydroxybenzene. Similarly, the adsorption of 4-chlorophenol was found to reduced by 5.0% and 12.5% in the presence of 4-nitophenol and 2,4,6-trinitrophenol. 4-chlorophenol was not affected by 1,3-dihydroxybenzene. The sorption capacity of 1,3-dihydroxybenzene decresed by 3.3%, 8.3%, and 16.7% in presence of 4-chlorophenol, 4-nitrophenol, and 2,4,6-trinitrophenol, respectively. The electron withdrawing nature of nitro as well as chloro reduced the electron density in the ring in phenols. The effect was highest in 2,4,6-trinitrophenol and lowest in 1,3-dihydroxybenzene. 4-nitophenol and 4-chlorophenol occupy the second and third position if a gradation of all four adsorbates is made vis-a-vis the reduction in electron density of the pi system of the ring, which explained that the removal of 2,4,6-trinitrophenol did not get reduced in the presence of the other three phenols. The observed fact that 1,3-dihydroxybenzene also did not reduce the uptake of other phenols could also be attributed to the above-mentioned reason.

MULTICOMPONENT KINETICS

Similar to equilibrium studies, multicomponent kinetics is also a very important aspect of any adsorption study. It is based on the single component kinetics model. Out of the various kinetic models, the film-solid diffusion model is the best one as far as theoretical background and optimum mathematical conveyance are concerned, and therefore opted by a number of researchers from time to time in multicomponent systems. The details about this model are also very much documented in various articles (12,15,66–68).

The kinetic adsorption of mixtures of phenolic compounds onto a polymeric adsorbent from aqueous solution was studied by Mijangos et al. (69). Van Laar's equation was applied to evaluate the influence of concentration on diffusion. The adsorption kinetics for phenol and p-cresol mixtures at different initial concentration ratios were studied and adjusted to the mentioned kinetic model. They concluded that adsorption from multicomponent aqueous solution is a surface diffusion-controlled process.

The binary soprtion of Cu-Cd, Cd-Zn, and Cu-Zn onto bone char has been studied using an equilibrium and batch agitation system (70). The sorption capacities and selectivity of metal ions follows the order Cu(II)>Cd(II)>Zn(II), which is a reverse order of the hydrated ionic radii. The binary sorption equilibria were predicted by the ideal adsorbed solution theory (IAST) on the basis of single component isotherm data using a Langmuir or Langmuir–Freundlich isotherm. The overall performance of IAST provided a reasonable curve fitting to the experimental data. The single component film-pore diffusion model was extended to the multicomponent systems to correlate the batch kinetic data by incorporating the shrinking core model and IAST. It was found that all the diffusivities in the binary systems are similar to or less than the pore diffusitivites in single component systems.

Table 14

Metal Ions	Single Component D_ρ (cm^2/s)	Cd-Cu	Cd-Zn	Cu-Zn
Cd	1.14×10^{-6}	1.20×10^{-6}	2.25×10^{-7}	—
Cu	1.59×10^{-6}	1.30×10^{-6}	—	1.50×10^{-6}
Zn	1.21×10^{-6}	—	1.10×10^{-6}	1.00×10^{-6}

The pore diffusivities of the multicomponent systems using the film-pore diffusion model and IAST are given in Table 14. Although the equal molar and unequal molar equilibrium data can generally be predicted by IAST, the results for the mole ratios 3:7 and 7:3 for the Cd-Cu systems cannot be predicted very well.

BIBLIOGRAPHY

1. Crittenden, J.C. and Weber, W.J., Jr. (1978). Predictive model for design of fixed bed adsorbers; Single-component model verification. *J. Environ. Eng. Div.* **104**(EE3): 433–443.
2. Crittenden, J.C. and Weber, W.J., Jr. (1978). Model for design of multi-component adsorption systems. *J. Environ. Eng. Div.* **104**(EE6): 1175–1195.
3. Crittenden, J.C., Wong, B.W.C., Thacker, W.E., Snoeyink, V.L., and Hinrichs, R.L. (1980). Mathematical modeling of sequential loading in fixed-bed adsorbers. *J. Water Pollution Control Fed.* **51**(11): 2780–2795.
4. Hand, D., Crittenden, J.C., and Thacker, W.E. (1984). Simplified models for design of fixed bed adsorption systems. *J. Environ. Eng. Div.* **110**(2): 441–456.
5. Butler, J.A.V. and Ockrent, C. (1930). Studies in electrocapillarity Part 3. The surface tensions of solutions containing two surface-active solutes. *J. Phys. Chem.* **34**: 2841–2859.
6. Wurster, D.E., Alkhamis, K.A., and Matheson, L.E. (2000). Prediction of adsorption from multicomponent solutions by activated carbon using single-solute parameters. Part 1. *AAPS Pharm. Sci. Tech.* **1**(3): E25.
7. Alkhamis, K.A. and Wurster, D.E. (2002). Prediction of adsorption from multicomponent solutions by activated carbon using single solute parameters. Part II. *AAPS Pharm. Sci. Tech.* **3**(3): 23.
8. Hsieh, C.P., Turian, R.M., and Tein, C. (1977). Multicomponent liquid phase adsorption in fixed bed. *Amer Inst. Chem. Eng. J.* **23**(3): 263–275.
9. Hsieh, C.P., Tsang, M.W., and Hsieh, Y.S. (1985). The removal of cobalt(II) from water by activated carbon. *Amer. Inst. Chem. Eng. Symp. Series.* **81**(243): 85–98.
10. Jain, J.S. and Snoeyink, V.L. (1973). Adsorption from bisolute systems on activated carbon. *J. Water. Pollut. Control. Fed.* **45**(12): 2463–2479.

11. Huang, J.-C. and Steffens, C.T. (1976). Competitive adsorption of organic materials by activated carbon. *Proceedings of the 31st Industrial Waste Conference*. Purdue University.
12. Mathew, A.P. (1975). *Mathematical Modeling of Multicomponent Adsorption in Batch Reactors*. Ph.D. Dissertation. University of Michigan, Ann Arbor, MI.
13. Redlich, O. and Peterson, D.L. (1959). A useful adsorption isotherm. *J. Phys. Chem.* **63**: 1024.
14. Fritz, W. and Schlunder, E.U. (1974). Simultaneous adsorption equilibria of organic solutes in dilute aqueous solutions on activated carbon. *Chem. Eng. Sci.* **29**: 1279–1282.
15. Fritz, W., Merk, W., and Schlunder, E.U. (1981). Competitive adsorption of two dissolved organics onto activated carbon, II Adsorption kinetics in batch reactors. *Chem. Eng. Sci.* **36**: 731–741.
16. Dastgheib, S.A. and Rockstraw, D.A. (2002). A systematic study and proposed model of the adsorption of binary metal ion solutes in aqueous solution onto activated carbon produced from pecan shells. *Carbon* **40**: 1853–1861.
17. Sheindorf, C.H., Rebhun, M., and Sheintuch, M. (1981). *J. Colloid. Interface Sci.* **79**: 136.
18. Sheindorf, C.H., Rebhun, M., and Sheintuch, M. (1982). *Water Res.* **16**: 357.
19. Myers, A.L. and Prausnitz, J.M. (1965). Thermodynamics of mixed-gas adsorption. *Amer. Inst. Chem. Eng. J.* **11**(1): 121–127.
20. Radke, C.J. and Prausnitz, J.M. (1972). Thermodynamics of multisolute adsorption from dilute liquid solutions. *Amer. Inst. Chem. Eng. J.* **18**(4): 761–768.
21. Crittenden, J.C. et al. (1985). Prediction of multi-component adsorption equilibria using ideal adsorbed solution theory. *Environ. Sci. Technol.* **19**: 1030–1043.
22. LeVan, M.D. and Vermeculen, T. (1981). Binary Langmuir like and Freundlich isotherms for ideal adsorbed solutions. *J. Phys. Chem.* **85**: 3247–3250.
23. Mohan, D. and Chander, S. (1999). *Recovery of Valuable Materials from Mine Drainage The Ben Franklin Partnership Program*, Project Number: 976C.1033R-1, Penn State University, University Park, State College, PA.
24. Budinova, T.K., Gergova, K.M., Petrov, N.V., and Minkova (1994). Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials. *J. Chem. Technol. Biotechnol*. **60**: 177–182.
25. Johns, M.M., Marshall, W.E., and Toles, C.A. (1998). Agricultural by-products as granular activated carbons by adsorbing dissolved metals and organic. *J. Chem. Technol. Biotechnol*. **71**: 131–140.
26. Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M., and Portier, R.J. (2003). Adsorption of metal ions by pecan shell-based granular activated carbons. *Bioresour. Technol.* **89**(2): 115–119.
27. Chen, J.P. and Lin, M. (2001). Equilibrium and kinetics of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modeling studies. *Water Res.* **35**(10): 2385–2394.
28. Choi, J.Y. and Kim, D.S. (2002). Adsorption behavior of zinc and cadmium ion on granular activated carbon in singular and binary systems and the influence of nitrilotricetic acid as a complexing agent. *J. Environ. Sci. Health Part A Tox Hazard Subst. Environ. Eng.* **37**(9): 1701–1719.
29. Yu, Q. and Kaewsarn, P. (1999). Binary adsorption of copper(II) and cadmium(II) from aqueous solutions by biomass of marine alga Durvillaea Potatorum. *Separation Sci. Technol.* **34**(8): 1595–1605.
30. Trujullo, E.M., Jeffers, T.H., Ferguson, C., and Stevenson, Q. (1991). Mathematically modeling the removal of heavy metals from a wastewater using immobilized biomass. *Environ. Sci. Technol.* **25**: 1559–1664.
31. Bunzl, K., Schmidt, W., and Sansoni, B. (1976). Kinetic of ion exchange in soil organic metter-IV. Adsorption and desorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}. *J. Soil. Sci.* **27**: 32–41.
32. Masslenilov, B.I. and Kiselva, S.A. (1989). Physicochemical basis for the use of peat in ion-excahnge technology and adsorption processes. *Torfianaia Promyshlennost* **5**: 23–25.
33. Ho, Y.-S., Wase, D.A.J., and Forster, C.F. (1996). Removal of lead ions from aqueous solution using sphagnum moss peat as adsorbent. *Water SA* **22**: 219–224.
34. Beveridge, A. and Fickering, W.F. (1983). The influence of surfactants on the adsorption of heavy metal ions by clays. *Water Res.* **17**: 215–255.
35. Allen, S.J. and Brown, P.A. (1995). Isotherm analyses for single component and multicomponent metal sorption onto lignite. *J. Chem. Tech. Biotechnol*. **62**: 17–24.
36. Tan, T.C., Chia, C.K., and Teo, C.K. (1985). Uptake of metal ions by chemically treated human hairs. *Water Res.* **19**(2): 157–162.
37. Krishnan, K.A. and Anirudhan, T.S. (2003). Removal of Cd(II) from aqueous solutions by steam activated sulphurised carbon prepared from sugar bagasse-pitch: kinetic and equilibrium studies. *Water SA* **29**(2): 147–156.
38. Mohan, D. and Singh, K.P. (2002). Single and multicomponent adsorption of zinc and cadmium from wastewater using activated carbon derived from bagasse-an agricultural waste material. *Water Res.* **36**(9): 2304–2318.
39. Mohan, D. and Chander, S. (2001). Single component and multicomponent metal ions adsorption by activated carbons. *Colloids Surfaces A* **177**: 183–196.
40. Srivastara, S.K., Tyagi, R., and Pant, N. (1989). Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plant. *Water Res.* **23**(9): 1161–1165.
41. Pant, N. (1988). *Studies on the Use of Activated Carbon Developed from a Fertilizer Waste for the Removal of Organic and Inorganic Pollutants*, Ph.D. Thesis, Indian Institute of Technology Roorkee, India.
42. Yen C-Y. and Singer, P.C. (1984). Competitive adsorption of phenols on activated carbon. *J. Environ. Engineer.* **119**(5): 976–989.
43. Sorial, G.A., Suidan, M.K., and Vidic, R.D. (1993). Competitive adsorption of phenols on GAC I: Adsorption equilibrium. *J. Environ. Engineer.* **119**(6): 1026–1043.
44. Sorial, G.A., Suidan, M.K., Vidic, R.D., and Maloney, S.W. (1993). Competitive adsorption of phenols on GAC I: Adsorption dynamics under anoxic conditions. *J. Environ. Engineer.* **119**(6): 1044–1058.
45. Garner, I.A., Watson-Craik, I.A., Kirkwood, R., and Senior, E. (2001). Dual solute adsorption of 2,4,6-trichlorophenol and N-[2-(2,4,6-trichlorophenoxy)propyl]amine onto activated carbon. *J. Chem. Tech. Biotechnol*. **76**: 932–940.
46. Srivastava, S.K. and Tyagi, R. (1993). Competitive effect of surfactants in the adsorption of phenols by activated carbon developed from fertilizer waste slurry. *Chem. Engineer. World* **28**(11): 83–86.
47. Jossens, L., Prausnitz, J.M., Fritz, W., Schlunder, E.U., and Myers, A.L. (1978). Thermodynamics of multicomponent adsorption from dilute aqueous solutions. *Chem. Engineer. Sci.* **33**: 1097–1106.

48. Barton, S.S. (1993). Adsorption from dilute, binary, aqueous solutions. *J. Colloid. Interface Sci.* **158**: 64–70.
49. García-Araya, J.F., Beltrán, F.J., Álvarez, P., and Masa, F.J. (2003). Activated carbon adsorption of some phenolic compounds present in agroindustrial wastewater. *Adsorption* **9**(2): 107–115.
50. Mameli, A., Cincotti, A., Lai, N., Crisafulli, C., Scire, S., and Cao, G. (2004). Adsorption of organic compounds onto activated carbons from recycled vegetables biomass. *Ann. Chim.* **94**(7–8): 547–554.
51. Kim, M-S. and Lordgooei, M. (2004). Modeling volatile organic compound sorption in activated carbon II. Multicomponent equilibrium. *J. Environ. Eng.* **130**(3): 223–230.
52. Kim, M-S. and Lodgooei, M. (2004). Modelling volatile organic compound sorption in activated carbon I: Dynamics and single component equilibrium. *J. Environ. Eng.* **130**(3): 212–222.
53. Semmens, M.J., Staples, A.B., Hohenstein, G., and Norgaard, G.E. (1986). Influence of coagulation on removal of organics by granular activated carbon. *J. Amer. Water Works Assoc.* **78**(8): 80–84.
54. Semmens, M.J., Norgaard, G.E., Hohenstein, G., and Staples, A.B. (1986). Influence of pH on the removal of organics by granular activated carbon. *J. Amer. Water Works Assoc.* **78**(5): 89–93.
55. Okazaki, M., Kage, H., Iijima, F., and Toei, R. (1981). Approximate description of multi solute adsorption equilibrium in organic aqueous solution. *J. Chem. Eng. Japan* **14**(1): 26–31.
56. Okazaki, M., Kage, H., and Toei, R. (1980). Prediction of liquid phase adsorption equilibria in muti-solutes in water. *J. Chem. Eng. Japan* **13**(4): 286–291.
57. Ha, S.R., Vinitnantharat, S., and Ishibashi, Y. (2001). A modeling approach to bioregeneration of granular activated carbon loaded with phenol and 2,4-dichlorophenol. *J. Environ. Sci. Health A Tox Hazard Subs. Environ. Eng.* **36**(3): 275–292.
58. Chern, J.M. and Chien, Y.W. (2003). Competitive adsorption of benzoic acid and p-nitrophenol onto activated carbon: isotherm and breakthrough curves. *Water Res.* **37**(10): 2347–2356.
59. Bulloch, J.L., Hand, D.W., and Crittenden, J.C. (1998). A model for predicting contaminant removal by adsorption within the International Space Station water processor: 1. Multicomponent equilibrium modeling. *Water Environ. Res.* **70**(1): 14–26.
60. Rozada, F., Calvo, L.F., Garcia, A.I., Martin-Villacorta, J., and Otero, M. (2003). Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems. *Bioresour. Technol.* **87**(3): 221–230.
61. Srivastava, S.K., Tyagi, R., Pal, N., and Mohan, D. (1997). Process development for the removal and recovery of substituted phenol from wastewater by a carbonaceous adsorbent developed from fertilizer waste material. *J. Environ. Engineer (ASCE)* **123**(9): 842–851.
62. Gupta, V.K., Srivastava, S.K., and Mohan, D. (1997). Equilibrium uptake, sorption dynamics, process optimization & column operation for the removal & recovery of malachine green from wastewater using activated carbon & activated slag. *Industr. Engineer. Chemistry Res. (ACS)* **36**(6): 2207–2221.
63. Sung-Ryong, H.A. and Vinitnantharat, S. (2000). Competitive removal of phenol and 2,4 dchlorophenol in biological activated carbon system. *Environ. Technol.* **12**(4): 387–396.
64. Harrison, I.M., Meadows, J., Robb, I.D., and Williams, P.A. (1995). Competitive adsorption of polymers and surfactants at the solid/liqud interface. *J. Chem. Soc. Farady Trans.* **91**(21): 3919–3923.
65. Srivastava, S.K. and Tyagi, R. (1995). Competitive adsorption of substituted phenols by activated carbon developed from fertilizer waste slurry. *Water Res.* **29**(2): 483–488.
66. Mckay, G. (1995). *Use of Adsorbents for the Removal of Pollutants from Wastewaters*. CRC Press, Boca Raton, FL.
67. Mackay, G. and Al-Duri, B. (1991). Multicomponent dye adsorption onto carbon using a solid diffusion mass transfer model. *Indust. Engineer. Chem. Research* **30**: 385.
68. Liapis, A.I. and Rippin, D.W.T. (1977). A general model for the simulation of multicomponent adsorption from a finite bath. *Chem. Eng. Sci.* **32**: 619.
69. Mijangos, F., Navarro, A., and Jodra, Y. (2001). Kinetic analysis of phenol adsorption from aqueous systems. *Can. J. Chem. Engineer.* **79**.
70. Cheung, C.W., Ko, D.C.K., Porter, J.F., and Mckay, G. (2003). Binary metal sorption on bone char mass transport model using IAST. *Langmuir* **19**: 4144–4153.

A REAL-TIME HYDROLOGICAL INFORMATION SYSTEM FOR CITIES

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Nowadays, many organizations collect hydrologic information for various purposes. But still, little information from the huge sources of data is made public in real time, and only a small fraction of the data is applied for real-time decision making. Once the hydrologic data have become "historical" (the data are no longer applicable for real-time decision making), the data are still very valuable for design and for evaluating and understanding the hydrologic environment. But if hydrological data are used only after they have become "history," the value of the data collection is not fully used.

Before starting to disseminate hydrologic information it is important to address the following questions:

1. What kind of real-time information should be shown to the public?
2. How and where should the real-time information be presented to the public?
3. When do hydrologic data change from valuable real-time information to less interesting (from a public point of view) historical hydrologic data?
4. What does it take in knowledge, technology, and hardware to provide real-time hydrologic information?

This article discusses experience gathered from a research project in Bangkok concerning provision of real-time rainfall data to the public through the Internet, hand-held computers, and mobile phones. It also provides an outline of the future use of hydrologic information in real time. The potential benefits from the described framework for using the information are

- a public rainfall and flood information service, like the daily weather forecast, and flood warning system
- traffic information about streets that have a potential risk for flooding,
- a decision support system for reducing flooding in the Bangkok area.

INTRODUCTION

Water is a basic necessity for sustaining life and developing society. Proper management, protection and development of water resources are challenges imposed by population growth, increasing pressure on water and land resources by competing usage, and degradation of scarce water resources in many parts of the world.

The cities in Asia are growing rapidly, so it is important to pay attention to the role of cities in integrated water resources management (IWRM). The infrastructure for water in cities consists of water supply networks, sewer systems, and purification and wastewater facilities. Many of the cities are old, and they have developed according to varying historical needs and visions. Hence, the layout and design of the infrastructure has gradually developed into rather complex systems covering large areas, and the systems often have inadequate capacities. The cities are located in the monsoon area, so they have to cope with very high rainfalls every year. Regular flooding during the rainy season is the rule rather than the exception in most areas. For smaller floods, the people seem to have adjusted their daily lives, although there is always a loss of income and property damage. However, when the floods are heavy, the socioeconomic and health impacts on the population are enormous. This requires information and tools that can handle such situations and describe flooding from local rainfall in cities.

An understanding of the physical system and its interaction with the environment is a prerequisite for effective planning and management of urban water resources. It is too expensive to eliminate flooding in urban areas by using only structural measures, such as building new sewers, embankments, and installation of pumps. To manage the existing infrastructure better, nonstructural measures, like real-time rain fall and flood risk information can minimize flooding and the impact of flooding. In addition, provision of flood risk information can help people make more intelligent decisions during floods, and hence reduce the stress and costs of floods.

Today's advances in computer technology can help many cities in the world manage local and minor flooding problems using computer-based solutions. This involves building computer models of the drainage/sewer system. These models are then used to understand the often rather complex interaction between rainfall and local flooding. Computer models provide the opportunity for well-structured analyses of rainfall/runoff/flooding, water availability, water demands, and wastewater disposal, and they offer a sound scientific framework for coordinated management and planning. Once the existing conditions have been analyzed and understood, alleviation schemes can be evaluated and the optimal scheme implemented. In addition to real-time information, modeling increases the value of the hydrologic data tremendously because the combination of models and real-time data provides a full cover of information over a catchment.

BACKGROUND

At present, the Asian Institute of Technology (AIT) is carrying out a research project to apply real-time rainfall information for Bangkok, Thailand. The Greater Bangkok area has a very high level of activity. Millions of people live in the area: On the outskirts of the city, there are a lot of big factories, and many national as well as international offices are situated in the center of town. When heavy rainfall occurs in the Bangkok area, some of the consequences are heavy traffic jams, waterlogging, blackouts, and property damage. If flooding follows, there is often great social impact as well. Many people might lose their jobs for a shorter or longer period due to temporary closing of businesses, and schools have to close because the streets are flooded.

A typical picture of flooding in the city after a minor heavy rain in Bangkok can be seen in Fig. 1. Knowing the condition of rainfall in Bangkok in advance can help in managing and dealing with these problems. Therefore, hydrometeorological forecasts and warnings are effective tools for preventing property damage caused by rainfall and subsequent flooding.

The objectives of the current project are to

1. provide a real-time information system concerning rainfall and flood risk, and

Figure 1. The Nontaburi area in Bangkok after a "minor" heavy rain on the April 27, 2002.

2. explore the possibilities of predicting rainfall and flooding in Bangkok.

The outcome of the project in economic and social impacts depends on the dissemination of the information to the people and the accuracy of the information supplied. The information system is designed to be generic, so that the concepts can be transferred easily and implemented at other Asian locations.

PROVISION OF REAL-TIME HYDROLOGICAL INFORMATION TO THE PUBLIC

Before embarking on a project to provide real-time hydrologic information to the public, it is important to assess which information the public would like to have as individuals and which information local authorities would like to have to manage the assets of the city. For example, a private person driving a car to work may be interested in knowing the approximate duration of the rain and the strength of the rain plus an assessment of the risk of flooding like "Probably small flooding" or "Flooding—Don't drive to zone A, B, etc.," whereas the local authority may want information about an accumulated rainfall of 60 mm during the past 60 minutes (which, by experience, provokes flooding) or other more specific numbers concerning the rainfall. The local authority may then want to process the rainfall information further and pass it to public information sources such as traffic radio and local news broadcasts.

In modern society, much information (maybe too much) surrounds us, and we must choose which information we would like to have. However, one of the basic principles is that information should be available at the time we need it and in a form that fits our demands. Providing rainfall information through a computer requires that we are in front of a computer, which rarely happens when we are walking or driving in the rain. We could stop and visit an Internet café to get the latest rainfall information, but that would be rather unrealistic. You would like rainfall information to be available wherever you are. Mobile phones provide the means of bringing the rainfall information directly to you wherever you are.

Technical Requirements to Transform Hydrologic Data to Real-Time Information

A prerequisite for turning hydrologic data into real-time hydrologic information is the basic infrastructure in terms of rain gauges and stable Internet connections. In addition, the communication between the rain gauges and the Internet service should be available at all times. If these components are available, it is possible to send the hydrologic data to a central place where the data can be processed into information. There are several ways of setting up such a communication system; it may be tailored depending on individual need and available hardware. Figure 2 shows the configuration of the real-time application that is under development at AIT.

Data from rain gauge stations and radar stations were sent to the center by radio and the Internet. After generating the data, Bangkok Metropolitan Administration (BMA) and Thai Meteorological Department (TMD) center sent data packages to AIT by the Internet. The server at AIT was set up to carry out all the main tasks: receiving, generating, and storing online data; creating applications based on data; and answering requests from users. The data are updated using a real-time Internet database (DIMS^{TM}). In DIMS^{TM}, macros have been developed to create the images and other information automatically for the web sites and then upload the results to the web sites, including WAP sites available to the public (Fig. 4). The forecasts of rainfall and flooding are at present based on 53 on-line rain gauges across Bangkok (Fig. 3) and a weather radar located in downtown Bangkok.

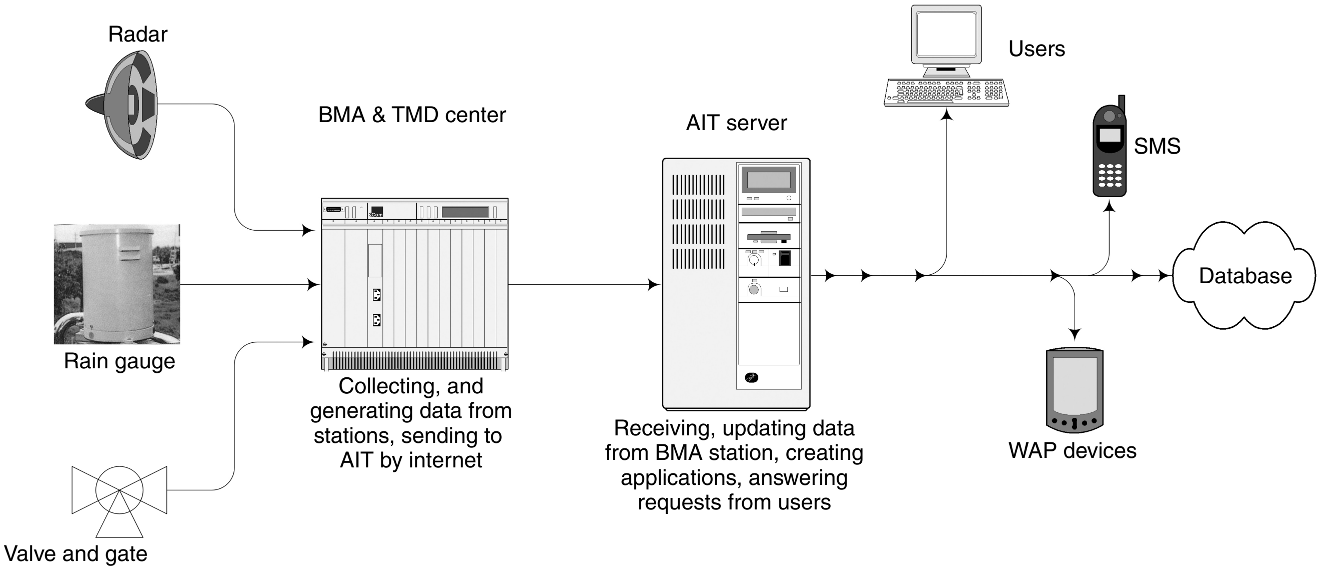


Figure 2. The layout of the real-time rainfall information application at AIT.

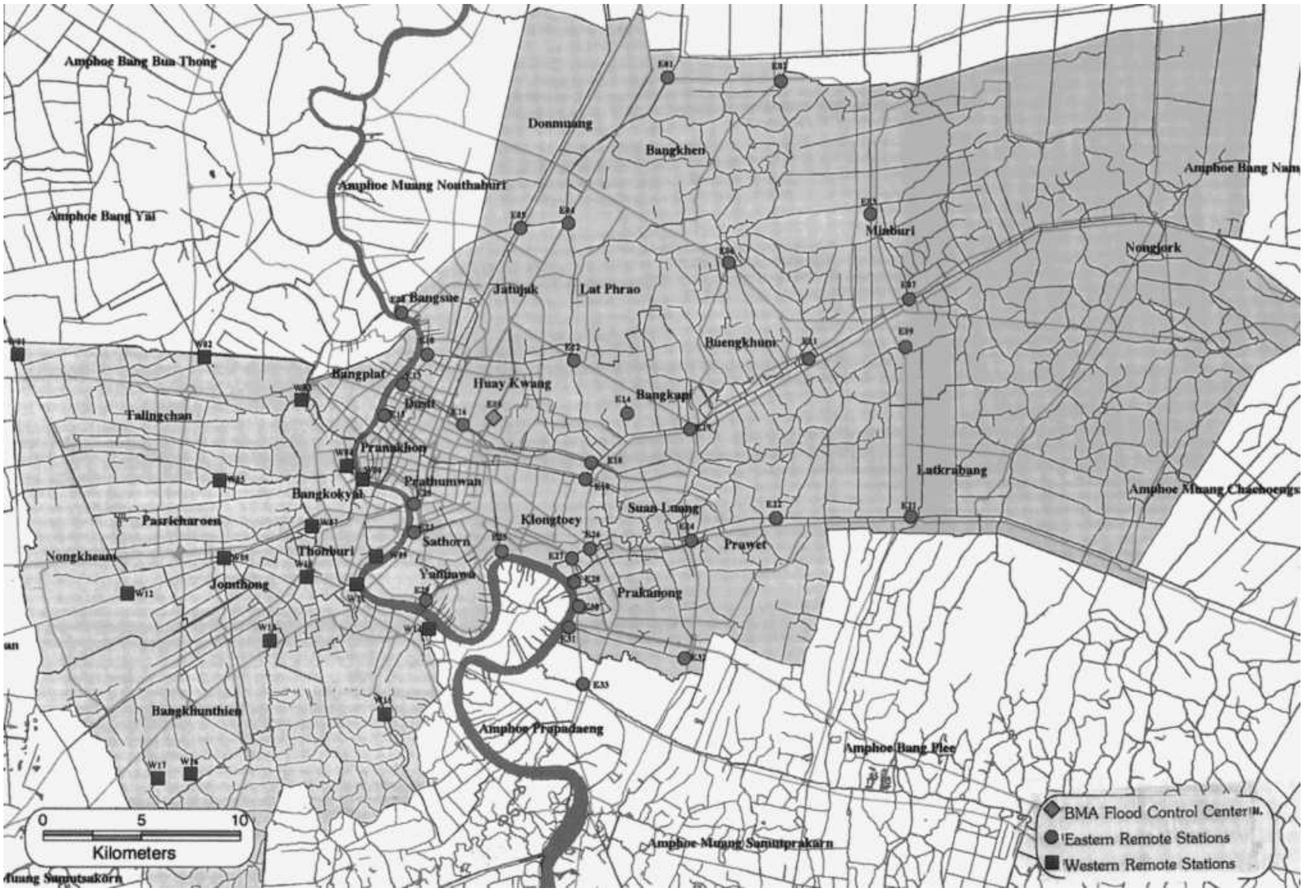
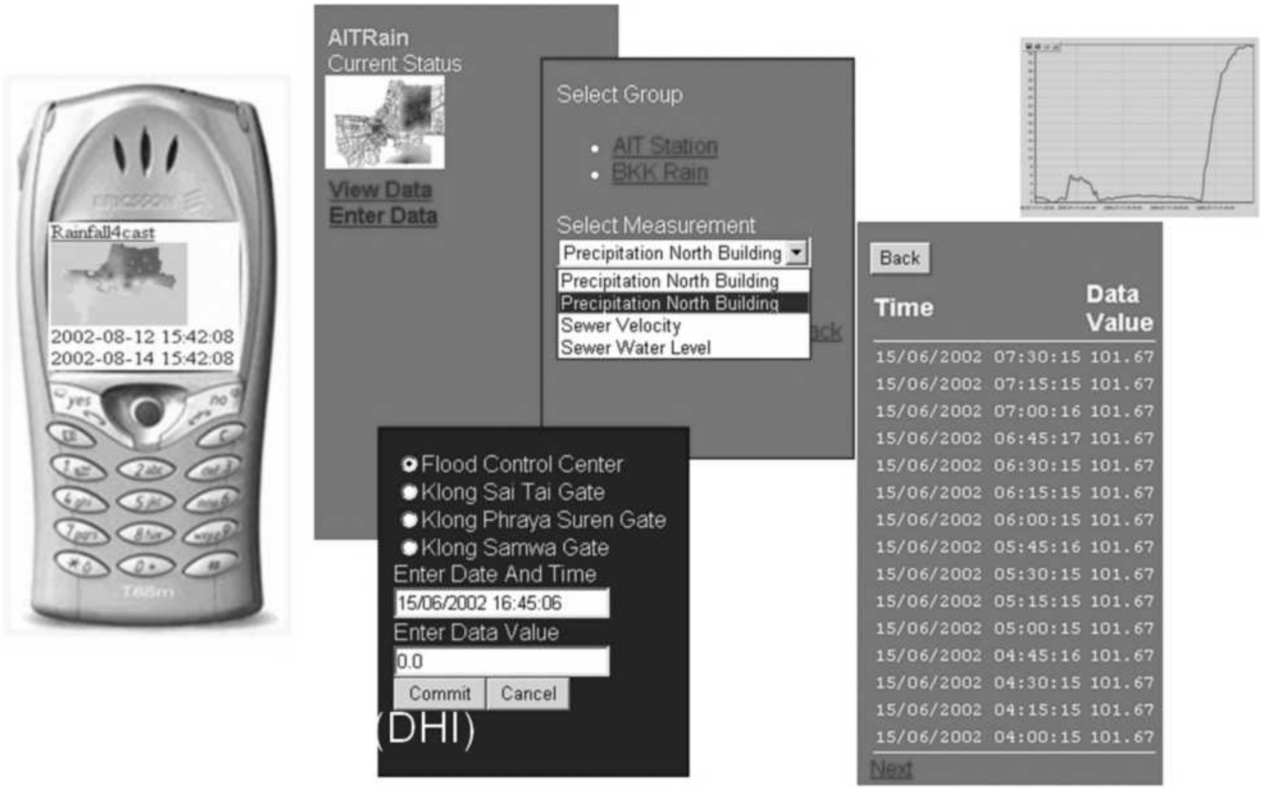


Figure 3. The locations of 47 Bangkok Metropolitan Administration rain gauges in Bangkok (source BMA).



2002-08-12 15:42:08
2002-08-14 15:42:08

Enter Date And Time: 15/06/2002 16:45:06
Enter Data Value: 0.0

Time	Data Value
15/06/2002 07:30:15	101.67
15/06/2002 07:15:15	101.67
15/06/2002 07:00:16	101.67
15/06/2002 06:45:17	101.67
15/06/2002 06:30:15	101.67
15/06/2002 06:15:15	101.67
15/06/2002 06:00:15	101.67
15/06/2002 05:45:16	101.67
15/06/2002 05:30:15	101.67
15/06/2002 05:15:15	101.67
15/06/2002 05:00:15	101.67
15/06/2002 04:45:16	101.67
15/06/2002 04:30:15	101.67
15/06/2002 04:15:15	101.67
15/06/2002 04:00:15	101.67

Figure 4. Information about the rainfall over Bangkok as presented on a mobile phone.

How Close to Real Time must Hydrologic Information be to Consider It Valuable Real-Time Information?

This is a question, which is extremely difficult to answer. So far, this article has used the term "real time" to describe the measurements, which were made, sent to the AIT computers, processed, and presented to the public. But the information presented to the public will always have a time delay because of the time it takes for measurements, data transmission, and processing. These time delays are discussed in detail below:

1. The rain gauges run by Bangkok Metropolitan Administration (BMA) measure the rainfall at 15 minute intervals. Thus, it may only rain the first 5 minutes of the sampling interval and the rainfall intensities from the first 5 minutes will be averaged over a period of 15 minutes. Hence, the sample over 15 minutes produces a significantly lower peak intensity, which according to the measurement, lasts 10 minutes longer than the actual rain.
2. The data transmission from the rain gauges to BMA and further to AIT is rather swift and takes only 1 to 2 minutes. But the AIT rain data server looks only for new data from BMA every 5 min, which on average means a time delay of 2.5 minutes.
3. The data processing at AIT and the transmission to the Internet, mobile phones, etc. takes only another minute, but then the hydrologic information stays on the Internet until new information has been measured, transmitted and processed through the loop described before.

The "real-time" information available to the public is updated only after the repetition of a new measurement cycle, as described above. Hence, the information presented as real-time information may in the worst case be around 20–30 minutes old!!! Is this acceptable? This is a question that is difficult to answer and depends on may local conditions such as the speed of the rain front, the uniformity of the rain; the density and number of rain gauges, and the use of the real-time hydrologic rainfall information. For example, if a rain cloud moves at 5 m/s, then it will travel 6 km in 20 minutes. This means that details within an area of travel distance will be difficult to describe accurately. Means to achieve a higher level of accuracy are to reduce the sampling interval from 15 minutes to 5 minutes or even to 1 minute to be able to present information to the public closer to real time. Alternatively, more rain gauges can be installed. One can imagine that the public will not gain faith in an information system, which tells them it is still raining where they are 20 min. after they have felt the last raindrop.

APPLICATION OF REAL-TIME HYDROLOGIC INFORMATION IN CONJUNCTION WITH URBAN DRAINAGE MODELS

Applying a model in conjunction with real-time rain data provides means for improving information about the current status of the hydrologic system. In general, the rain gauges provide information only at specific locations. The application of a model provides the possibility for gap-filling of information between rain gauges. The simplest kind of modeling is an inverse-distance-based interpolation between the rainfall measurements in real time. At present, that is the method applied at AIT for generating hyetographs. In the near future, more interpolative methods will be evaluated and compared.

In addition to interpolation of the rain intensity between the spatial network of rain gauges, surface runoff and urban drainage models can easily be added to the hydrologic information system. The models are automatically executed when the rainfall at specified locations exceeds preset threshold values. Based on a forecast by the hydrologic model or the urban drainage model, the level of information about the hydrologic system can be extended into the future. The general approach behind the level of information about the hydrologic system as a function of the availability of rain gauges, models, and a forecast is shown in Fig. 5. The figure shows how the information level increases and extends in time when more rain gauges and a model are applied.

The present status of the research project in Bangkok, is that rain gauges reporting in real time together with a simple model predict the spatial variation of the rainfall. In addition, forecast tests in real time have been carried out on a small scale. First, the procedures were tested with a small urban drainage model covering AIT only where all the real-time information is measured directly at AIT. Second, the urban flood model for Bangkok was set up and made operational based on real-time data from BMA and TMD. The forecast has shown promising results and will be made operational during November–December 2003.

The ongoing work on flood forecasting for specific areas of Bangkok is based on real-time rainfall data and a deterministic hydrodynamic urban flood model. The urban flood model has already been established during 2001–2002 as part of the AIT research in modeling urban flooding (1,2). The urban flood model builds on a 1-D hydrodynamic urban drainage modelling package, MOUSE (3) from DHI—Water & Environment. Based on input in terms of time series of rainfall, the MOUSE model for Bangkok produces flood inundation maps, showing flooded areas and depths for the Sukhumvit business area in Bangkok. Layout of the system is shown in Fig. 6. The model has been successfully set up and applied to off-line studies of flooding in Bangkok.

WARNING SYSTEMS FOR FLOODING, FLASH FLOODS, AND LANDSLIDES

Real-time hydrologic information makes it possible to detect potential hazards shortly before they happen, for example, heavy rainfall recorded in certain parts of the catchment may indicate potential flooding, a potential flash flood, or a landslide in hilly areas. However, the level of data and information from a real-time hydrologic system is overwhelming, and it is not really suitable for decision support until targeted data processing has taken place. By keeping the rainfall information in a database, it is easy to write scripts, which automatically keeps track of

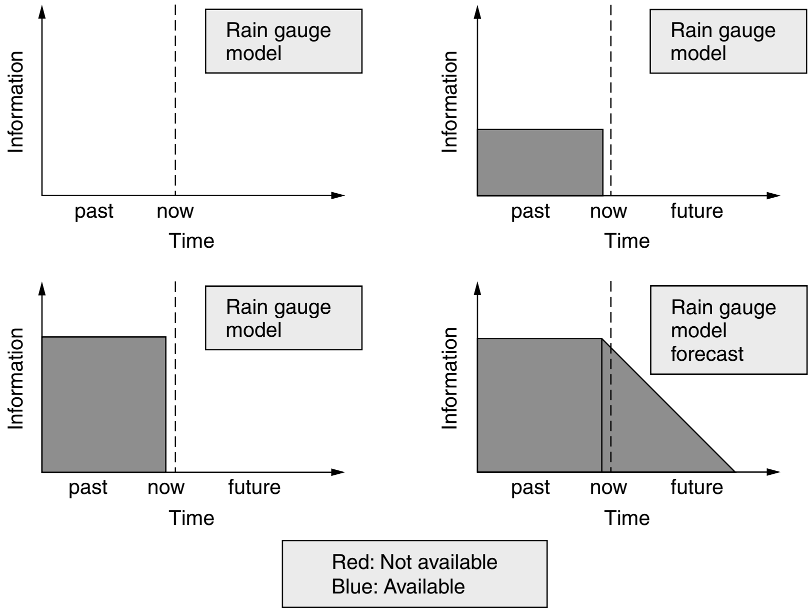


Figure 5. The level of information as a function of the application of (1) no rain gauges and no model available; (2) only rain gauges available; (3) rain gauges and a model available; and (4) rain gauges, a model, and a forecast available.

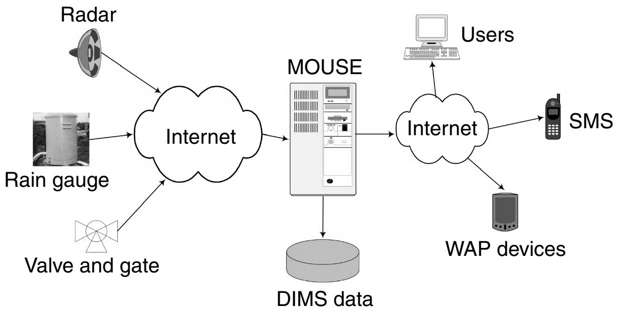


Figure 6. The layout of the real-time data transmission and real-time model.

the accumulated rainfall within the last hour. In Bangkok, experience says that if the accumulated rain within 1 hour is more than 60 mm, then flooding occurs. This criterion has been implemented in the rainfall information system, and warnings are automatically sent to BMA officers, whenever this criterion is exceeded. The warning system is built so that it both sends information about the rain and a personalized message in an e-mail and a SMS message to mobile phones when the criterion is exceeded. Whoever the BMA officer on duty is, he will be alerted about the rainfall conditions either by his email system or by a ringing phone. It is possible to let the information system automatically control gates, weirs, pumps, or other devices in the drainage system, but that is not considered for the moment.

APPLICATION OF WEATHER RADAR FOR HYDROLOGIC REAL-TIME INFORMATION

During the last decade, the use of weather radar has emerged as a tool for rainfall forecasting and at present, research on the use of weather radar for estimating rainfall is carried out at several locations (4–6). A weather radar measures the reflectivity from raindrops in the sky. It does not measure the actual rainfall, and a calibration between the reflectivity and the rainfall is always required for each individual weather radar. A radar provides the potential for getting the spatial variation of rainfall over a large catchment area. For example, the weather radar location in Bang Na, Bangkok, has a range of 60 km, and radar pictures from the Bang Na radar are presently updated every 15 minutes. However, weather radars are still a rather new topic for research in forecasting rainfall. Until now, it has not really been possible systematically to forecast rainfall dynamics (convective effects) with notable success, and operational application of weather radar is rare. However, even though the radar information at present is not highly accurate, radar can still be part of a warning system, where a human is automatically alerted (through the e-mail and SMS warning system described above) when very high rainfall intensities are measured by the weather radar. It will then be up to the duty officer to assess the flood/flash flood risk based on local data, guidelines, and experience. At present, a number of weather radars are already available in Thailand, so there is a good basis for making a warning system that covers the country.

FUTURE PERSPECTIVES FOR HYDROLOGIC DATA IN REAL TIME

At present, hydrologists working in urban areas are facing many new challenges imposed by the ever changing hydrologic environment in cities. Emphasis should be put on managing the urban systems as well as possible by applying currently available information and technology, for example, by implementing real-time hydrologic information systems, like that outlined above. Apart from managing urban hydrology in real time, many other challenges have to be addressed in the near future. An example is Dhaka city, which relies heavily (up to 97%) on groundwater for its water supply (7). During the last 25 years, the groundwater table has dropped by about 25 m. If this drop in the water table continues, it may generate problems for the city's water supply, and surface waters may be needed as additional resources. This is complicated by the growth of Dhaka city. Areas that used to be permeable are being transformed into hard, impermeable surfaces. Such impermeable surfaces prevent replenishing groundwater storage and further aggravate groundwater problems. In turn, the runoff from the new impermeable surfaces generates additional surface runoff, which again increases the flooding in Dhaka city. If the water supply pipes are under low pressure during a period of flooding, polluted floodwater may enter the water supply network. This poses an additional health risk to the population on top of the diseases spread by the floodwater. In addition, there are considerable losses from the water supply network, so quite a large amount of drinking water is lost. This means that being an urban hydrologist does not only involve one problem, but a group of strongly interrelated problems, that have major impacts on the people living in the cities.

The application of real-time hydrologic information is not the solution to all problems mentioned above, but it may mitigate flood problems and in this way reduce the economic losses and health problems the public faces from urban flooding. Finally, the information generated by a real-time hydrologic information system can be applied by using the historical data for design and maintenance analyses to achieve better functionality of the urban hydrologic system before the next heavy rain arrives.

SUMMARY

Making hydrological information publicly available on the Internet and mobile phone is at present a feasible task, which makes data collection more valuable and the work of hydrologists more highly appreciated by the public. In this project, the essential backbone for forecasting rain and urban flooding is established, and it can easily be extended to achieve more accurate forecasts, by adding online rain gauges to the system or by changing the sampling time for the rain gauges to a shorter period. In addition, the hydrologic information can be applied in conjunction with real-time hydrologic and urban drainage models providing decision support and warning systems to deal with urban flooding and flash floods. The authors believe that hydrologic information systems like that described in this article, in the future, may be part of the infrastructure of any major city around the world.

Acknowledgments

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BIBLIOGRAPHY

1. Mark, O., Apirumanekul, C., Kamal, M., and Praydal, P. (2001). *Modelling of Urban Flooding in Dhaka City*, *UDM*, Orlando, FL, May 20–24.
2. Boonya-Aroonnet, S., Weesakul, S., and Mark, O. (2002). *Modelling of Urban Flooding in Bangkok*. *9th Int. Conf. Urban Drainage*, Portland, OR, September 8–13.
3. Lindberg, S., Nielsen, J.B., and Carr, R. (1989). *An Integrated PC-Modelling System for Hydraulic Analysis of Drainage Systems*. *1 Aust. Conf. Tech. Comp. Water Ind.: Watercomp '89*, Melbourne, Australia.
4. Braga, B. and Massambani, O. (1997). *Weather Radar Technology for Water Resources Management*. UNESCO, Unesco Press, Montevideo, Uruguay, p. 516.
5. Einfalt, T., Krejci, V., and Schilling, W. (1998). Rainfall data in urban hydrology. In: *Hydroinformatics Tools for Planning, Design, Operation and Rehabilitation of Sewer Systems*. J. Marsalek, C. Maksimovics, E. Zeman, and R. Price (Eds.). *NATO ASI Series 2: Environment*, Vol. 44. Kluwer, Dordrecht, pp. 129–168.
6. Collier, C.G. (1989). *Application of Weather Radar Systems: A Guide to Uses of Radar Data in Meteorology and Hydrology*. Ellis Harwood, Chichester, England.
7. Khan, H.R. and Siddique, Q.I. (1999). Urban water management problems in developing countries with particular reference to Bangladesh. *Int. J. Water Res. Dev.*, special issue.

READING LIST

Mark, O., Boonya-Aroonnet, S., Hung, N.Q., Buranautama, V., Weesakul, U., Chaliraktraku, C., and Larsen, L.C. (2002). *A Real-Time Hydrological Information System for Bangkok*. *Int. Conf. Urban Hydrol. 21st Century*. Kuala Lumpur, Malaysia, October 14–18.

Mark, O., Weesakul, S., and Hung, N.Q. (2002). *Modelling the Interaction Between Drainage System, Wastewater Treatment Plant and Receiver Water in Pattaya Beach*. *9th Int. Conf. Urban Drainage*, Portland, OR, September 8–13.

Mark, O., Hung, N.Q., and Helwigh, A.B. (2002). Waiting for a swim—the handling of wastewater in Asia. *WaterLines* **20**(4).

Moraes, L.R.S. (1996). *Health Impacts of Drainage and Sewerage in Poor Urban Areas in Salvador, Brazil*. Ph.D. Thesis. London School of Hygiene and Tropical Medicine, London.

CHLORINE AND CHLORINE RESIDUALS

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INTRODUCTION

Chlorine, being a powerful oxidant, is capable of destroying biological molecules (1). It is universally used as a disinfectant for drinking water treatment and as a biocide for cooling water treatment (2). However, the very oxidizing nature of chlorine involves it in a number of side reactions with organic and inorganic substances present in water. A certain fraction of the chlorine actually dosed into water may therefore disappear and not be available for estimation by the normal methods employed. These methods actually estimate chlorine concentration by measuring the amount of oxidants present. The fraction of chlorine that is used in such side reactions is called chlorine demand. Chlorine residual refers to the amount of chlorine (as well as its reaction products, which retain some oxidation potential) that remains after such side reactions.

Chlorine, when dissolved in natural waters, gives rise to various oxidizing compounds depending on the reaction of hydrolysis and oxidation of ammonia, which leads to the production of free chlorine (as hypochlorous acid or its dissociated form) as well as various chloramines, all of which retain oxidant property. The oxidants also react with organic matter to produce halogenated organics. Therefore, chemistry of water chlorination is complex and involves many molecular and ionic species, with often confusing terminology. In literature, chlorine dissolved in water may be described as “free,” “active,” “available,” “combined,” or “residual”—or a combination of the above. A brief explanation of the nomenclature associated with water chlorination is given below.

Free Chlorine/Free Available Chlorine (FC/FAC)

This refers to the amount of hypochlorous acid present in water in its dissociated or undissociated form:

$$\mathrm{Cl_2 + H_2O \longrightarrow HOCl + HCl} \tag{1}$$

$$\mathrm{HOCl \rightleftharpoons H^+ + OCl^-} \tag{2}$$

In seawater (which contains about 65 mg/L bromide), the following reactions will also take place:

$$\mathrm{HOCl + Br^- \longrightarrow HOBr + Cl^-} \tag{3}$$

Therefore, in seawater chlorination, HOBr (as well as hypobromite ion, $\mathrm{OBr^-}$) is also categorized into FC/FAC.

Combined Chlorine/Combined Available Chlorine

Combined chlorine refers to chloramines, which result from the reaction of free chlorine with ammonia (or other nitrogenous compounds with an N-C link) present in water:

$$\mathrm{HOCl + NH_3 \longrightarrow NH_2Cl + H_2O} \tag{4}$$

$$\mathrm{NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O} \tag{5}$$

Additionally, the following reactions are also possible in seawater environments:

$$\mathrm{NH_3 + HOBr \longrightarrow NH_2Br + H_2O} \tag{6}$$

$$\mathrm{NH_2Br + HOBr \longrightarrow NHBr_2 + H_2O} \tag{7}$$

$$\mathrm{2NH_2Cl + Br^- \longrightarrow NHBrCl + NH_3 + Cl^-} \tag{8}$$

Chloramines are much less reactive (that is, less effective as biocides) when compared with bromamines. Combined forms of chlorine are, in general, less efficient biocides than free chlorine, but are more persistent than it. Hence, they are very important from the environmental point of view.

Total Available Chlorine (TAC)

This refers to the sum of the two terms just defined and represents a major part of the biocidal capacity of the chlorinated water.

Residual Chlorine

This term is analogous to TAC and is often used to represent the oxydisinfectant capacity of water (consisting of free and combined oxidants) at that point in time (Fig. 1). It must be kept in mind that this capacity goes on reducing as a function of time because of what is known as chlorine decay. The dosed chlorine continuously engages in a series of reactions with substances present in water, which in due time will result in complete disappearance of all measurable chlorine.

Chlorine Demand (CD)

It is defined as the difference between the amount of chlorine added and the useful residual chlorine that remains at the end of a specified contact time. It refers to the amount of chlorine “lost” in side reactions referred to earlier. As the CD of a given sample of water varies with the chlorine dose applied and the contact time (that is, the interval between chlorine dosing and chlorine measurement), it is always denoted with reference to the dose and the contact time. For example, for a chlorine dose of 1 mg/L, a sample of water may return a CD value of 0.6 mg/L after a contact time of 30 minutes. In natural sea or fresh water, chlorine demand also varies as a function of season (Fig. 2) because of the seasonal changes in the concentration of oxidizable substances present in natural waters. The dosed chlorine continuously engages in a series of reactions with substances present in water, which in due time will result in complete disappearance of all measurable chlorine.

Total Residual Chlorine/Total Residual Oxidant (TRC/TRO)

Chlorine estimation in water is carried out indirectly by measuring the oxidant capacity via the stoichiometric iodide/iodine. As the method determines all oxidants produced in Equations 1–7, it is appropriate to use the term total residual oxidants (TRO) rather than total residual chlorine (TRC) in the case of seawater chlorination (Fig. 1). Although different in nomenclature, TRO numerically equals TRC.

Chlorine Produced Oxidants (CPO)

This term is used to distinguish oxidants produced in water after addition of chlorine from those naturally present in a given parcel of water. The latter appear as “background” in blank determination, but because their normal concentrations are very low, they can be generally ignored.

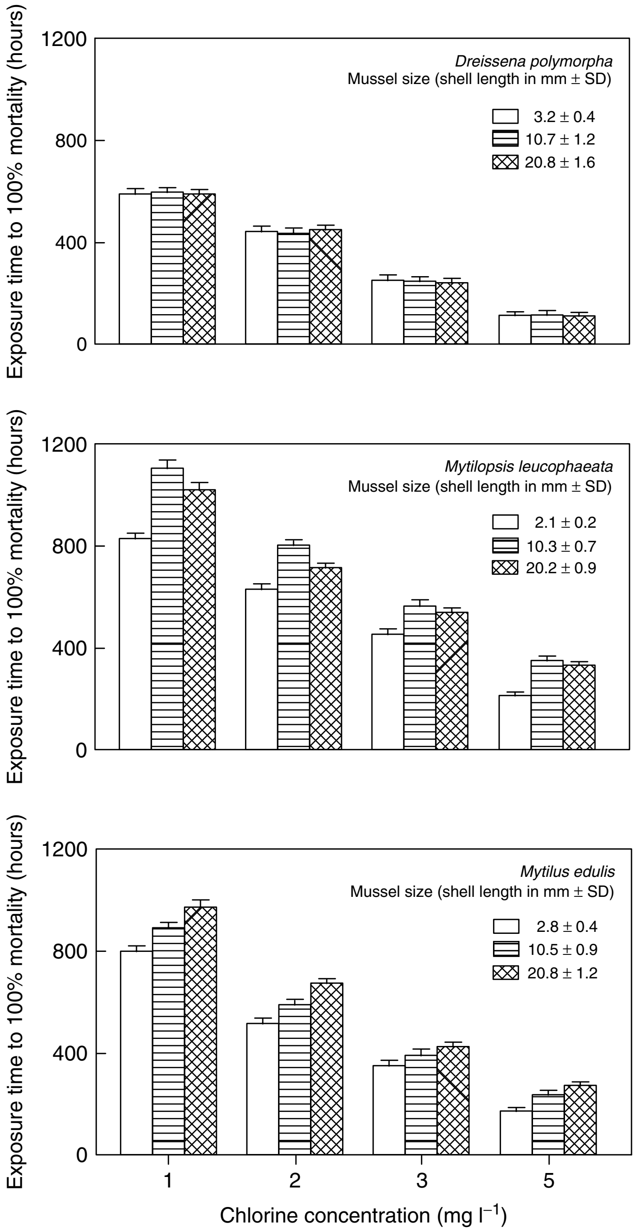

Figure 1. (**a**) Example of a chlorination curve in freshwater containing ammonia [modified after (2)]; (**b**) Experimental chlorination of seawater from intake canals of Gravelines power station. N ammonia = 0.21 mg/L; Contact time = 20 min [modified after (2,3)].

Nonoxidizing Chlorine Byproducts (CBP)

These are byproducts of chlorination that result from the reaction of chlorine with organic matter present (especially humic substances) in water. Several of these compounds exist, but the majority of them come under the category organohalogens called trihalomethanes (THM) (Fig. 3).

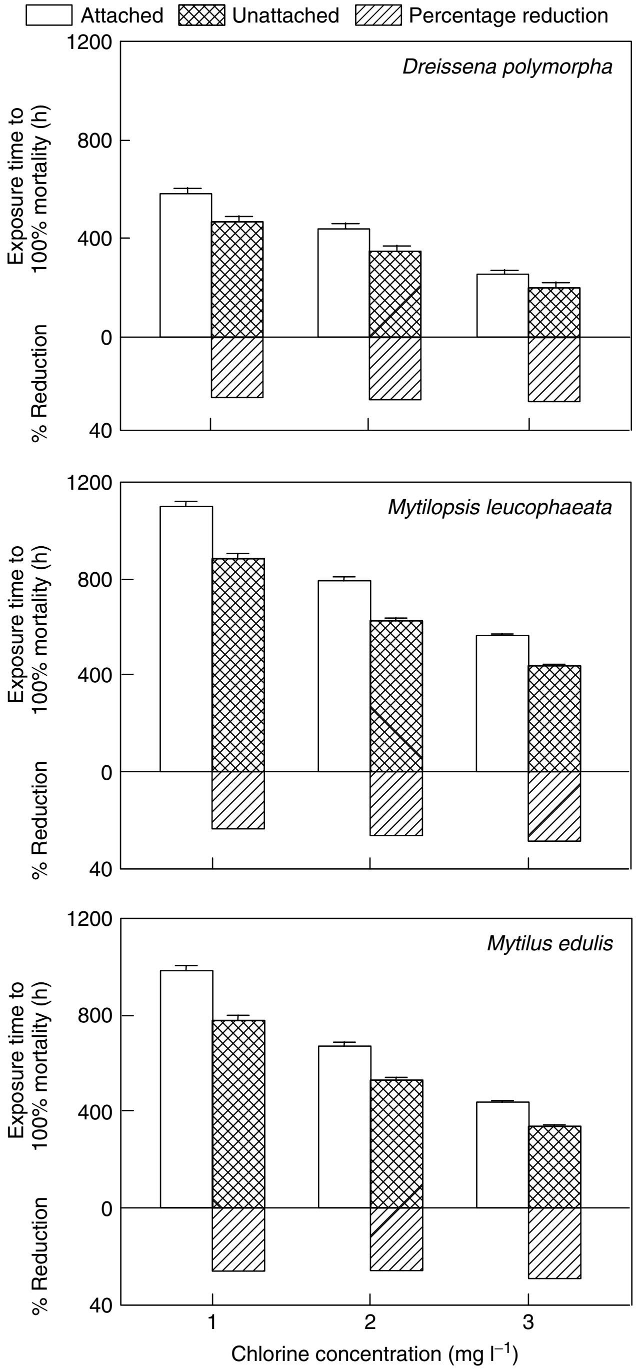

Figure 2. Seasonal variations of chlorine demand at three different chlorine doses in Kalpakkam coastal waters, east-coast of India from February 1989 to January 1990 [modified after (4)]. Total chlorine residuals were measured after 5 min for calculation of the chlorine demand.

From the above discussion, it is clear that the most important term that one comes across in the context of chlorination for disinfection/biofouling control is "chlorine residual," which denotes the biocidal capacity of water in terms of its oxidizing nature. Both HOCl and OCl^- (hypochlorite ion), produced in Reactions 1 and 2 above, are oxidants and constitute free residuals. However, HOCl is more effective than its ionized form, because being neutrally charged, it can penetrate cells more easily than OCl^- (Fig. 4). The dissociation of HOCl is a pH- and temperature-dependent reaction, higher pH and temperature favoring ionization of the acid. The ionization also increases with increasing total

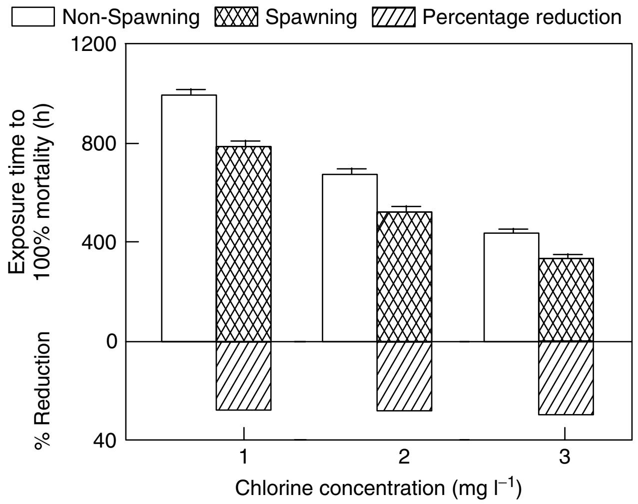

Figure 3. Average distribution of organohalogens measured by gas chromatography in seawater (chlorine dose = 0.8 mg/L) at the Gravelines power station [modified after (2,3)].

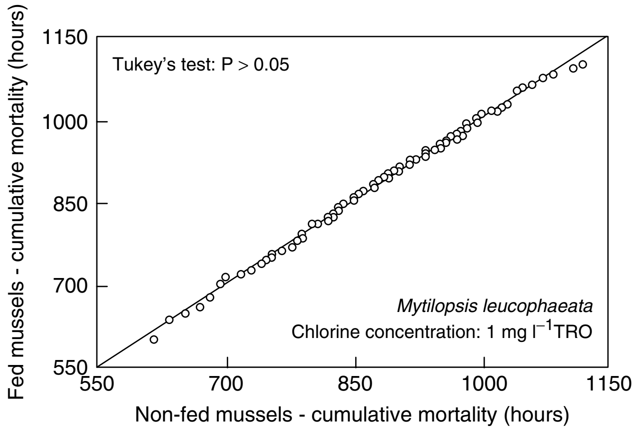

Figure 4. Comparison of the dissociation of hypochlorous acid and hypobromous acid with changing pH at a temperature of 20 °C [modified after (2)].

dissolved salts (TDS) or salinity, in the case of estuarine brackish water.

MEASUREMENT OF CHLORINE RESIDUALS

Several techniques are available for the measurement of chlorine residuals in water. Amperometric titration, potentiometric titration, or colorimetric titration using FAS-DPD (ferrous ammonium sulphate/N,N-diethyl-p-phenylene diamine) can be used. Simple colorimetry (using DPD) can also be used, especially under field sampling conditions, which has the ability to differentiate between free and combined forms of chlorine. Additionally, it allows rapid analysis after sample collection, reducing the chances of chorine loss through decay reactions. The required reagents are currently available commercially as portable kits, ready for field use. Although this method can theoretically detect a chlorine concentration of 0.01 mg/L, threshold detection level in practice is about 0.02 mg/L (2). Details of the various methods are available in APHA-AWWA-WPCF (5). Accurate and reliable instruments for continuous monitoring of residual chlorine levels in water are currently not available.

ENVIRONMENTAL DISCHARGE LIMITS

Several reports are available on the effects of residual chlorine in aquatic systems (6–9). Therefore, environmental release of chlorine residuals (for instance, in cooling water discharge from electric power plants) is tightly controlled in many countries through legislation. However, the permitted levels vary from country to country. For example, in the Netherlands, the permitted limit of chlorine residuals (0.2 mg/L for 2 h per day) is much less than that in India (0.5 mg/L).

BIBLIOGRAPHY

1. White, G.C. (1999). *Handbook of Chlorination and Alternative Disinfectants*. John Wiley & Sons, New York, p. 1569.
2. Jenner, H.A., Whitehouse, J.W., Taylor, C.J.L., and Khalanski, M. (1998). Cooling water management in European power stations: biology and control. *Hydroecologie Appliquée* **1–2**: 1–225.
3. Allonier, A.S. and Khalanski, M. (1997). *Chlorination By-Products in Sea Water*. EDF DER Report HE/31/97/027, Electricité de France, Chatou, Paris.
4. Rajagopal, S. (1997). *The Ecology of Tropical Marine Mussels and Their Control in Industrial Cooling Water Systems*, Ph.D. Thesis, University of Nijmegen, the Netherlands, p. 184.
5. APHA-AWWA-WPCF. (1992). *Standard Methods for the Examination of Water and Wastewater*, 17th Edn. Washington, DC.
6. Brook, A.J. and Baker, A.L. (1972). Chlorination at power plants: impact on phytoplankton productivity. *Science* **176**: 1414–1415.
7. Carpenter, E.J., Peck, B.B., and Anderson, S.J. (1972). Cooling water chlorination and productivity of entrained phytoplankton. *Mar Biol.* **16**: 37–40.
8. Eppley, R.W., Ringer, E.H., and Williams, P.M. (1976). Chlorine reaction with seawater constituents and the inhibition of photosynthesis of natural marine phytoplankton. *Estuar Coast Mar Sci.* **4**: 147–161.
9. Choi, D.H. et al. (2002). Effects of thermal effluents from a power station on bacteria and heterotrophic nanoflagellates in coastal waters. *Mar Ecol Prog Ser.* **229**: 1–10.

READING LIST

Allonier, A.S., Khalanski, M., Camel, V., and Bermond, A. (1999). Characterization of chlorination by-products in cooling effluents of coastal nuclear power stations. *Mar. Pollut. Bull.* **38**: 1232–1241.

Mattice, J.S. and Zittel, H.E. (1976). Site-specific evaluation of power plant chlorination. *J Water Pollut. Cont. Fed.* **48**: 2284–2308.

MODELING CHLORINE RESIDUALS IN URBAN WATER DISTRIBUTION SYSTEMS

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INTRODUCTION

The water to be supplied to a community should be adequate in quantity to satisfy their demands and potable in quality to safeguard their health. It is not enough to treat water in the treatment works for safeguarding the health of consumers without trying to take adequate steps in preventing deterioration of the water quality in a distribution system. Treatment can be adequate to provide an excellent product for the consumer at the plant outlet, but it is inadequate to overcome inferior protective measures in the distribution system (1). There are various causes for which the potable water may turn to an obnoxious liquid in the distribution system and become unfit for drinking as could be found after quality assessment. The various causes of deterioration of water quality are pipe materials, constituents of water, intermittent supply, cross connections, dead-end pipes, service reservoirs, commissioning of new distribution system without disinfection, and breakages (2). The significant constituents of water generally include residual chlorine, natural organic matter, nutrient concentrations, temperature, and pH of water. The distribution system plays an important role in assuring a good quality of water to the consumer.

It is well known that the quality of drinking water can change within a distribution system. The movement or lack of movement of water within the distribution system may have deleterious effects on a once acceptable supply. These quality changes may be associated with complex physical, chemical, and biological activities that take place during the transport process. Such activities can occur either in the bulk water column, the hydraulic infrastructure, or both, and they may be internally or externally generated (3). An ability to understand these reactions and model their impact throughout a distribution system will assist water suppliers in selecting operational strategies and capital investments to ensure delivery of high-quality drinking water (4). Water quality modeling provides an engineering insight into the distribution system activities.

The water quality in a distribution system can be represented in the form of a constituent, water age and source trace (in case of multiple sources) analysis. For constituent concentration, the residual chlorine is considered to be important to represent the overall quality of water. Chlorination is a form of disinfection that reduces the risk of infection to an acceptable level by controlling the number of bacteria. The alternative disinfection options available are ozonation and ultraviolet radiation. But these two have no residual action to protect the water during distribution and are expensive. Although the chlorine is not as powerful as ozone, it has a lasting residual effect, is relatively easy to use, and is cost effective. Hence, chlorine happens to be the most predominant water treatment disinfectant. Because of chlorine's oxidizing potential, minimum levels of chlorine residual must be maintained in the distribution system to preserve both chemical and microbial quality of treated water (5). It is well known that as chlorine travels through the distribution system, it reacts with different materials inside the pipe. Free chlorine is consumed on the one hand by water (oxidation of dissolved organic compounds) and on the other hand by the internal walls of pipes (6). For the age-old distribution systems made up of unlined cast iron pipes, the wall component of reaction plays an important role in chlorine reaction kinetics.

CHLORINE REACTION KINETICS

The chlorine disappearance in a drinking water distribution system is governed by both the quality of water (bulk decay) and the chlorine demand of the pipe (wall decay). The chlorine demand exerted in the bulk flow and at the pipe wall is caused by the reaction of chlorine with organic content and materials associated with the pipe wall, respectively. The reactions in bulk flow occur within the fluid volume and are a function of constituent concentration, reaction rate and order, and concentration of the formation products. The various reaction kinetic models that represent bulk decay of chlorine include first-order, second-order with respect to chlorine only, parallel first-order, nth order, limited first-order (7), and two component second-order (8). The variability of bulk reactions with the temperature and organic matter concentration was studied by Kiéné et al. (9). An empirical kinetic model predicted the bulk reaction parameter by taking into account the TOC and temperature. To summarize, the kinetic models are either a single-parameter or a multiple-parameter decay equation. The multiple-parameter decay equations are shown to have an edge over the single-parameter models in describing the chlorine decay in bulk water.

The applicable reaction kinetics for chlorine in the aqueous (bulk) phase can be determined experimentally by conducting the bottle tests, which consist of placing a sample of water in a series of nonreacting glass bottles and analyzing the contents of each bottle at different points in time. The results of these bottle tests are then used for selecting an appropriate kinetic model, and thereby the bulk reaction parameter(s) involved in the model are estimated.

The chlorine decay at the pipe wall is controlled by the mass transfer mechanism from bulk to the pipe wall. The mass transfer expressions are based on either a two-dimensional radial diffusion (10) or a lumped-mass transfer (4) approach. The radial diffusion model can produce more accurate results than those using a lumped-mass transfer coefficient, but it is less suitable for inclusion in network models applied to large systems (11). After the lumped-mass transfer approach, the wall reaction kinetics for chlorine with the materials associated with the pipe wall can be modeled by assuming an active reaction zone located on the wall or in an adjacent molecular layer. The transport of chlorine to the wall is represented by a film resistance model of mass transfer using a mass transfer coefficient suitable to the flow regime in the pipe (4). The reaction at the pipe wall can be modeled according to either first-order or zero-order kinetics. The reactivity of the pipe wall is a function of pipe radius, hydrodynamic conditions, nature of pipe materials, and amount and nature of deposits (12). The first-order wall model may best represent a process in which chlorine is the limiting reactant, as might be the case with reactions involving complex organic compounds that are found in the exocellular enzymes and metabolic products produced by the biofilm on the pipe wall. The zero-order model would better represent the case in which chlorine immediately oxidizes some reductant (such as ferrous compound), and the rate is dependent on how fast the reductant is produced by the pipe. This mechanism would more likely apply to corrosion-induced reactions. These two wall reaction models are further simplified by relating the wall reaction constant inversely with the pipe roughness and thereby converting the equations into a single unknown parameter (5).

MODELING CHLORINE RESIDUALS WITHIN A WATER DISTRIBUTION SYSTEM

The hydraulic analysis of the system is a prerequisite for attempting to model water quality in a distribution system. Steady-state network hydraulic analysis determines the operating behavior of the system under unchanging conditions. Dynamic-state network hydraulic analysis is usually carried out by an extended period simulation that determines the effects on the system over time and is more significant as possible flow reversals in the pipes may affect the quality of water drastically. Steady- or dynamic-state chlorine residual modeling is a direct extension of the corresponding hydraulic network modeling. Basically, the chlorine residual modeling is done in two environments, namely, steady and dynamic. In steady-state modeling, the external conditions of a distribution network are constant in time and the nodal concentrations of the constituents that will occur if the system is allowed to reach equilibrium are determined. The steady-state models determine the ultimate spatial distributions of chlorine concentrations throughout the network. These models (13–18) are based on the law of mass conservation. Dynamic modeling, on the other hand, represents both spatially and temporally varied chlorine concentrations in a distribution system. In dynamic models, the external conditions are temporally varied and the time-varying nodal concentrations of the constituents are determined. Dynamic models rely on a system-simulation approach to determine the movement and fate of chlorine under time-varying demand, supply, and hydraulic conditions. The dynamic-state algorithms developed include (3,9,19–26) models. Because water distribution systems and the processes within them are usually categorized as continuous systems, dynamic modeling provides a more accurate and realistic portrayal of the actual operation of the system.

Flow rates in pipes and the flow paths that define the movement of water through the network can determine mixing, residence times, and other hydraulic characteristics that affect the chlorine transport and reactions. The residence time of water within the system also has its impact on the chlorine concentration. In the chlorine transport models, the physical processes like transport and mixing, and chemical reactions like chlorine decay, are typically represented. The transport of chlorine in water along the length of a pipe takes place by advection and dispersion aided by the reactions involved. Although dispersion of chlorine in water supply pipes with very low flows has been shown to be important (25,27,28), the flows in the water distribution pipes are generally considered to be advection dominated and the dispersion term is negligibly small in most models. Hence, the water quality modeling is generally based on one-dimensional advective–reactive transport through a pipe. A water distribution system, typically represented as a network model, consists of links (pipes, pumps and control valves) interconnected by nodes (junctions, storage tanks and reservoirs) in some particular branched or looped configuration.

STEADY-STATE MODELING

The principle of mass conservation along with the suitable bulk and wall chlorine reaction kinetics are used in formulating the chlorine residual model. The basic governing equation required to determine the steady-state concentration of chlorine at any node j can be formulated as

$$C_j = \frac{\sum_{i=1}^{Ninp_j} C_{nu_i} Rec_i Q_i}{\sum_{i=1}^{Ninp_j} Q_i}; \quad j = 1, \ldots Njn \tag{1}$$

where C_j = chlorine concentration at node j (mg/L); C_{nu_i} = chlorine concentration at node nu_i (mg/L); $Ninp_j$ = number of incoming pipes at node j; nu_i = upstream node of incoming pipe i; Q_i = flow in pipe i (m^3/s); Njn = number of nodes in the network; and Rec_i = reaction coefficient for pipe i. The expression for the reaction coefficient depends on the kinetics used for bulk and wall reactions. For first-order bulk and wall reactions, it is given by

$$Rec_i = Exp - \left[k_{bi} + \frac{k_{wi} k_{f_i}}{r_{h_i}(k_{wi} + k_{f_i})}\right] ptt_i \tag{2}$$

where ptt_i = travel time in pipe i (s); r_{hi} = hydraulic radius of pipe i (m); k_{wi} = first-order wall reaction parameter of pipe i (m/s); k_{bi} = first-order bulk reaction parameter of pipe i (s^{-1}); k_{fi} = mass transfer coefficient of pipe i(m/s) = $(D/d_i)S_{hi}$, where, d_i = diameter of pipe i (m); D = molecular diffusivity of chlorine (m^2/s); and S_{hi} = Sherwood number of pipe i and is given by Rossman (29), for $R_{ei} \leq 2300$ (Laminar flow);

$$S_{hi} = 3.65 + \frac{0.0668\left(\dfrac{d_i}{L_i}\right)R_{ei}S_c}{1 + 0.04\left[\left(\dfrac{d_i}{L_i}\right)R_{ei}S_c\right]^{2/3}} \qquad (3)$$

for $R_{ei} > 2300$;

$S_{hi} = 0.0149{R_{ei}}^{0.88}{S_c}^{1/3}$;

$S_c =$ Schmidt number $= \nu/D$; and $\nu =$ kinematic viscosity (m^2/s); $L_i =$ length of pipe i.

The reaction coefficients for other combinations of bulk and wall reactions are given in Ref. 25.

If Nsn is the number of source nodes, then Equation 1 with appropriate reaction kinetics results in $(Njn - Nsn)$ number of linear equations. An iterative procedure based on the Gauss–Siedel algorithm can be adopted to solve the equations. The converged solution gives steady-state chlorine concentrations at all nodes for given source chlorine concentrations.

DYNAMIC-STATE MODELING

The unsteady advection–reaction process for the transport of chlorine in a pipe flowing full is given by the following classic equation:

$$\frac{\partial C_i(x,t)}{\partial t} = -v_i\frac{\partial C_i(x,t)}{\partial x} - R[C_i(x,t)] \qquad (4)$$

where $C_i(x,t) =$ chlorine concentration in pipe i (mg/L) as a function of distance x and time t; $v_i =$ mean flow velocity in pipe i (m/s); and $R[C_i(x,t)] =$ reaction rate expression. For the first-order bulk and wall chlorine reaction kinetics, it is given by the following equation:

$$R[C_i(x,t)] = k_{bi}C_i(x,t) + \frac{k_{wi}k_{fi}}{r_{h_i}(k_{wi}+k_{fi})}C_i(x,t) \qquad (5)$$

k_{fi} can be calculated using expressions as described earlier.

Instantaneous and complete mixing of chlorine at the node j and time t is given by the following expression:

$$Cnc_{j,t} = \frac{\sum_{i=1}^{Ninp_j} Q_iC_i(L_i,t) + Q_EC_E}{\sum_{i=1}^{Ninp_j} Q_i + Q_E}; \quad j = 1, \cdots Njn \qquad (6)$$

where $Q_i =$ flow in the pipe i (m^3/s); $Q_E =$ external source flow in to node j (m^3/s); $C_E =$ external source chlorine concentration into node j (mg/L); and $Njn =$ total number of nodes in the network.

The numerical approaches adopted to solve the above-formulated problem can be classified spatially as either Eulerian or Lagrangian and temporally as time driven or event driven (30). Eulerian models divide the pipe into a series of fixed, interconnected control volumes and record changes at the boundaries or within these volumes as water flows through them. Lagrangian models track changes in a series of discrete parcels of water as they travel through the pipe network. Event-driven simulation updates the state of the system only at times when a change actually occurs, such as when a new parcel of water reaches the end of a pipe and mixes with water from other connecting pipes, and at the output reporting time (30). The Eulerian methods include the finite difference method (FDM) (30) and the discrete volume element method (DVEM) (21), and the Lagrangian methods are the time-driven method (TDM) (19) and the event-driven method (EDM) (22). The Lagrangian methods are more efficient for simulating the chemical transport in a water distribution system (30).

The input to the dynamic simulation model essentially consists of the system demands, source chlorine concentrations, and reaction parameters (bulk and wall) of the network. The outputs of this model are the spatially and temporally varying nodal chlorine concentrations.

APPLICATION OF THE CHLORINE TRANSPORT MODEL

The Brushy plains zone of the South Central Connecticut Regional Water Authority is chosen to illustrate the application and is shown in Fig. 1. The pipe and node data of the network are taken from EPANET [distributed by USEPA, (29)] example networks. The first-order bulk

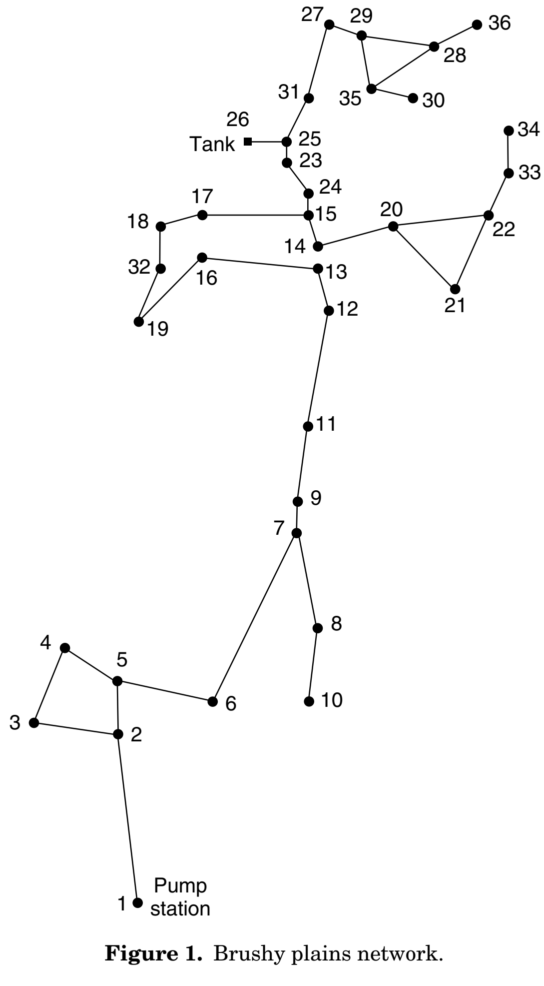

Figure 1. Brushy plains network.

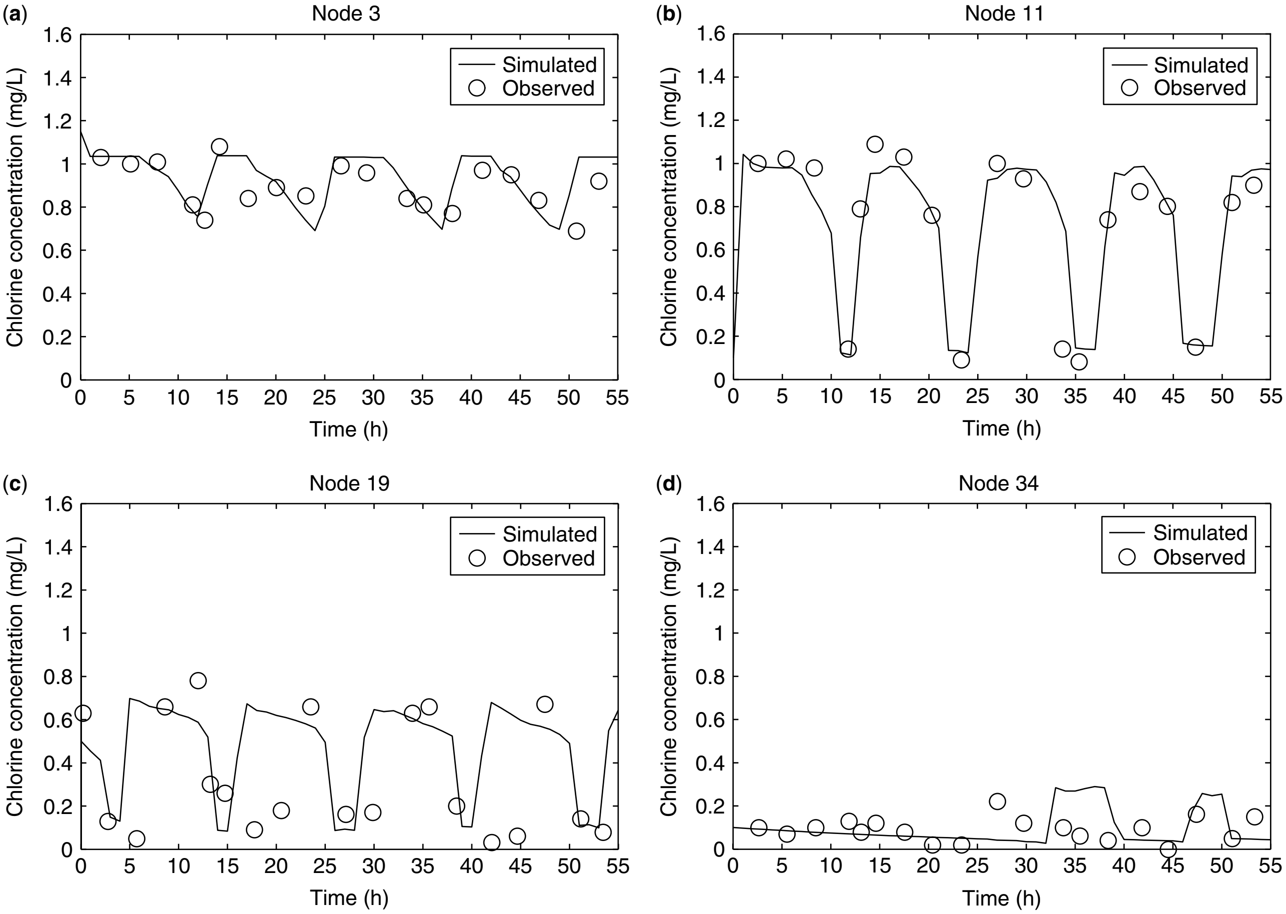

Figure 2. Simulated and observed chlorine concentration at nodes (**a**) 3, (**b**) 11, (**c**) 19, and (**d**) 34.

and wall reaction parameters used are 0.55 d^{-1} and 0.15 m/d, respectively. The system has been hydraulically well calibrated, with most pipes having been assigned roughness coefficients (HWC) of 100. The chlorine input at node 1 (Fig. 1) to the network has a constant value of 1.15 mg/L. The chlorine transport model is run using the time-driven method for a hydraulic time step of 1 hr and a water quality step of 3 min. The results are obtained for a simulation period of 55 hr. The chlorine concentrations at a few network nodes are represented in Fig. 2.

CHLORINE REACTION PARAMETER ESTIMATION

The chlorine transport model described earlier predicts the constituent concentrations throughout the distribution system under steady or dynamic state. The reliability of these predicted concentrations when compared with the field observations depends on the assigned parameter values involved in the type of reaction kinetics used in the model. The parameters that control the chlorine reaction kinetics within the system can be broadly classified into the bulk and wall reaction parameters. Bulk reaction parameters (first- or non-first-order) are associated with individual pipes and storage tanks, assigned to groups of pipes in an area, which is contributed more by a particular source, or applied globally. Wall reaction parameters (first- or zero-order) are associated with individual pipes, applied globally, or assigned to a group of pipes with similar material/age/roughness factors. The wall reaction parameter can also be related inversely to the Hazen–Williams roughness coefficient and represented in the wall reaction pipe-roughness parameter. The advantage of using this sort of representation is that it requires only a single parameter to allow wall reaction parameters to vary throughout the network in a physically meaningful way (5).

The parameters involved in the single-parameter or multiple-parameter bulk reaction expressions can be determined with the data sets observed by conducting the bottle tests on the water samples. By performing measurements in the distribution system, the researchers have calculated the decay rate constant (overall first-order) for site-specific tests (such as fixed pipe diameter, pipe material, or water source). This process may yield reasonable results; however, a wide range of values for this constant is obtained, thus severely limiting its use as a predictive tool (31). The determination of an overall reaction parameter (which represents the combined effect of bulk and wall reactions) and a wall reaction parameter is much more difficult than is establishing a bulk reaction parameter. Hence, these reaction parameters are more a product of calibration. Calibration is a process of adjusting a model so that the simulation reasonably predicts system behavior. The objective of water quality calibration is to capture the steady/transient dynamic behavior of the network. Wall reaction parameters are similar to pipe roughness coefficients in that they can and do vary from pipe to pipe. Unfortunately, unlike the head loss test for pipe roughness values, direct measurements of wall reaction parameters are extremely difficult to make (32). Because these parameter values are difficult to measure, they need to be estimated with the field measurements. The various techniques adopted to estimate these parameters include the trial-error (33), gradient-descent-based search technique (34), method of Lagrange multiplier (35), Gauss–Newton sensitivity analysis technique (36), and stochastic-based genetic algorithm (GA) technique (37). Gradient-based methods are generally faster, but they are more difficult to formulate because either an analytical expression must be derived or the gradient must be approximated. Stochastic search methods are more robust and simpler to formulate and use, but they are generally slower (32).

The parameter estimation can be formulated as an optimization problem so that the difference between the observed and computed chlorine concentrations at the monitoring nodes are minimized in the least-squares sense. Thus, the objective function is given by

$$Minimize\ E = \sum_{j=1}^{M} \sum_{k=1}^{N(j)} [Cno_{j,t_k} - Cnc_{j,t_k}]^2 \qquad (7)$$

where M = number of monitoring nodes; $N(j)$ = number of monitoring times at node j; Cno_{j,t_k} = computed chlorine concentration at node j at time t_k (mg/L); and Cno_{j,t_k} = measured chlorine concentration at node j at time t_k (mg/L).

The simulation-optimization inverse modeling technique, which uses the field measurements and simulated chlorine concentrations at monitoring nodes, can be adopted to solve this unconstrained optimization problem. The flow diagram in Fig. 3 illustrates the simulation-optimization procedure if GA is used in its optimization module.

The various unknown reaction parameters constitute a set of decision variables to be evaluated by GA, and this can work by evaluating the fitness of each potential solution that consists of values for the set of unknown reaction parameters. Fitness is determined by comparing how well the simulated chlorine concentrations that result from the candidate solution match the measured values collected in the field. The computationally intensive step involved in the GA technique is the determination of fitness that is somehow related to the objective function value. The GA continues to spawn generations of potential solutions until comparison of solutions from successive generations no longer produces a significant improvement. In addition, the GA process eliminates most routine and tedious aspects of the calibration process. GA will generally achieve better fits to the available data if the correct set of variables is included in the solution and it can establish the correct range of possible solutions.

APPLICATION OF THE INVERSE MODEL FOR PARAMETER ESTIMATION

The network used earlier is chosen for applying the inverse model. The time-varying chlorine concentrations were observed for this network at the nodes 3, 6, 10, 11, 19, 25, 28, and 34 for a period of 55 hr (10). These measurements become input observed data to the inverse model, and the unknown global wall reaction parameter for the first-order reaction kinetics, which is assumed to be applicable for the system, is estimated. The inverse model is run with a zero concentration tolerance, quality time step of 3 min, and hydraulic step of 1 hr. The estimated value of the global first-order wall reaction parameter is found to be 0.3654 m/d, which results in the lowest possible RMS

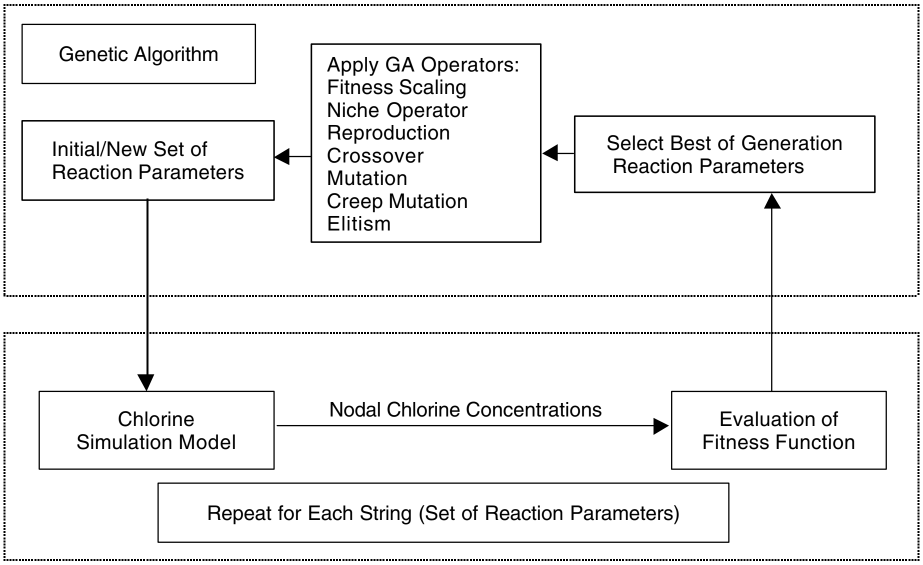

Figure 3. GA implementation.

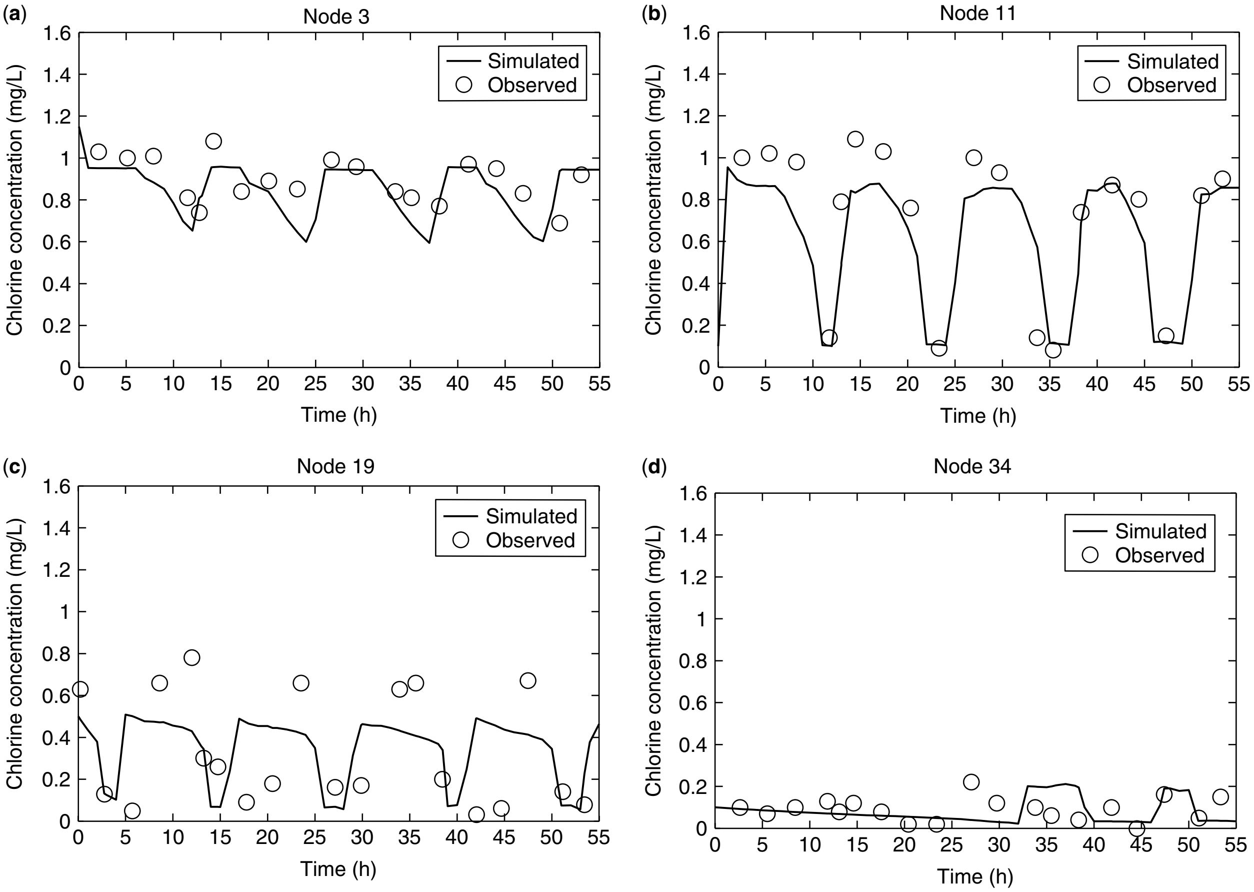

Figure 4. Simulated and observed chlorine concentration at nodes (**a**) 3, (**b**) 11, (**c**) 19, and (**d**) 34.

residual error of 0.172 mg/L without any tedious trial-and-error computations. The comparison of observed and simulated chlorine concentrations for this parameter estimated at node 3, 11, 19, and 34 are represented in Fig. 4.

CLOSURE

The maintenance of chlorine residual is needed at all points in the distribution system supplied with chlorine as a disinfectant. Chlorine is subjected to bulk flow and pipe wall reactions as it propagates through the pipes of the distribution system. The bulk flow reaction term depends on the organic content of the water, whereas the wall reaction term is related to the material and age of the distribution pipe. Because of these reactions, the loss of chlorine is significant between the outlet of the treatment plant and the consumer end. Thus, the study of spatial and temporal distribution of chlorine forms an important aspect of modeling. The chlorine simulation model forms the base for the reaction parameter estimation. The application of the inverse model is more relevant as any combination of bulk and wall reaction kinetics is possible for best fit with field chlorine observations. The inverse model is significant in deciding the operational strategy for real life systems. The chlorine simulation together with the inverse model provides the water supply agencies a tool for better management of their systems.

BIBLIOGRAPHY

1. Larson, T.E. (1966). Deterioration water quality in distribution systems. *J. AWWA.* **58**(10): 1307–1316.
2. Pathak, P.N. (1969). Deterioration of potable water quality in distribution system and its remedial measures. *Environmental Health* **11**(10): 220–228.
3. Boulos, P.F., Altman, T., Jarrige, P.A., and Collevatti, F. (1995). Discrete simulation approach for network water quality models. *J. Water Resour. Plng. Mgmt., ASCE* **121**(1): 49–60.
4. Rossman, L.A., Clark, R.M., and Grayman, W.M. (1994). Modeling chlorine residuals in drinking water distribution systems. *J. Envir. Eng., ASCE* **120**(4): 803–820.
5. Vasconcelos, J.J. et al. (1997). Kinetics of chlorine decay. *J. AWWA.* **89**(7): 55–65.
6. Frateur, I. et al. (1999). Free chlorine consumption induced by cast iron corrosion in drinking water distribution systems. *Water Res.* **33**(8): 1781–1790.
7. Powell, J.C. et al. (2000). Performance of various kinetic models for chlorine decay. *J. Water Resour. Plng. Mgmt., ASCE* **126**(1): 13–20.
8. Clark, R.M. and Sivaganesan, M. (1998). Predicting chlorine residuals and the formation of TTHMs in drinking water. *J. Envir. Eng., ASCE* **124**(12): 1203–1210.
9. Kiéné, L., Lu, W., and Lévi, Y. (1998). Relative importance of the phenomena responsible for chlorine decay in drinking water distribution systems. *Water Res.* **38**(6): 219–227.

10. Ozdemir, O.N. and Ucak, A. (2002). Simulation of chlorine decay in drinking-water distribution systems. *J. Envir. Eng., ASCE* **128**(1): 31–39.
11. Vasconcelos, J.J., Boulos, P.F., Grayman, W.M., Kiéné, L., Wable, O., Biswas, P., Bhari, A., Rossman, L.A., Clark, R.M., and Goodrich, J.A. (1996). Characterization and modeling of chlorine decay in distribution systems. AWWA Research Foundation, Denver, CO.
12. Zhang, G.R., Kiéné, L., Wable, O., Chan, U.S., and Duguet, J.P. (1992). Modeling of chlorine residuals in the water distribution network of Macao. *Environ. Technol.* **13**: 937–946.
13. Chun, D.G. and Selznick, H.L. (1985). Computer modeling of distri-bution system water quality. *Proc. Comp. Appl. Water Resour., ASCE*, NewYork, pp. 448–456.
14. Males, R.M., Clark, R.M., Wehrman, P.J., and Gates, W.E. (1985). Algorithm for mixing problems in water systems. *J. Hydr. Eng., ASCE* **111**(2): 206–219.
15. Clark, R.M., Grayman, W.M., and Males, R.M. (1988). Contaminant propagation in distribution system. *J. Envir. Eng., ASCE* **114**(4): 929–943.
16. Shah, M. and Sinai, G. (1988). Steady state model for dilution in water networks. *J. Hydraulic Eng., ASCE* **114**(2): 192–206.
17. Wood, D.J. and Ormsbee, L.E. (1989). Supply identification for water distribution systems. *J. AWWA.* **81**(7): 74–80.
18. Boulos, P.F., Altman, T., and Sadhal, K. (1992). Computer modeling of water quality in large networks. *J. Appl. Math. Modeling* **16**(8): 439–445.
19. Liou, C.P. and Kroon, J.R. (1987). Modeling the propagation of waterborne substances in water distribution networks. *J. AWWA.* **79**(11): 54–58.
20. Grayman, W.M., Clark, R.M., and Males, R.M. (1988). Modeling distribution system water quality: Dynamic approach. *J. Water Resour. Plng. Mgmt., ASCE* **114**(3): 295–311.
21. Rossman, L.A., Boulos, P.F., and Altman, T. (1993). Discrete volume element method for network water quality models. *J. Water Resour. Plng. Mgmt., ASCE* **119**(5): 505–517.
22. Boulos, P.F., Altman, T., Jarrige, P.A., and Collevatti, F. (1994). An event-driven method for modeling contaminant propagation in water networks. *J. Appl. Math. Modeling* **18**(2): 84–92.
23. Islam, M.R. and Chaudhary, M.H. (1998). Modeling of constituent transport in unsteady flows in pipe networks. *J. Hydr. Eng., ASCE* **124**(11): 1115–1124.
24. Shang, F., Uber, J.G., and Polycarpou, M.M. (2002). Particle backtracking algorithm for water distribution system analysis. *J. Environ. Eng., ASCE* **128**(5): 441–450.
25. Tzatchkov, V.G., Aldama, A.A., and Arreguin, F.I. (2002). Advection-dispersion-reaction modeling in water distribution networks. *J. Water Resour. Plng. Mgmt.* **128**(5): 334–342.
26. Munavalli, G.R. and Mohan Kumar, M.S. (2004). Modified Lagrangian method for water quality in distribution systems. *Water Res.* **38**(8): 2973–2988.
27. Axworthy, D.H. and Karney, B.W. (1996). Modeling low velocity/high dispersion flow in water distribution systems. *J. Water Resour. Plng. Mgmt., ASCE* **122**(3): 218–221.
28. Ozdemir, O.N., and Ger, A.M. (1999). Unsteady 2-D chlorine transport in water supply pipes. *Water Res.* **33**(17): 3637–3645.
29. Rossman, L.A. (2000). EPANET 2 Users manual. Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.
30. Rossman, L.A. and Boulos, P.F. (1996). Numerical methods for water quality in distribution systems: A comparison. *J. Water Resour. Plng. Mgmt., ASCE* **122**(2): 137–146.
31. Biswas, P., Lu, C.S., and Clark, R.M. (1993). Chlorine concentration decay in pipes. *Water Res.* **27**(12): 1715–1724.
32. Walski, T.M., Chase, D.V., and Savic, D.A. (2001). *Water Distribution Modeling*. Haestad Press, Baltimore, MD.
33. Clark, R.M., Rossman, L.A., and Wymer, L.J. (1995). Modeling distribution system water quality: Regulatory implications. *J. Water Resour. Plng Mgmt., ASCE* **121**(6): 423–428.
34. Al-Omari, A.S. and Chaudhry, M.H. (2001). Unsteady-state inverse chlorine modeling in pipe networks. *J. Hydrol. Eng., ASCE* **127**(8): 669–677.
35. Zeirolf, M.L., Polycarpou, M.M., and Uber, J.G. (1998). Development and autocalibration of an input-output model of chlorine transport in drinking water distribution systems. *IEEE Trans. Control Syst. Technol.* **6**(4): 543–553.
36. Munavalli, G.R. and Mohan Kumar, M.S. (2003). “Water quality parameter estimation in a steady state distribution system”, *J. Water Resour. Plng and Mgmt., ASCE*, **129**(2), 124–134, 2003.
37. Mohan Kumar, M.S. and Munavalli, G.R. (2003). Autocalibration of chlorine transport model for steady state distribution system by genetic algorithm. *Seventh International Water Technology Conference IWTC-2003*, Egypt, May 1–3.

PARTICULATE MATTER REMOVAL BY COAGULATION

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Particulate matter in natural water varies in size, concentration, and surface chemistry. The particle size may range from a few tens of nanometers to a few hundred micrometers. Discrete particles less than one micron in size are called colloidal. Colloidal particles have significantly higher external surface area per unit area and move in a random diffusional motion known as Brownian motion. In colloidal suspension, surface phenomena dominate over mass phenomena. The most important surface property is the accumulation of electrical charges at the particle surface. Loss of atoms due to abrasion, molecular arrangement within the crystal, and imperfections within the molecular structure may result in surfaces being charged. The colloidal particles in most surface water are negatively charged. Because of hydration and/or electrostatic surface charges, colloidal particles repel other material and thereby remain suspended. Surface waters that are turbid due to colloidal particles cannot be clarified without special treatment.

Coagulation is a process for enhancing the tendency of particulate matter in aqueous suspension to attach to one another and/or to attach to collector surfaces. Coagulation promotes destabilization of surface charges on colloidal particles. Destabilization and aggregation of particulate matter and precipitation or adsorption of NOM in subsequent solid–liquid separation processes are the primary functions of the coagulation process. The coagulation process involves two steps: (1) the addition of chemical coagulants to destabilize particulate matter and react with NOM and (2) the physical transport of collisions among particulate matter, resulting in aggregation or floc formation. In the water treatment literature, coagulation refers to all reactions and mechanisms that result in aggregation, and the physical transport step of producing interparticle aggregation is called flocculation. In a water treatment plant, coagulation is achieved by rapid or flash mixing of coagulants followed by flocculation.

The two most common types of coagulants are metallic salts and polymers; the most common metallic salt coagulants are aluminum sulfate (alum) and ferric chloride. The selection of a particular coagulant depends on the required level of effectiveness. A standard jar test is a recommended method for determining the relative effectiveness of coagulants for a particular raw water supply. The factors that are considered normally in selecting a coagulant include cost, availability, overall safety, ease of storage, handling, and application.

Alum is the most widely used coagulant because of its availability, low cost, ease of use, and ease of storage. Ferric chloride, other metallic salts, and polymers are less widely used. Alum's performance, however, is greatly affected by the pH of the influent. The commonly used dosage of alum ranges from 5 to 150 mg/L, but the problem of sludge disposal increases at higher alum dosages. Due to special raw water characteristics and because of health concerns about aluminum, some water utilities use ferric chloride. Although ferric chloride is not always as effective as alum in reducing trihalomethane formation potential (THMFP) and total organic carbon (TOC), it is more effective than alum for water that has high dissolved color, low turbidity, and a moderate pH.

Polymers are effective coagulants, coagulant aids, and filter aids. They consist of monomers and are classified according to their charge or lack of charge. A polymer that has a charge is an ionized polymer, or a polyelectrolyte. Polymers can be cationic, anionic, or nonionic. In applications where polymers are effective, dosages are generally lower than alum dosages for the same effect. Typical polymer dosages range from 1.5 to 10 mg/L. Consequently, polymer coagulants produce less residual sludge than alum.

Coagulant aids are added to the influent after or simultaneously with the primary coagulants to improve particle capture efficiency during flocculation, sedimentation, and filtration. Nonionic and anionic polymers are commonly used as coagulant aids. The ratio of alum to coagulant aid dosages ranges from 100:1 to 50:1. Standard jar tests are required to determine precise coagulant aid dosages.

There are four coagulation mechanisms that, it is thought, occur in destabilizing colloidal particles: double layer compression, surface charge neutralization, sweep coagulation, adsorption and interparticle bridging.

The double layer model is used to understand the ionic environment near a charged colloid particle. The surface charge on the colloid attracts ions of opposite charge and forms a dense layer adjacent to the particle known as the Stern layer. Excess positive ions are still attracted by the negatively charged colloids but are repelled by the Stern layer. This dynamic equilibrium results in creating a diffuse layer of counterions. The Stern and the diffuse layer in the interfacial region around colloidal particles are referred to collectively as the double layer. The electrical potential at the junction of the Stern layer and the diffuse layer, called the zeta potential, can be measured experimentally. It correlates with colloid particle stability. Highly stable colloidal systems are characterized by a high zeta potential, whereas lower zeta potentials reflect less stable systems. The DLVO theory (named after Derjaguin, Landau, Verwey, and Overbeek) governs the net interactive force between colloidal particles by combining the van der Waals attractive force and the electrostatic repulsion force. The double layer can be compressed by adding a coagulant that has a positive charge (to counteract negatively charged colloids). In water treatment practice, destabilization by double layer compression is not a dominant mechanism because it requires an extremely high salt concentration. This is an important destabilization mechanism in natural systems, for instance, delta formation in estuaries.

Destabilization by surface charge neutralization involves reducing the net charge of colloidal particles in the suspension. The net surface charge can be reduced by adjusting the solution chemistry. In other cases, colloidal particles can be destabilized by neutralizing using counterions of coagulants. In water treatment practice, a similar type of surface charge destabilization occurs that is called heterocoagulation. The distribution of charges on a colloidal surface is not uniform. Large particles that have high negative surface charges may come in contact with smaller particles that bear relatively low positive charges. These particles may be destabilized by simple electrostatic interaction.

Sweep coagulation or sweep-floc coagulation is also known as enmeshment in a precipitate. At higher coagulant doses, excess metal salts hydrolyze into metallic hydroxides. These hydroxides are extremely insoluble in water, amorphous, heavier than water, and gelatinous. As the hydroxide precipitate forms and accumulates, the colloidal particles are enmeshed or entrapped in the hydroxide floc. This destabilization mechanism is called sweep coagulation.

Interparticle bridging destabilization occurs when high-molecular-weight polymers are used as coagulants or coagulant aids. These polymers are highly surface-active, and their surface structure may be linear or branched. The polymers destabilize particles by first adsorbing at one or more sites on the colloidal particle surface and then extending the chain length into solution and attaching to other particles. This results in forming an interparticle bridge. Sometimes an excessive dosage of polymer may cause restabilization due to surface saturation or sterical stabilization.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, New York.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, New York.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold Company, New York.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000). *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

SELECTIVE COAGULANT RECOVERY FROM WATER TREATMENT PLANT RESIDUALS USING THE DOMAIN MEMBRANE PROCESS

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BACKGROUND

During the last two decades, pressure-driven membrane processes, namely, reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF), have found increased applications in water utilities and chemical industries. Unlike RO, NF, and UF, Donnan membrane process (DMP) or Donnan dialysis is driven by an electrochemical potential gradient across an ion exchange membrane. Theoretically, the Donnan membrane process is not susceptible to fouling because particulate matter or large organic molecules do not concentrate on the membrane surface, as commonly observed with pressure-driven membrane processes. Although information on several applications of DMP is available in the open literature (1,2), no work is reported on the use of DMP to treat a sludge or slurry with a high concentration of suspended solids or large organic molecules. It was conceived that a single-step Donnan membrane process could selectively recover coagulant alum ($Al_2(SO_4)_3 \cdot 14H_2O$) (3,4) from water treatment plant sludge or water treatment plant residuals (WTR), which are the endproduct of coagulation. WTR contain insoluble aluminum hydroxide (50–75%) along with suspended inorganic particles, natural organic matter (NOM), and trace amounts of heavy metal precipitates (5).

Several efforts were made to recover alum from WTR. The acid digestion process is the most commonly tried process at the laboratory, pilot-scale, and plant level (6). In this process, WTR are sufficiently acidified with sulfuric acid, dissolving insoluble aluminum hydroxide in the form of alum up to aluminum concentration levels of 360–3700 mg/L. However, the process is nonselective; with the dissolution of aluminum hydroxide, NOM-like humates and fulvates get dissolved too, and the resulting dissolved organic carbon (DOC) concentration ranges from 326 to 1800 mg/L (7). This recovered alum, if reused as a coagulant, may impart a high trihalomethane formation potential (THMFP) during the chlorination stage of water treatment. The trihalomethanes are suspected carcinogens regulated by the USEPA (8). As an alternative to the acid digestion process; the amphoteric nature of aluminum oxide also permits alum recovery from the WTR under alkaline conditions. However, the alkali digestion process suffers from the same limitation as the acid digestion process; i.e., NOM concentration is very high in the recovered solution. Figure 1 shows both DOC and aluminum concentrations of the Allentown Water Treatment Plant (AWTP) in WTR at different pH levels. The Donnan membrane process is uniquely capable of recovering alum from WTR in a single-step process using sulfuric acid and a cation-exchange membrane.

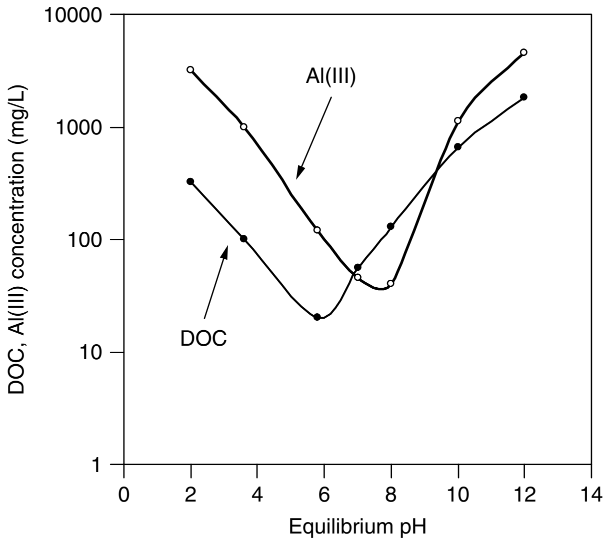

Figure 1. Variation of dissolved organic carbon (DOC) and aluminum concentration with pH for water treatment residuals (WTR) from Allentown Water Treatment Plant (AWTP).

THEORY

Let us consider solutions of aluminum sulfate (feed) and sulfuric acid (recovery) in a Donnan membrane cell divided into two chambers by a cation-exchange membrane that allows only cations to migrate from one side to the other but rejects any passage of anions according to Donnan's co-ion exclusion principle (9). At equilibrium, the electrochemical potential of aluminum ion Al^{3+} ion ($\overline{\mu}$) in the feed solution will be the same as that in the recovery solution for both aluminum and hydrogen ions, which corresponds to the following Donnan equilibrium condition:

$$\left(\frac{C^{R}_{Al}}{C^{L}_{Al}}\right) = \left(\frac{C^{R}_{H}}{C^{L}_{H}}\right)^{3}$$

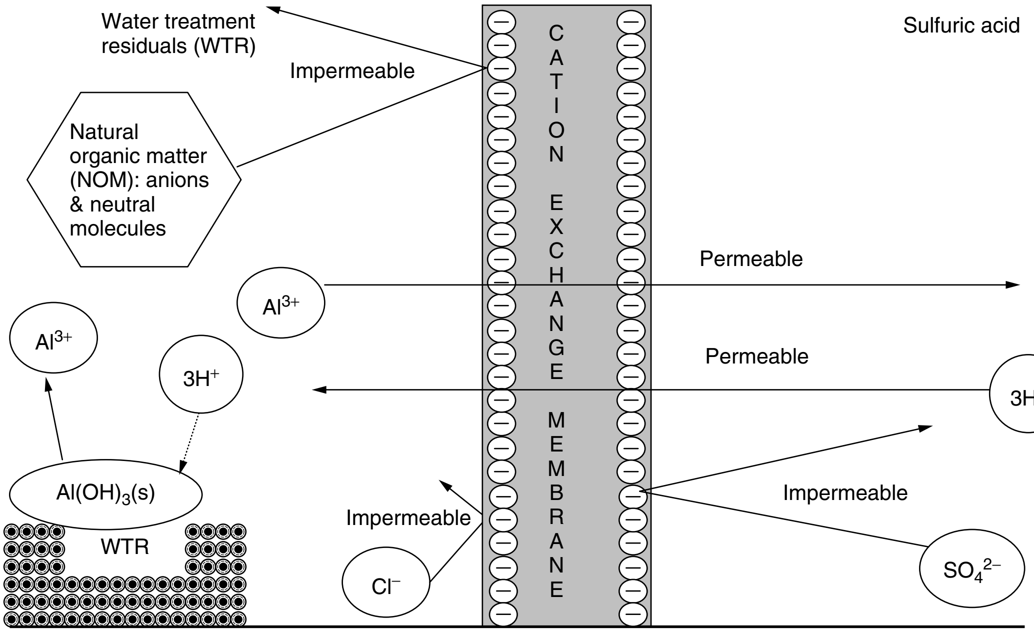

Figure 2. A schematic of Donnan membrane process illustrating selective alum recovery from WTR.

If the ratio $\frac{C_H^R}{C_H^L}$ is 10, it means C_{Al}^R is 1000 times greater than C_{Al}^L. Thus, by maintaining high hydrogen ion concentration in the recovery solution, aluminum ions can be driven from the feed to the recovery side even against a positive concentration gradient, i.e., from a lower concentration region to a higher concentration one. Figure 2 depicts the conceptualized selective alum recovery from WTR, highlighting the following.

KEY FINDINGS

In the Donnan membrane cell, the feed side of the membrane contained 6 L of the decanted and slightly acidified WTR collected from the AWTP, whereas the recovery side contained 1.5 L of 10% sulfuric acid solution, separated by a cation-exchange membrane Nafion 117. At the start, pH of the WTR side was between 3.0 and 3.5. With the progress of the run, aluminum ions from the WTR side moved to the recovery side through the cation-exchange membrane, whereas an equivalent amount of hydrogen ions permeated to the WTR side, thus further reducing the pH. Under the experimental conditions of the Donnan run, free aluminum ions, Al^{3+}, was the predominant aluminum species. Figure 3 shows the results of the process for a period of 24 hours; the percentage aluminum recovery and the concentration of aluminum in the two chambers were plotted against time. It can be seen that over 70% recovery (72%) was attained in 24 hours. The noteworthy observation is that the

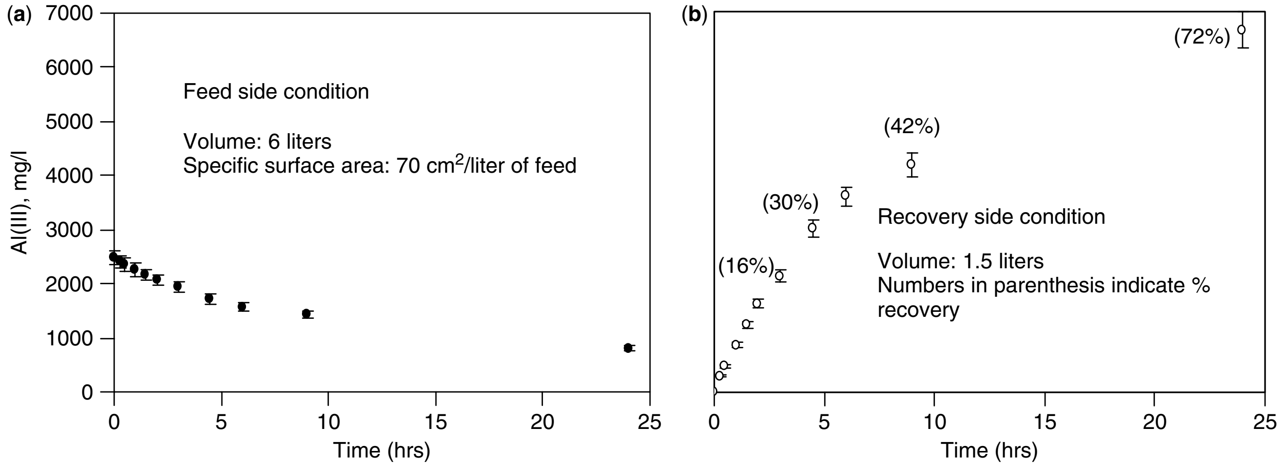

Figure 3. Aluminum recovery from AWTP residuals during Donnan membrane process: (**a**) decrease in Al concentration in feed; (**b**) percentage recovery and increase in Al concentration in recovery solution.

recovered aluminum concentration was 6,650 mg/L as Al, and it was significantly greater than the total aluminum concentration (2400 mg/L) present in the parent sludge. It was also noted that the recovery was selective with respect to trace heavy metal ions. The recovered alum did not contain any suspended solids, whereas NOM expressed as DOC was consistently less than 5 mg/L. The ratio of individual contaminants to aluminum in the recovered alum was comparable, and in some cases lower, than in the commercial alum currently being used in AWTP. Similar results were obtained with WTR received from the Baxter Plant (Philadelphia, PA), which used $FeCl_3$ as a coagulant, where over 75% recovery was made in 24 hours.

Figure 4(a,b) show the visual comparison of recovered coagulants, both alum and ferric sulfate, between the traditional acid digestion process and the Donnan membrane process. Higher transparency of the coagulants from AWTP and the Baxter Plant, recovered by Donnan membrane process, is readily noticeable because of the absence of turbidity and NOM.

CONCLUSIONS

In this work, it was worthy to note that (a) aluminum (ferric) hydroxide precipitates could be dissolved and coagulant ions concentrated in the recovery solution; (b) negatively charged NOM, sulfate, and chloride could not permeate the membrane because of Donnan exclusion; and (c) the recovered alum was sufficiently pure and reuseable in water treatment plants.

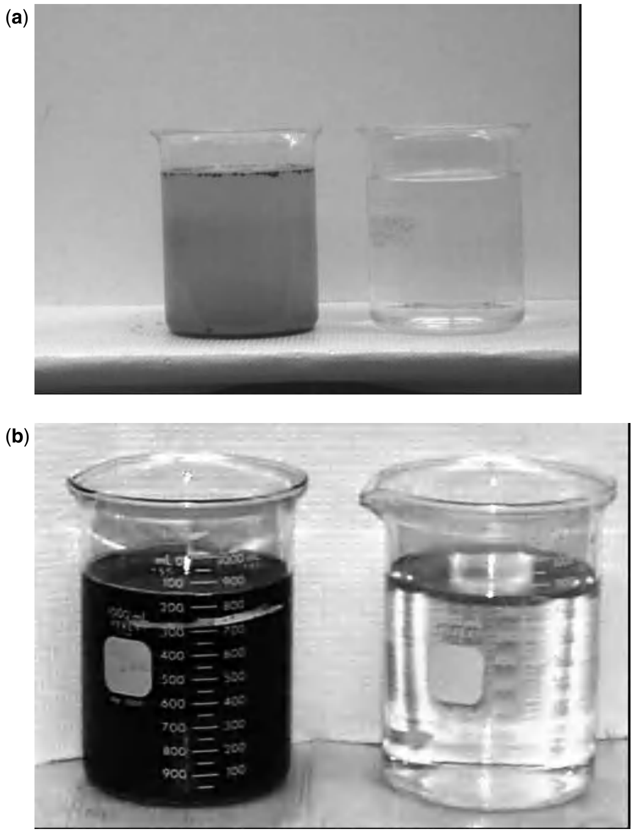

Figure 4. (**a**) Visual comparison of recovered alum coagulant from AWTP residuals by acid digestion process (left) and Donnan membrane process (right) (**b**) Visual comparison of recovered ferric coagulant from Baxter Plant residuals by acid digestion process (left) and Donnan membrane process (right).

BIBLIOGRAPHY

1. Wallace, R.M. (1967). *Ind. Eng. Chem. Process Des. Dev.* **6**(4): 423–431.
2. Kim, B.M. (1979). *AIChE Symposium Series* **76**(197): 184–192.
3. Prakash, P. and SenGupta, A.K. (2003). *Environ. Sci. Technol.* **37**: 4468–4474.
4. SenGupta, A.K. and Prakash, P. (2002). Process for selective coagulant recovery from water treatment plant sludge. U.S. Patent 6,495,047.
5. Cornwell, D.A and Westerhoff, G.P. (1981). Management of water treatment plant sludges. In: *Sludge and Its Ultimate Disposal*, J.A. Borchardt (Ed.). Ann Arbor Science, Ann Arbor, MI.
6. Bishop, M.M., Rolan, A.T., Bailey, T.L., and Cornwell, D.A. (1987). *J. AWWA.* **79**(6): 76–83.
7. Saunders, F.M. (1989). *Coagulant Recovery from Alum WTR at North Area Plant*. Final Report for Bureau of Water, City of Atlanta, GA.
8. Christman, R.F., Norwood, D.L., Millington, J.D.S., Stevens, J.D., and Stevens, A.A. (1983). *Environ. Sci. Technol.* **17**: 625–628.
9. Helfferich, F. (1995). *Ion Exchange*. Dover Publication, New York, pp. 134–135.

PHYSICAL WATER CONDITIONING

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Magnetic water treatment technology that was used two centuries ago to control hard water scale is now being used in hundreds of different kinds of beneficial applications throughout the world. Permanent magnetic water conditioning (PMWC) does not change the chemistry of the water; only a *physical* change takes place. It is therefore referred to as physical water conditioning (Fig. 1) (1).

Physical water conditioning (PWC) has been highly controversial for many years; however, due to numerous successful installations on boilers, cooling towers, and other HVAC equipment, the technology has gained credibility throughout the industry in recent years. The ASHRAE Handbook (considered the "bible" of the industry) states, "Equipment based on magnetic, electromagnetic, or electrostatic technology has been used for scale control in boiler water, cooling water, and other process applications."

Several laboratory tests have been conducted to evaluate the results of magnetically treated water for scale and corrosion control in heat transfer equipment. The purpose of one such test was to determine the physical or chemical differences between treated and untreated residues. Emission spectrographic analyses of

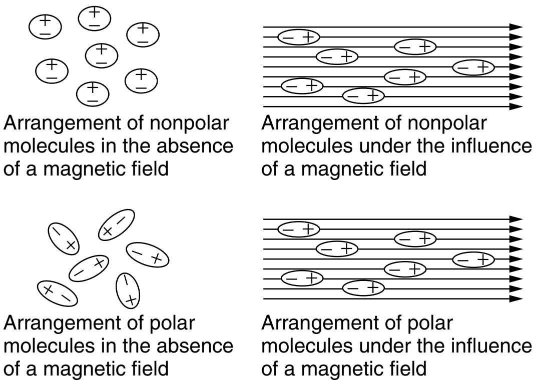


Figure 1. The effect of a magnetic field.

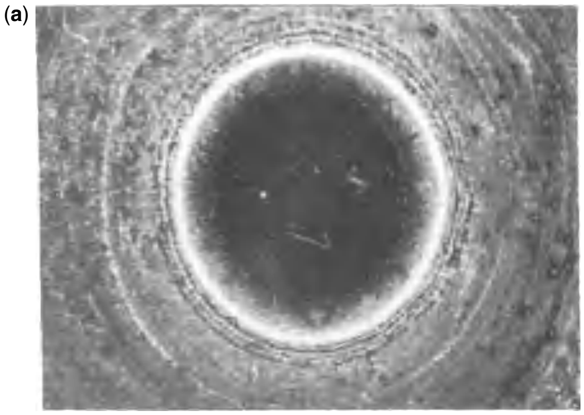
the two water residues, it was found, have the same chemical constituents; however, a distinctive difference was observed in the crystalline structure. The residue from the magnetically conditioned water was a soft powder (when dry), whereas the untreated water deposit was typical boiler scale (2).

Disassociated dissolved molecules of $CaCO_3$ in water have a tendency to recombine by forming scale that adheres to the inner walls of the piping system, containers, steam vessels, etc. When water flows through a magnetic field of relatively low intensity, the formation of scale in the treated water is prevented in many instances. Instead, aragonite is formed within the flowing bulk water (aragonite forms a dilute slurry in the water, and the sediment can be easily removed by blowdown or bleed-off). The magnetochemical reaction is only one of the many cross effect reactions that enable the transformation of calcite to aragonite. Other reactions include thermochemical and mechanochemical reactions (Fig. 2).

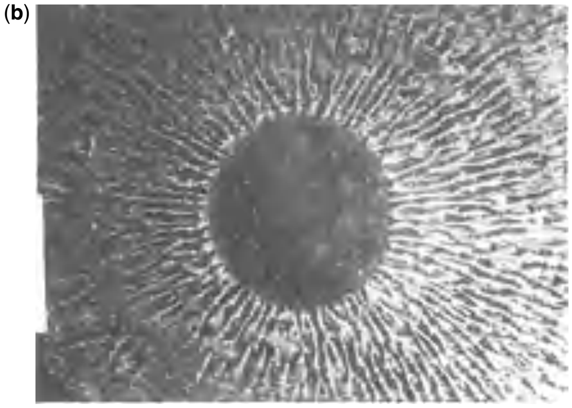
One of the benefits of PWC is energy savings from keeping the heat transfer area clean and free of scale, which prevents efficient transfer from the energy side to the water (see Fig. 3).

Billions of dollars are lost in the United States every year due to corrosion. Laboratory tests and field installations, using corrosion coupons, as a comparison, have proven that magnetic water treatment reduces corrosion rates in HVAC equipment. This is accomplished by eliminating the aggressive chemicals used to control scale, and aragonite talc, a by-product of calcium, which puts a microscopic film on all wetted parts and provides protection against oxygen pitting. The $CaCO_3$ with the PMWC does not build upon itself; however, a thin transparent coating deposits on the metal water side and dries as a fine white or gray powder.

The National Aeronautics and Space Administration (NASA), using their Dynamic Corrosion Test System in an evaluation study, compared magnetically conditioned water to chemical treatment. Corrosion coupon #42 in the magnetically conditioned water loop had a corrosion rate of 0.0 mils per year; #41 and #43, treated with chemical corrosion inhibitors in the loop, had 5 and 6 mils loss per year respectively (Fig. 4) (3).

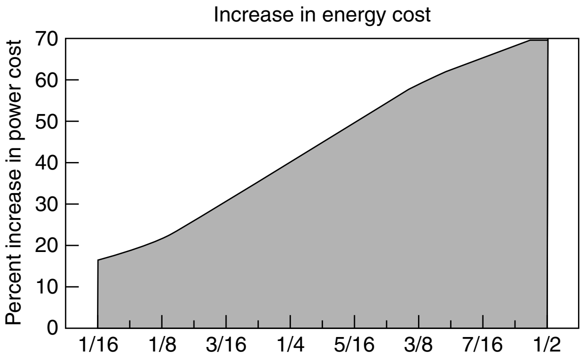


Untreated raw water



Magnetically treated water

Figure 2. Partially evaporated water droplets magnified to the 40th power.



(Above data from the University of Illinois and the Bureau of Standards)

Figure 3. Additional fuel consumed with scale accumulation.

An independent laboratory used a test rig consisting of two 48 inch glass cylinders filled with steel wool and tapered at one end to evaluate the effect of magnetically treated water on corrosion. The flow rate of the water entering the top of each cylinder (one treated and one untreated) was adjusted to make the water head in the cylinders about 10 inches. After 72 hours, water in the untreated system overflowed the glass cylinder. The flow rate was then determined (4).

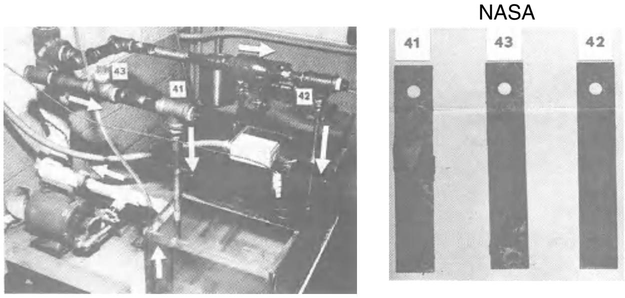


Figure 4. NASA dynamic corrosion test stand and # C-75-1495 photos of coupons.

	Untreated Tap Water	Treated Tap Water
Flow Rate	25 mL per 58.0 s	25 mL per 7.5 s
Water height	46 inches	20 inches

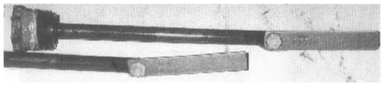
A PMWC system was installed on a 4-year-old, 1500-ton cooling tower and chillers that had moderate scale buildup in the tower and condenser tubes. There was also a considerable amount of corrosion and pitting on the inside of the chiller end caps. The chemical company that treated the system during the first four years of operation suggested that they monitor the results of the PMWC system.

Six months after the installation, the chillers were opened for inspection. The end caps did not require wire brushing to remove the hard brittle scale as previously found, and the small accumulation of mud in the tubes was easily flushed out of the system by a garden hose.

Prior to the PMWC installation, the average corrosion rate of the copper coupon ID # 10008 16-S was 0.01 MPY. After the PMWC installation, the copper coupon ID # 10007 A0882 corrosion rate was also 0.01 MPY; however, the loss was even and general and had an average penetration of 0.15 mils versus 0.50 mils penetration using the previous chemical treatment.

The prior steel coupon ID #10008 48 V had a corrosion rate of 0.36 MPY and an average pit depth of 0.500 mils. The PMWC steel coupon ID # 10007 A3379 had a corrosion rate of 0.22 MPY and an even and general average penetration of 0.150 mils. A 100% return on investment took only 27 months in chemical cost alone (Fig. 5)

In recent years, *pollution prevention* has taken on a new meaning. The transfer of polluted material from one place to another was, at one time, considered “prevention” if the contaminated water was prevented from entering our freshwater streams. However, true prevention is now understood as *eliminating the generation* of toxic waste. The 200-year-old technology is now being used to replace chemicals previously used for water treatment. Research has been spurred recently due to public awareness and concern for the environment. Several different types of applications have been discovered since the turn of the century. The science laid dormant for many years; however, it is now considered “state of the art technology” and is gaining momentum in numerous industrialized countries.



Copper and mild steel corrosion coupons

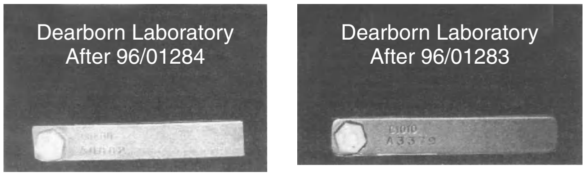


Figure 5. Nissan/Dearborn corrosion coupons.

The arrangement of the magnetic fields is a very important factor to provide adequate and effective treatment for most applications. To a multiple reversing polarity field that has a N–SS–NN–S arrangement is the most successful in controlling hard water scale deposition (Fig. 6) (5).

In addition to the multiple reversing fields, research has shown that scale can be best controlled when the water containing the minerals cuts through the magnetic lines of force at right angles. A steel pipe (magnetic material) surrounding the magnet pulls the magnetic lines of force at right angles through the water passageway. The pipe directs the water flow perpendicular to the magnetic fields (Figs. 7 and 8) (6).

Since the turn of the century, there have been dozens of new beneficial applications for magnetically treated water found through new research discoveries and hundreds more in the field. There are numerous case histories of PMWC installations on various types of equipment that have been documented by third parties as successful applications (7). Most convincing are the original equipment manufacturers (OEM) who install magnetic water conditioners on their equipment to extend the period of time between maintenance service calls.

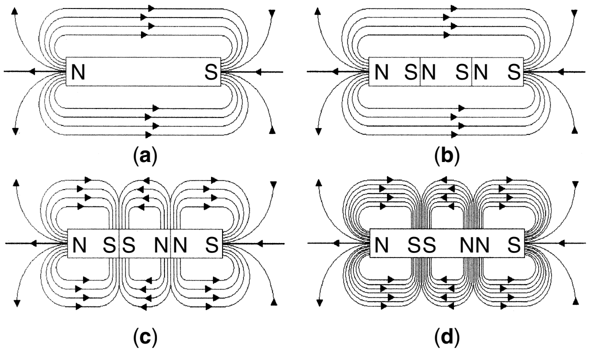


Figure 6. (**a**) One 2 pole, single field; (**b**) Three 2 pole, single field; (**c**) Three 2 pole, three separate fields; (**d**) One 6 pole, three dense fields.

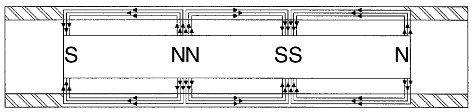


Figure 7. One 6 pole, three dense fields, with steel shield.

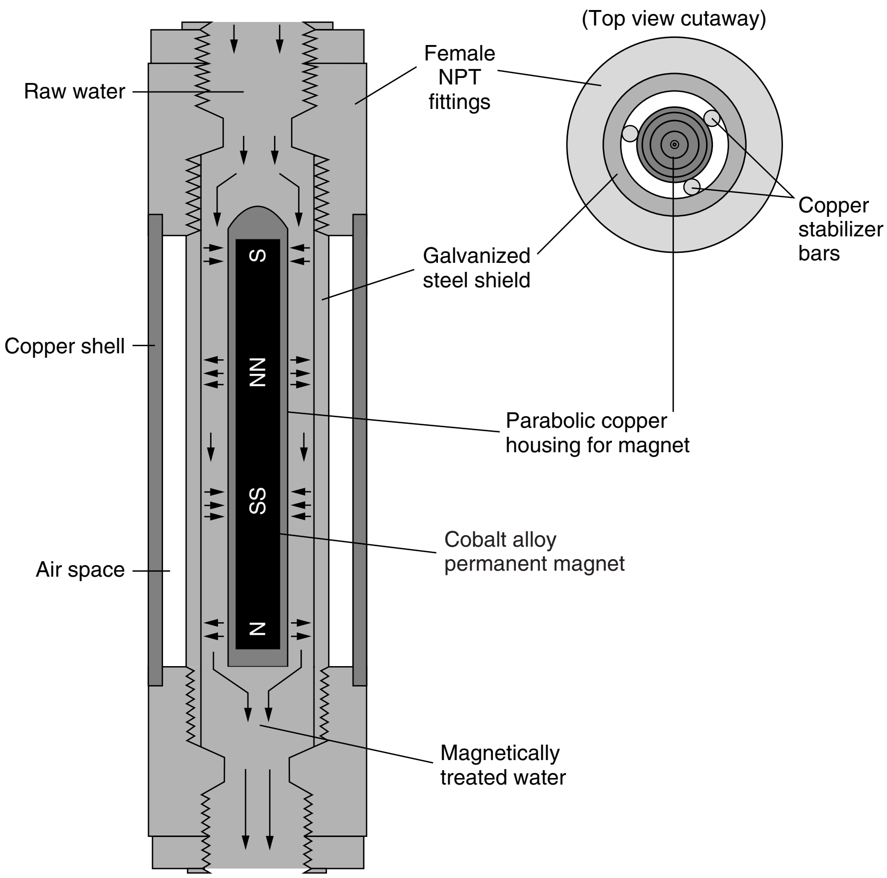


Figure 8. Cutaway view of a PMWC unit showing the water path perpendicular to the magnetic fields.

Water softeners that weighed over 100 pounds, plus bags of salt that were carried in carpet cleaning vans, are being replaced by small magnetic water conditioners (only $1\frac{1}{4}$ inches in diameter and 12 inches long), weighing less than 2 lb. Thousands of these small specially designed units for truck-mounted applications have been installed to prevent scale in steam boilers and related equipment by the manufacturer of a turnkey carpet steam cleaning equipment package.

Hard water is one of the most common causes of truck-mounted heating system failure. Untreated hard water causes loss of performance in heat exchangers and, many times, permanent damage to components (8). Several manufacturers of carpet cleaning systems throughout the United States have installed thousands of PMWC units on their truck-mounted systems during the last 5 years and reported excellent scale control and corrosion protection. Several manufacturers of the truck-mounts now encourage the use of PMWC by their customers who purchased their equipment with water softeners prior to the changeover.

Magnetic water conditioning is believed to be the wave of the future by many proponents, especially environmental groups. It is nonpolluting, does not require energy for continued operation, and needs very little, if any, maintenance. The total value of the overall benefits of PMWC is still not known. There are hundreds of different types of successful applications now in use, and there are dozens more evaluations of laboratory studies and field installation presently underway. The PMWC system has the ability to enhance our environment by reducing chemical use (true pollution prevention) and also helps save energy. The technology is cost-effective and plays a big role in water conservation. (9).

The steel industry is reportedly the single largest consumer of PMWC technology in *total gallons treated per day* due to the high demand for water needed to cool its furnaces. Units are presently available in sizes up to 50,000 gallon per minute with 72 inch flanges.

Economics is also one of the deciding factors in reducing chemical usage; the cost of preventing contaminated process wastewater from entering our freshwater rivers, lakes, and underground aquifers is very high. Transportation to another location can be as much as three times the cost of the chemical, depending on how hazardous the discharge water is.

The food service industry is the largest user of the PMWC in *total number of units*; installations are on ice machines, coffee makers, dish washers, proofers, steamers, and drink dispensers. Sizes usually range from 1 gpm up to 15 gpm (10). Original equipment manufacturers that supply the food service industry have found that adding a small specially designed unit to their water using product eliminates the majority of service calls and replacement of parts under warranty that are prone to scaling or corrosion (11).

As a result of millions of successful installations reported (many documented by qualified professionals), **the question of whether or not magnetic water**

conditioners work has been put to rest. However, the issue of how they work is still being debated. ASHRAE funded a comprehensive research study in 2000, titled *"Efficiency of Physical Water Treatment for the Control of Scale"* This report, published in 2003, confirms the results of several PMWC units performing under very rigid conditions and identifies the most effective velocity through each unit to control scale on heat transfer surfaces (12).

BIBLIOGRAPHY

1. Quinn, C.J. (1986). Professor Emeritus, Indiana University-Purdue University Chairman, Manufacturing Technology. *Magnetic Water Treatment For Heating, Refrigeration, and Air-Conditioning Systems*. DOE/CE/40568-T1 (DE86014306).
2. Schmutzer, M.A. and Hull, G.W. (1969). *Water Residues After Evaporation*. Report # 28258. United States Testing Company, Inc.
3. Kuivinen, D.E. (1975). *Dynamic Corrosion Test System*. Report # 70112. National Aeronautics and Space Administration, Lewis Research Center.
4. Levinsky, H.L. and Schmutzer, M.A. (1968). *Evaluation Of Steel Wool Corrosion With Magnetic Treated Water versus Untreated Water*. Report # 27421-2. United States Testing Company, Inc.
5. Lin, I.J. (1982). *Faculty of Civil Engineering*, Mineral Engineering Department, Technion Institute of Technology, Haifa, Israel.
6. Young, I.C. (2002). *Efficiency of Physical Water Treatments in Controlling Calcium Scale Accumulation in Recirculating Open Cooling Water System*. Department of Mechanical Engineering, and Mechanics, Drexel University, College of Engineering.
7. Craine, J.E. (1984). Professor Emeritus, Ohio State University, International Foodservice Consultants Society, *Control Lime/Scale Build-Up With Magnetic Water Treatment*, Volume XVII, Number 2.
8. HydraMaster Corporation, Manufacturers of Truck Mounted Steam Machine Carpet Cleaning Systems, *Instructions How To Retrofit Magnetic Water Conditioners* (1998).
9. Evers, D. (1998). *Technology for Improving Energy Efficiency Through the Removal or Prevention of Scale. DOE/EE-0162* Battelle Columbus Operations, United States Department of Energy—Federal Technology Alert.
10. Ferlin, J. (1982). *Magnetic Water Conditioning Will Do Many Thing For The Foodservice Operator*. President, Ferlin and Hopkins, USPWCA National Seminar Presentation.
11. Kappus, J. (1997). *Taylor Freezer Food Service*, Henny Penny Steamers.
12. ASHRAE Research Project 1155 TRP (2000).

CONSUMER CONFIDENCE REPORTS

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On August 19, 1998, the U.S. Environmental Protection Agency (USEPA) promulgated a final rule (40 CFR Parts 141 and 142) requiring community water systems to prepare and provide annual water quality reports to their customers. Mandated by the 1996 amendments to the Safe Drinking Water Act, these "Consumer Confidence Reports" (CCRs) provide the missing link for consumers to have easy access to valuable water quality information. Just as food products have labeling requirements, CCRs are the public's "right-to-know" resource.

The federal rule outlines a number of required elements, including information on the source(s) of drinking water and any source water assessment that has been completed, plainly worded definitions of industry terminology, information on all regulated contaminants detected in the water, health effects language, notice for non-English-speaking residents, and specific language on vulnerable subpopulations and the reasonably expected presence of some contaminants. The CCR also gives the public direct access to their water system professionals by requiring the inclusion of information on public participation opportunities, local contacts, and additional water-related resources, such as USEPA's toll-free Safe Drinking Water Hotline. In addition to the federal requirements, some states mandate supplementary guidelines.

The first CCRs, due to customers on October 19, 1999, covered test results from January 1, 1998—December 31, 1998. Subsequent annual reports are due to consumers by July 1 each year and include data from the prior calendar year. Detections of contaminants that are tested for less frequently should also be included; however, no data more than 5 years old are permitted.

All community water systems that have at least 15 service connections serving residents year-round must prepare a CCR. Water wholesalers must provide monitoring data and other required information to their retail customers by April 1 of each year. The retail system is responsible for ensuring that its customers receive a CCR containing all required content, whether they produce the report themselves or contract with their wholesaler to provide the report. After completing the CCR, each utility must certify to the state that they have complied with the CCR rule; each state determines the method for certification. A copy of the CCR is shared with the local health department, and the utility must keep the report on file for 5 years.

CCR mailing and distribution requirements are based on the size of the water utility as outlined in the federal guidelines or as modified by the state. The governor of the state has the option to waive the mailing requirements for systems that serve fewer than 10,000 people; however, these systems must still prepare a CCR, inform customers that the report is available upon request, and publish the report in a local newspaper each year. Systems that receive the waiver and serve fewer than 500 customers are not required to publish the report in the newspaper. Systems that serve more than 10,000 people must mail one copy of the report to each customer must and make a "good faith effort" (mailing to all postal patrons in the service area, posting the CCR in public places, delivering multiple copies to apartment buildings or to large employers for distribution) to get reports to non-bill-paying customers. Systems that serve 100,000 or more people must also post their CCR on the Internet.

CCRs are promoted by industry organizations, such as the American Water Works Association (AWWA), as “a timely opportunity for utilities to deliver straight talk to the consumer on quality and other issues affecting drinking water” (1). The AWWA offered training on how to prepare a CCR when the rule was issued, and it commissioned a series of six qualitative focus groups in 1997 to assess public perception and reaction to prototype CCRs in anticipation of the final rule. Their findings suggested that CCRs be called “Water Quality Reports” to let customers decide for themselves whether or not they are confident in the water system; to keep the report basic, simple, and honest; to avoid self-serving or alarming statements; and to gear the materials toward the needs of the system’s customers.

According to the USEPA (2), there are more than 54,000 community water systems in the United States. Most Americans (263 million) get their drinking water from one of these community water systems and use about 370 billion gallons of water daily. Approximately $22 billion is spent annually to make tap water fit to drink. CCRs are the first nationwide commitment to educate the public about these important drinking water quality issues.

BIBLIOGRAPHY

1. AWWA. (1998). Preparing the Consumer Confidence Reports—One Day Seminar, August.
2. USEPA Office of Water. (2001). Factoids: Drinking Water and Ground Water Statistics for 2000, EPA 816-K-01-004, June.

WATER CONSERVATION MEASURES

National Drinking Water
Clearinghouse

Water is a finite resource, and in many areas, future water supplies are uncertain. Individuals are usually aware when there is a drought; however, because water is inexpensive, there are often few incentives to reduce water loss. Water has no viable substitutes, and its depletion bodes profound economic and social impacts. Citizens and utilities need to consider water conservation programs.

This fact sheet considers the role of water conservation as an integral part of long-term resource planning. It might be more appropriate to use the term “water demand management.” Traditional water supply management seeks to provide all the water the public wants, which, in some sections of the country, translates to a constant search for untapped sources.

WHAT METHODS CONSERVE WATER?

The water demand management methods described in this fact sheet incorporate the methods the August 1998 U.S. Environmental Protection Agency (EPA) *Water Conservation Plan Guidelines* recommend for water systems serving 10,000 or fewer people. EPA’s Basic guidelines suggest (1) metering, (2) water accounting and loss control, (3) pricing and costing, and (4) education or information.

EPA’s Guidelines are not regulations, but recommendations that suggest 11 different conservation methods. How appropriate and desirable any given method is must, in the end, be accepted by the individual community and utility. Pricing may be the primary way to encourage conservation, however, utilities should not automatically rely on any single method.

METER ALL WATER

Metering is a most important part of water demand management. In fact, unless a utility is 100 percent metered, it is difficult to enforce any conservation program. According to a U.S. Housing and Urban Development document, metered customers use an average of 13–45 percent less water than unmetered customers because they know they must pay for any misuse or negligence. A U.S. General Accounting Office report states that metering also assists in managing the overall water system, since it can help to:

- locate leaks in a utility’s distribution system by identifying unaccounted-for blocks of water,
- identify high use customers, who can be given literature on opportunities for conserving, and
- identify areas where use is increasing, which is helpful in planning additions to the distribution system.

Once water meters are installed, equipment begins to deteriorate. Eventually meters will fail to measure flows accurately. The question of how long to leave a meter in service has long troubled the waterworks industry. According to a *Journal of the American Water Works Association* (AWWA) article by Tao and a Community Consultants report, average losses of accuracy, for periods greater than 10 years, range from 0.03–0.9 percent per year. To be fair to both customers and the utility, meters must be maintained at regular intervals.

ACCOUNT FOR WATER, REPAIR LEAKS

The EPA Guidelines recommend that all water systems—even smaller systems—implement a basic system of water accounting. The cost of water leakage can be measured in terms of the operating costs associated with water supply, treatment, and delivery. Water lost produces no revenues for the utility. Repairing larger leaks can be costly, but it also can produce substantial savings in water and expenditures over the long run.

Water accounting is less accurate and useful when a system lacks source and connection metering. Although the system should plan to meter sources, unmetered source water can be estimated by multiplying the pumping rate by the time of operation based on electric meter readings.

A utility may want to consider charging for water previously given away for public use or stepping up efforts to reduce illegal connections and other forms of theft.

Drinking water systems worldwide have begun to implement programs to address the problem of water loss. Utilities can no longer tolerate inefficiencies in water distribution systems and the resulting loss of revenue associated with underground leakage, water theft, and under registration. As pumping, treatment, and operational costs increase, these losses become more and more expensive.

If a utility does what it can to conserve water, customers will tend to be more cooperative in other water conservation programs, many of which require individual efforts. In *Economics of Leak Detection*, Moyer states that of the many options available for conserving water, leak detection is a logical first step. A highly visible leak detection program that identifies and locates water system leakage encourages people to think about water conservation before they are asked to take action to reduce their own water use. When leaks are repaired, water savings result in reduced power costs to deliver water, reduced chemicals to treat water, and reduced costs of wholesale supplies.

According to Le Moigne's technical paper *Using Water Efficiently: Technologies Options*, old and poorly constructed pipelines, inadequate corrosion protection, poorly maintained valves and mechanical damage are major factors contributing to leaks. In addition to loss of water, water leaks reduce pressure in the supply system. Raising pressure to compensate for such losses increases energy consumption and can make leaking worse, as well as causing adverse environmental impacts.

A World Bank technical paper by Okun and Ernst shows that, in general, it is normal to be unable to account for 10–20 percent of water. However a loss of more than 20 percent should raise a red flag. It should be noted that percentages are great for guidelines, but volume of water lost is probably more meaningful. According to AWWA's *Leak Detection and Water Loss Reduction*, once a utility knows the volume of water lost, it can determine revenue losses and decide the best way to correct the problem.

EPA's Guidelines recommend that each system institute a comprehensive leak detection and repair strategy. This strategy may include regular onsite testing using computer-assisted leak detection equipment, a sonic leak-detection survey, or another acceptable method for detecting leaks along water distribution mains, valves, services, and meters. Divers can inspect and clean storage tank interiors.

Increasingly, water systems are using remote sensor and telemetry technologies for ongoing monitoring and analysis of source, transmission, and distribution facilities. Remote sensors and monitoring software can alert operators to leaks, fluctuations in pressure, problems with equipment integrity, and other concerns.

Each system should institute a loss-prevention program, which may include pipe inspection, cleaning, lining, and other maintenance efforts to improve the distribution system and prevent leaks and ruptures. Whenever possible, utilities might also consider methods for minimizing water used in routine water system maintenance procedures.

COSTING AND PRICING

In a Journal of the *American Water Works Association* article "Long-Term Options for Municipal Water Conservation," Grisham and Fleming stress that water rates should reflect the real cost of water. Most water rates are based only on a portion of what it costs to obtain, develop, transport, treat, and deliver water to the consumer. Experts recommend that rates include not only current costs but those necessary for future water supply development. Only when rates include all costs can water users understand the real cost of water service and consequently, the need to conserve.

When utilities raise water rates, among other factors, they need to consider what members of the community can afford. According to Schiffler, the ability to pay for water depends on a number of variables, including its intended use. In households, the assumption is that if the share of water costs does not exceed 5 percent of total household revenue it can be considered as socially acceptable. This rule of thumb has no specific foundation, but is widely used.

Many utility managers argue, correctly, that an effective water conservation program will necessitate rate increases. In *Water Conservation*, Maddaus states that a reduction in water use by customers in response to a water conservation program can decrease a water utility's revenues, and the utility may need to re-examine the water rate structure needs and possibly raise rates to compensate for this effect.

Water charges have typically been looked at as a way of financing the operation and maintenance (O&M) costs of a water agency, rather than as a demand management measure to encourage water-use efficiency. As a World Bank document states, political objections and constraints to increasing water charges are often seen as insurmountable. However, low water charges encourage consumption and waste and can put pressure on O&M budgets, leading to poor water treatment and deterioration in water quality.

In *Water Strategies for the Next Century*, Rogers et al. advocate a positive price for water that is less than the cost of desalination, but not zero. Desalination presently costs about $2 a cubic meter. The ideal is to charge a reasonable amount that sends the message to the users.

EPA suggests that systems consider whether their current rate structures promote water usage over conservation. Nonpromotional rates should be implemented whenever possible.

Systems that want to encourage conservation through their rates should consider various issues, such as the allocation between fixed and variable charges, usage blocks and breakpoints, minimum bills and whether water is provided in the minimum bill, seasonal pricing options, and pricing by customer class.

Numerous sources recommend tying sewer prices to water prices. Billing for wastewater is not included in this analysis; however, it is expected to become a more significant motivation for reducing water use over the next 15 years.

INFORMATION AND EDUCATION

According to Maddaus, water conservation initiatives are more likely to succeed if they are socially acceptable. Measuring social acceptability, an exercise in anticipating public response to a potential water conservation measure, may be measured with a two-part survey technique. First, conduct interviews with community leaders to assess the political and social atmosphere. Second, assess the response to selected specific measures via a questionnaire mailed to a random sample of water customers.

The public tends to accept lawn watering restrictions, education, home water-saver kits, low-flush toilet rebates, and a low-flow fixtures ordinance for new construction. Overall acceptance of conservation is strongly related to attitudes about the importance of water conservation, as well as to age, income, and type of residence.

Howe and Dixon note that, “Public participation is now widely understood to be a necessary input for both efficiency and equity.” Public participation should be part of any long-term public education program, as well as an element of plan development. A plan responsive to public needs usually receives continuing support.

The EPA Guidelines state that water systems should be prepared to provide information pamphlets to customers on request. Consumers are often willing to participate in sound water management practices if provided with accurate information. An information and education program should explain to water users all of the costs involved in supplying drinking water and demonstrate how water conservation practices will provide water users with long term savings.

An informative water bill goes beyond the basic information used to calculate the bill based on usage and rates. Comparisons to previous bills and tips on water conservation can help consumers make informed choices about water use. Systems can include inserts in their customers’ water bills that provide information on water use and costs or tips for home water conservation.

School programs can be a great way to get information out. Systems can provide information on water conservation and encourage the use of water conservation practices through a variety of school programs. Contacts through schools can help socialize young people about the value of water and conservation techniques, as well as help systems communicate with parents.

Workshops and seminars can be used to solicit input, and water equipment manufacturers can be invited to these sessions to exhibit their equipment. Maddaus suggests that a number of groups may have a role in water conservation planning:

- Elected officials from all jurisdictions immediately affected by the process;
- Staff persons from private water companies, key personnel from local government agencies, and state agency people;
- Representatives of major local economic interest groups—major industries, chambers of commerce, builders’ associations, farm bureaus, boards of realtors, and landscape contractors;
- Representatives of major community forces, such as federated civic associations, neighborhood associations, school boards, local unions, churches, and local press and media owners;
- Representatives of local government interest groups;
- Local professionals, such as economists and engineers; and
- Representatives of major water users, for example, food processing plants and homeowners’ associations.

WHERE CAN I FIND INFORMATION?

Information in this fact sheet was obtained from the following sources:

American Water Works Association. 1986. *Leak Detection and Water Loss Reduction*. Distribution System Symposium Proceedings, Minneapolis, MN.

American Water Works Association Leak Detection and Water Accountability Committee, 1996. “Committee Report: Water Accountability.” *Journal of American Water Works Association*.

American Water Works Association. 1992. “Alternative Rates.” *Manual of Water Supply Practices*, Manual No. 34. Denver, CO.

Baumann D., J. Boland, and M. Hanemann. 1998. *Urban Water Demand Management and Planning*: McGraw Hill.

Community Consultants. 1986. “Testing of Residential Meters.” *Consultants Report for the City of Tempe*, Arizona.

Grisham, A., and M. Fleming. 1989. “Long-Term Options for Municipal Water Conservation.” *Journal of American Water Works Association*.

Howe, C. and J. Dixon. 1993. “Inefficiencies in Water Project Design and Operation in the Third World: An Economic Perspective.” *Water Resources Research* 29: 1889–1894.

Le Moigne, G., U. Kuffner, M. Xie, et. al. 1993. *“Using Water Efficiently: Technological Options.”* Technical Paper 205, World Bank.

Maddaus, W. 1987. Water Conservation. Denver: American Water Works Association.

Moyer, E. E. 1985. *Economics of Leak Detection: A Case Study Approach*. Denver: American Water Works Association.

Okun, D. A., W. Ernst. 1987. *Community Piped Water Supply Systems in Developing Countries: A Planning Manual*. World Bank Technical Paper 60.

Rogers, P., K. Frederick, G. Le Moigne, D. Seckler, and J. Keller. 1994. *Water Strategies for the Next Century: Supply Augmentation vs. Demand Management*. A debate sponsored by the U.S.

Agency for International Development and ISPAN. Washington, DC.: U.S. Department of State.

Schiffler, M. 1995. "Sustainable Development of Water Resources in Jordan: Ecological and Economic Aspects in a Long-Term Perspective." in J. A. Allan and C. Mallat, eds. *Water in the Middle East: Legal, Political and Commercial Implications*. New York: I.B. Tauris Publishers.

Tao, P., 1982. "Statistical Sampling Technique for Controlling the Accuracy of Small Water Meters." *Journal of American Water Works Association*.

U.S. Department of Housing and Urban Development. 1984. *Residential Water Conservation Projects-Summary Report*. Report No. HUD-PDR-903, Prepared by Brown and Caldwell Consulting Engineers for the Office of Policy Development and Research, Washington, DC.

U.S. Environmental Protection Agency. 1998. *Water Conservation Plan Guidelines*. EPA-832-D-001. Office of Water. Washington, DC.

U.S. General Accounting Office. 1978. *Municipal and Industrial Water Conservation—The Federal Government Could Do More*. Report CED-78-66; B-114885. Report to the Congress of the U.S. by the Comptroller General, Washington, DC.

Vickers, A. 1990. "Water Use Efficiency Standards for Plumbing Fixtures: Benefits of National Legislation." Journal of American Water Works Association 82: 53.

World Bank. 1994. A Strategy for Managing Water in the Middle East and North Africa. Washington, DC.

For further information or comments about this fact sheet, call the National Drinking Water Clearinghouse (NDWC) at (800) 624-8301 or (304) 293-4191. Additional copies of the Water Conservation Measures fact sheets are free; however, postal charges are added to orders. To order, call one of the above numbers. You may also order online at ndwc_orders@estd.wvu.edu, *or download it from our Web site at* http://www.ndwc.wvu.edu *where the fact sheet is available in the Products section.*

PREVENTING WELL CONTAMINATION

Vipin Bhardwaj
NDWC Engineering Scientist

Nearly 80% of communities rely on groundwater as their primary drinking water source. Wells extract groundwater for use in homes and businesses. In addition, about 42 million Americans use private wells for drinking water. In light of this information, preventing groundwater contamination is of utmost importance, especially since a number of factors can contribute to groundwater contamination. To prevent well contamination, one of the first steps is to construct it properly. This Tech Brief presents tips about how to site a well and includes information about design issues; material selection and location, such as screens and filter pack; appropriate well sealing methods; and the use of pitless adaptors to prevent contamination

INTRODUCTION

To prevent well contamination, one of the first steps is to construct it properly. This tech brief presents tips on siting a well, its design, choosing proper materials, proper location of screens, filter pack and appropriate method of sealing a well and use of pitless adaptors to prevent contamination.

SITE SELECTION

To prevent groundwater contamination, the first step is to locate the well so that surface water and contaminants cannot flow into it. Site engineers try to install the well uphill from any potential contamination source. This means avoiding potential pollution sources, such as industrial plants, home septic systems, landfills, and underground storage tanks. Hiring a qualified hydrogeologist to investigate potential contaminant sources and likely subsurface conditions makes locating a well easier.

For most private wells, the primary contaminant source is the owner's septic system. The best protection practice is to locate the well above the area where contaminants can enter it, usually about 50 to 100 feet away. In addition, install a surface seal into a fine-grained layer or non-fractured zone above the aquifer.

To prevent water from collecting near the casing, the ground surrounding the well should slope away from the wellhead on all sides. In addition, most states regulate how far a well must be located from potential contamination sources. For instance, most states require that wells be a minimum of 50 feet away from a septic system.

WELL DESIGN

Proper selection of well casings, seals, screens, filter packs, and pump chamber casings are important factors that determine the efficiency of the well and prevent contamination. Figure 1 shows the components of a well that prevent pollutants from entering the well. Most states have well construction standards and permitting processes that must be followed. The American Water Works Association has a standard A100-90 that deals with construction design.

CASING

A casing is a pipe that is usually made of steel or plastic. It lines the borehole dug in the earth and keeps the well from caving in and prevents runoff and other material from getting into the well.

When contactors select casing, they must take into account the forces that are exerted while installing. In addition, the surrounding materials, such as soil and rocks, tend to collapse into the hole. If possible, the driller should

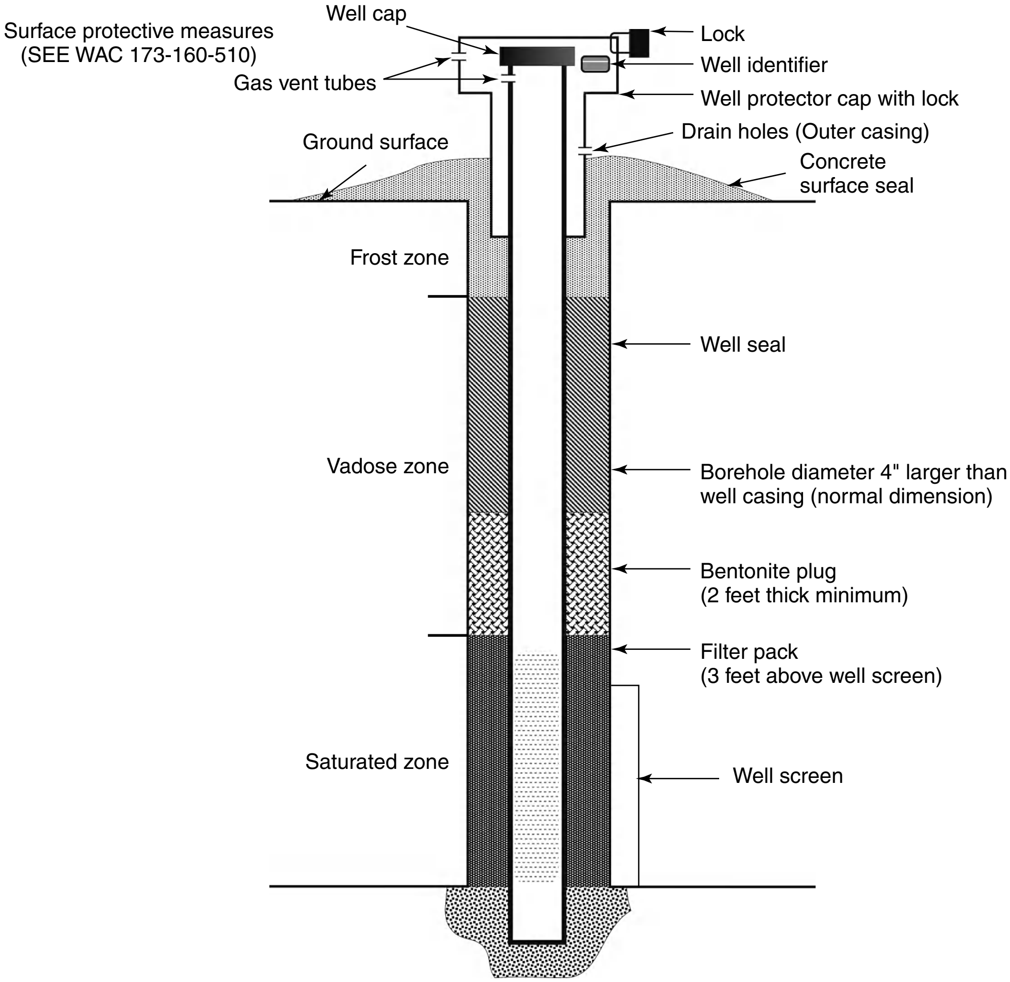

Figure 1. General resource protection well—cross section

Definitions

Well Seal: A seal is a cylindrical layer of material, usually cement, bentonite, or clay, that surrounds the casing up to a certain depth in the well. It prevents runoff or other contaminants from entering the well, and serves to further protect the casing.

Well Screen: Well screen is a cylindrical sieve-like structure that serves as the intake portion of the well. It is a metallic pipe that has holes or perforated sections or slotted sections that is placed on the water- carrying zones of the aquifer.

Filter Pack: A filter pack is made up of sand or gravel that is smooth, uniform, clean, well-rounded, and siliceous. It is placed in the annulus of the well between the bore-hole wall and the well screen to prevent formation material from entering the screen.

Vadose Zone: This is the zone that contains water under pressure less than that of the atmospheric pressure. It is the layer of soil between the water table and the ground surface.

Potentiometric Surface: This is an imaginary surface representing the total head of groundwater in a confined aquifer that is defined by a level to which water will rise in the well.

use a temporary casing for the borehole. The temporary casing diameter must be at least four inches larger than the permanent casing to provide sufficient space for a good well seal.

The American Society for Testing and Materials, the American Petroleum Institute, and the American Iron and Steel Institute have specifications for casings. Most state standards require steel casing of a specified wall thickness for wells, whether for a community or private individual.

The diameter of the casing must leave enough room to install the submersible pump and still have space for maintenance. The size of the pump depends upon the desired well yield.

Casing depth also helps prevent well contamination. Logs of any other nearby wells and the local geology can help determine how deep the casing should go. The casing should extend at least 12 inches above the ground for sanitary protection. Reducing the casing's diameter requires a minimum of eight feet of casing overlap. A watertight well cap should be placed on top of the casing. The Water Systems Council (WSC) has standards for well caps and other well components.

WELL SCREEN

A well screen is a cylindrical sieve-like structure that serves as the intake portion of the well. It is a metallic pipe that has holes or perforated sections or slotted sections that is placed on the water carrying zones of the aquifer. Proper selection, design, placement, and development of the screened section are very important and determine the well's efficiency and yield.

Since certain sections of the ground are more porous than others and, hence, carry more water, placing the screens in these sections will yield higher flow rates. By looking at the data collected during drilling, a good well driller can locate and place the screen in the proper zones.

To better understand conditions at the site, use borehole geophysical logs to grasp the subsurface conditions. In addition, visual inspection of the cuttings or samples can show if the layers of earth are sandy, coarse, or clayey. And to help determine well yield, use sieve analysis and hydraulic conductivity tests.

FILTER PACK

A filter pack is typically made up of sand or gravel that is smooth, uniform, clean, well rounded. It is placed in the area between the borehole wall and the well screen to prevent formation material from entering the screen.

To enhance the permeability of the zone surrounding the screen, place a filter pack around it. A good filter pack keeps sediment out and decreases friction losses around the screen and is especially important if the aquifer consists of uniform fine sand. A filter pack allows for larger openings in the screen and improves well yield. To install a filter pack, start from the bottom of the screen, filling in to at least three feet above the top of the screen. Domestic wells do not require a filter pack.

WELL SEALS

The most important components that prevent contaminants from entering the well are well seals. A seal is a cylindrical layer of material, usually cement, bentonite, or clay, that surrounds the casing up to a certain well depth. It prevents runoff or other contaminants from entering the well and serves to further protect the casing. The drilled hole must be four inches larger in diameter than the outer diameter of the casing so that the seal can be placed in the space between casing and the hole.

Well construction standards specify the material that well installers must use to seal the well, as well as the depth to which the well is grouted. Typically, public water supply wells are grouted to a depth of 50 feet. A cement slurry is pumped in the ring-shaped space between casing and hole and the well is sealed from the bottom up. Grout is placed using a small diameter pipe called a tremie. A layer of bentonite two feet thick should be placed on top of the filter pack.

PITLESS ADAPTORS

Pitless adapters and pitless units are devices that attach to the well casing below the frost line and provide sanitary connections. They prevent entry of contaminants into the well near the surface. These devices provide access to the well for servicing. The adapter connects the casing with a horizontal line that supplies water through a removable seal joint. This connection allows the drop pipe and pumping equipment in the well to be easily removed for repair or maintenance work without digging the ground around the well.

WSC has performance standards for pitless adapters, pitless units, and watertight well caps. A list of manufacturers that meet those standards can be obtained from the WSC.

DISINFECTION PROCEDURES

Well installers must disinfect all equipment and tools using a chlorine solution before any drilling operation to prevent bacterial contamination. The well must be disinfected after it's completed. Some types of bacteria, such as *E. coli*, are found in soils and can contaminate the well. By dissolving calcium hypochlorite or sodium hypochlorite, installers can make a chlorinated water solution. The strength of the solution can range from 50–200 milligrams per liter of available chlorine.

WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1999. *Design and Construction of Water Systems, An AWWA Small System Resource Book, Second Edition*. Denver, Colorado: AWWA.

Driscoll, FG. 1995. *Groundwater and Wells*. St. Paul, MN: U.S. Filter/Johnson Screens.

U.S. Environmental Protection Agency. 1991. *Manual of Individual and Non-Public Water Supply Systems*. Washington, DC: EPA. (Available from the National Drinking Water Clearinghouse, order product #DWBKDM06).

U.S. Environmental Protection Agency. 1975. *Manual of Water Well Construction Practices*. Washington, DC: EPA. (Available from the National Drinking Water Clearinghouse, order product #DWBKDM01).

National Ground Water Association, Westerville, OH: NGWA. (www.ngwa.org)

Water Systems Council, National Programs Office, Washington, DC: WSC. (www.wellcarehotline.org)

Acknowledgments

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Tech Brief: **Water Quality in Distribution Systems**, item #DWFSOM25
Tech Brief: **Water Treatment Plant Residuals Management**, item #DWBLPE65

CORROSION CONTROL

National Drinking Water
Clearinghouse

Corrosion occurs because metals tend to oxidize when they come in contact with water, resulting in the formation of stable solids. Corrosion in water distribution systems can impact consumers' health, water treatment costs, and the aesthetics of finished water.

Various methods can be used to diagnose, evaluate, and control corrosion problems. Techniques for controlling it include distribution and plumbing system design considerations, water quality modifications, corrosion inhibitors, cathodic protection, and coatings and linings.

CORROSION CAN CAUSE SYSTEM PROBLEMS

What Problems Does Corrosion Cause?

Corrosion can cause higher costs for a water system due to problems with:

- decreased pumping capacity, caused by narrowed pipe diameters resulting from corrosion deposits;
- decreased water production, caused by corrosion holes in the system, which reduce water pressure and increase the amount of finished water required to deliver a gallon of water to the point of consumption;
- water damage to the system, caused by corrosion-related leaks;
- high replacement frequency of water heaters, radiators, valves, pipes, and meters because of corrosion damage; and
- customer complaints of water color, staining, and taste problems.

How is Corrosion Diagnosed and Evaluated?

The following events and measurements can indicate potential corrosion problems in a water system:

Consumer Complaints: Many times a consumer complaint about the taste or odor of water is the first indication of a corrosion problem. Investigators need to examine the construction materials used in the water distribution system and in the plumbing of the complainants' areas (See Table 1).

Corrosion Indices: Corrosion caused by a lack of calcium carbonate deposition in the system can be estimated using

Table 1. Typical Water Quality Complaints That Might Be Due to Corrosion

Customer Complaint	Possible Cause
Red water or reddish-brown staining of fixtures and laundry	Corrosion of iron pipes or presence of natural iron in raw water
Bluish stains on fixtures	Corrosion of copper lines
Black water	Sulfide corrosion of copper or iron lines or precipitations of natural manganese
Foul taste and/or odors	Byproducts from microbial activity
Loss of pressure	Excessive scaling, tubercle (buildup from pitting corrosion), leak in system from pitting or other type of corrosion
Lack of hot water	Buildup of mineral deposits in hot water system (can be reduced by setting thermostats to under 60 degrees C [140 degrees F])
Short service life of household plumbing	Rapid deterioration of pipes from pitting or other types of corrosion

Source: U.S. Environmental Protection Agency indices derived from common water quality measures. The Langelier Saturation Index (LSI) is the most commonly used measure and is equal to the water pH minus the saturation pH (LSI = pH water − pH saturation). The saturation pH refers to the pH at the water's calcium carbonate saturation point (i.e., the point where calcium carbonate is neither deposited nor dissolved). The saturation pH is dependent upon several factors, such as the water's calcium ion concentration, alkalinity, temperature, pH, and presence of other dissolved solids, such as chlorides and sulfates. A negative LSI value indicates potential corrosion problems.

Sampling and Chemical Analysis: The potential for corrosion can also be assessed by conducting a chemical sampling program. Water with a low pH (less than 6.0) tends to be more corrosive. Higher water temperature and total dissolved solids also can indicate corrosivity.

Pipe Examination: The presence of protective pipe scale (coating) and the condition of pipes' inner surfaces can be assessed by simple observation. Chemical examinations can determine the composition of pipe scale, such as the proportion of calcium carbonate, which shields pipes from dissolved oxygen and thus reduces corrosion.

Can System Design Affect the Potential for Corrosion?

In many cases, corrosion can be reduced by properly selecting distribution and plumbing system materials and by having a good engineering design. For example, water distribution systems designed to operate with lower flow rates will have reduced turbulence and, therefore, decreased erosion of protective layers. In addition, some piping materials are more resistant to corrosion in a specific environment than others. Finally, compatible piping materials should be used throughout the system to avoid electrolytic corrosion.

Other measures that help minimize system corrosion include:

- using only lead-free pipes, fittings, and components;
- selecting an appropriate system shape and geometry to avoid dead ends and stagnant areas;
- avoiding sharp turns and elbows in the distribution and plumbing systems;
- providing adequate drainage (flushing) of the system;
- selecting the appropriate metal thickness of piping, based on system flow and design parameters;
- avoiding the use of site welding without replacing the pipe lining;
- reducing mechanical stresses, such as flexing of pipes and "water hammer" (hydraulic pressure surges);
- avoiding uneven heat distribution in the system by providing adequate coating and insulation of pipes;
- providing easy access for inspection, maintenance, and replacement of system parts; and
- eliminating the grounding of electrical circuits to the system, which increases the potential for corrosion.

How Can System Corrosion be Reduced?

Corrosion in a system can be reduced by changing the water's characteristics, such as adjusting pH and alkalinity; softening the water with lime; and changing the level of dissolved oxygen (although this is not a common method of control). Any corrosion adjustment program should include monitoring. This allows for dosage modification, as water characteristics change over time.

pH Adjustment: Operators can promote the formation of a protective calcium carbonate coating (scale) on the metal surface of plumbing by adjusting pH, alkalinity, and calcium levels. Calcium carbonate scaling occurs when water is oversaturated with calcium carbonate. (Below the saturation point, calcium carbonate will redissolve: at the saturation point, calcium carbonate is neither precipitated nor dissolved. See the section on "corrosion indices,".) The saturation point of any particular water source depends on the concentration of calcium ions, alkalinity, temperature, and pH, and the presence of other dissolved materials, such as phosphates, sulfates, and some trace metals.

It is important to note that pH levels well suited for corrosion control may not be optimal for other water treatment processes, such as coagulation and disinfection. To avoid this conflict, the pH level should be adjusted for corrosion control immediately prior to water distribution, and after the other water treatment requirements have been satisfied.

Lime Softening: Lime softening (which, when soda ash is required in addition to lime, is sometimes known as lime-soda softening) affects lead's solubility by changing the water's pH and carbonate levels. Hydroxide ions are then present, and they decrease metal solubility by promoting the formation of solid basic carbonates that "passivate," or protect, the surface of the pipe.

Using lime softening to adjust pH and alkalinity is an effective method for controlling lead corrosion. However, optimum water quality for corrosion control may not coincide with optimum reduction of water hardness. Therefore, to achieve sound, comprehensive water treatment, an operator must balance water hardness, carbonate levels, pH and alkalinity, as well as the potential for corrosion.

Dissolved Oxygen Levels: The presence of excessive dissolved oxygen increases water's corrosive activity. The optimal level of dissolved oxygen for corrosion control is 0.5 to 2.0 parts per million. However, removing oxygen from water is not practical because of the expense. Therefore, the most reasonable strategy to minimize the presence of oxygen is to:

- exclude the aeration process in the treatment of groundwater,
- increase lime softening,
- extend the detention periods for treated water in reservoirs, and
- use the correct size water pumps in the treatment plant to minimize the introduction of air during pumping.

What About the Use of Corrosion Inhibitors?

Corrosion inhibitors cause protective coatings to form on pipes. Although they reduce corrosion, they may not totally arrest it. Therefore, the success of any corrosion inhibitor hinges upon the water operator's ability to:

- apply double and triple the design doses of inhibitor during initial applications to build a protective base coat that will prevent pitting; (Note that initial coatings typically take several weeks to form.)
- maintain continuous and sufficiently high inhibitor doses to prevent redissolving of the protective layer; and
- attain a steady water flow over the system's metal surfaces to allow a continuous application of the inhibitor.

There are several commercially available corrosion inhibitors that can be applied with normal chemical feed systems. Among the most commonly used for potable water supplies are inorganic phosphates, sodium silicates, and mixtures of phosphates and silicates.

Inorganic Phosphates: Inorganic phosphate corrosion inhibitors include polyphosphates, orthophosphates, glassy phosphates, and bimetallic phosphates. Zinc, added in conjunction with polyphosphates, orthophosphates, or glassy phosphates, may help to inhibit corrosion in some cases.

Silicates: The effectiveness of sodium silicates depends on both pH and carbonate concentrations. Sodium silicates are particularly effective for systems with high water velocities, low hardness, low alkalinity, and pH of less than 8.4. Typical coating maintenance doses of sodium silicate range from 2 to 12 milligrams per liter. They offer advantages in hot-water systems because of their chemical stability, unlike many phosphates.

Before installing any technology for delivering corrosion inhibitors, several methods or agents first should be tested in a laboratory environment to determine the best inhibitor and concentration for each water system.

Is Cathodic Protection an Option?

Cathodic protection is an electrical method for preventing corrosion of metallic structures. However, this expensive corrosion control method is not practical or effective for protecting entire water systems. It is used primarily to protect water storage tanks. A limitation of cathodic protection is that it is almost impossible for cathodic protection to reach down into holes, crevices, or internal corners.

Metallic corrosion occurs when contact between a metal and an electrically conductive solution produces a flow of electrons (or current) from the metal to the solution. The electrons given up by the metal cause the metal to corrode rather than remain in its pure metallic form. Cathodic protection stops this current by overpowering it with a stronger, external power source. The electrons provided by the external power source prevent the metal from losing electrons, forcing it to be a "cathode," which will then resist corrosion, as opposed to an "anode," which will not.

There are two basic methods of applying cathodic protection. One method uses inert electrodes, such as high-silicon cast iron or graphite, which are powered by an external source of direct current. The current impressed on the inert electrodes forces them to act as anodes, thus minimizing the possibility that the metal surface being protected will likewise become an anode and corrode. The second method uses a sacrificial anode. Magnesium or zinc anodes produce a galvanic action with iron, so that the anodes are sacrificed (or suffer corrosion), while the iron structure they are connected to is protected.

Are Commercial Pipe Coatings and Linings Effective?

The nearly universal method of reducing pipe corrosion involves lining the pipe walls with a protective coating. These linings are usually mechanically applied, either when the pipe is manufactured or in the field before it is installed. Some linings can be applied even after the pipe is in service, but this method is much more expensive.

Mechanically applied coatings and linings differ for pipes and water storage tanks. The most common types of pipe linings include coal-tar enamels, epoxy paints, cement mortar, and polyethylene.

Water storage tanks are most commonly lined to protect the inner tank walls from corrosion. The most common types of water storage tank coatings and linings include coal-tar paints and enamels, vinyls, and epoxy.

Where Can I Find More Information?

Information for this fact sheet was obtained from three primary sources: *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, EPA/625/4-89/023; Corrosion Manual for Internal Corrosion of Water Distribution Systems, EPA/570/9-84/001; and Corrosion in Potable Water Supplies*, EPA/570/9-83/013. All of these documents are free and may be ordered from the U.S. Environmental Protection Agency (EPA) Office of Research and Development by calling (513) 569-7562.

If these publications are no longer available from the EPA, call the National Drinking Water Clearinghouse (NDWC) at (800) 624-8301. A photocopied version of the 209-page document Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, item #DWBKDM04, costs $30.05. There is no charge for the other two documents listed above; however, postage charges apply to all orders.

Also, the NDWC's Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS), version 2.0, is a public reference database that contains information about technologies—including those related to corrosion—in use at small water systems around the country. For further information about accessing or ordering RESULTS, call the NDWC at (800) 624-8301 or (304) 293-4191. You may also obtain more information from the NDWC's World Wide Web site at www.ndwc.wvu.edu.

For additional copies of "Tech Brief: Corrosion Control," item #DWBRPE52, or for a copy of the previously published "Tech Brief: Filtration," item #DWBRPE50, or "Tech Brief: Disinfection," item #DWBRPE47, call the NDWC at the number printed above.

CROSS CONNECTION AND BACKFLOW PREVENTION

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When drinking water is transported to a consumer, it is possible for contaminants to be introduced in the distribution system. This situation may occur due to connections between potable water lines and non-potable water sources or by a water flow reversal, resulting in contaminated water. This Tech Brief, discusses cross connections and backflow, and explores ways to prevent these situations.

WHAT IS A CROSS CONNECTION?

A cross connection is a link or structural arrangement where potable water in a distribution system can be exposed to unwanted contaminants. It is the point at which it is possible for a non-potable substance to come in contact with the drinking water system. Cross connections are generally unintentional and can happen anywhere pipes supply water.

WHAT IS A BACKFLOW?

Backflow is the reverse flow of undesirable materials and contaminants into the water mains. Backflow can happen because of two conditions: backpressure and backsiphonage.

Backpressure occurs when pressure in a pipe connected to a main pipe in the distribution system becomes greater than the pressure in the main pipe itself. When this happens, a net force acts on the volume of liquid in the connecting pipe, allowing unwanted material to enter the main pipe.

Backsiphonage refers to a situation where the pressure in a service pipe is less than the atmospheric pressure. If water in a supply line is turned off, such as when a pump fails, backsiphonage can cause contamination to be sucked into the system due to a vacuum in the service line.

If a cross connection exists in a system, it does not mean that there will be a backflow every time. But, where cross connections exist, there is always the possibility.

BACKFLOW CONTROL METHODS AND DEVICES

If possible, cross connections must first be eliminated before installing any backflow prevention devices. The device chosen depends on the degree of hazard involved, accessibility to the location of the device, and whether the backflow is due to backpressure or backsiphonage. Basic types of backflow prevention devices are:

- air gaps,
- reduced pressure principle devices,
- double check valves,
- vacuum breakers, and
- barometric loops

Air Gap

Air gaps are one of the most effective ways to prevent backflow and backsiphonage. An air gap is a vertical separation between a water outlet and the highest level of a potential fluid contamination source. However, because of air gaps, flow of water is interrupted and loss of pressure occurs. Because of this, air gaps are used at the end of a pipe. Air gaps should be twice the size of the supply pipe diameter or at least one inch in length, whichever is greater (see Fig. 1).

Reduced Pressure Principle Backflow Preventer

The reduced pressure zone backflow-preventing (RPBP) device has two spring check valves with a pressure-relief valve located between them that can be vented to the atmosphere.

During normal flow of water through this arrangement, the water flows through the two valves (see Fig. 2). The spring action of the first valve opposes the pressure of water as the water flows from left to right and enters the central chamber. Pressure in the central chamber is maintained lower than that in the incoming line by the operation of the relief valve.

The second check valve to the right is designed to open with a pressure drop of one pound per square inch (psi) in the direction of flow and is independent of the pressure required to open the relief valve. If the pressure downstream from the device increases for some reason (backpressure), the second check valve will close because of the spring action. Reverse flow of water or backflow is thus prevented. In case the pressure in the supply line on the left decreases abruptly or if there is a vacuum in the supply line (backsiphonage), the check valves close because of spring action, and backflow is prevented.

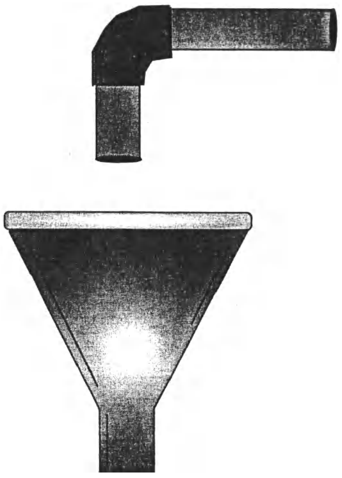

Figure 1. Air gap.

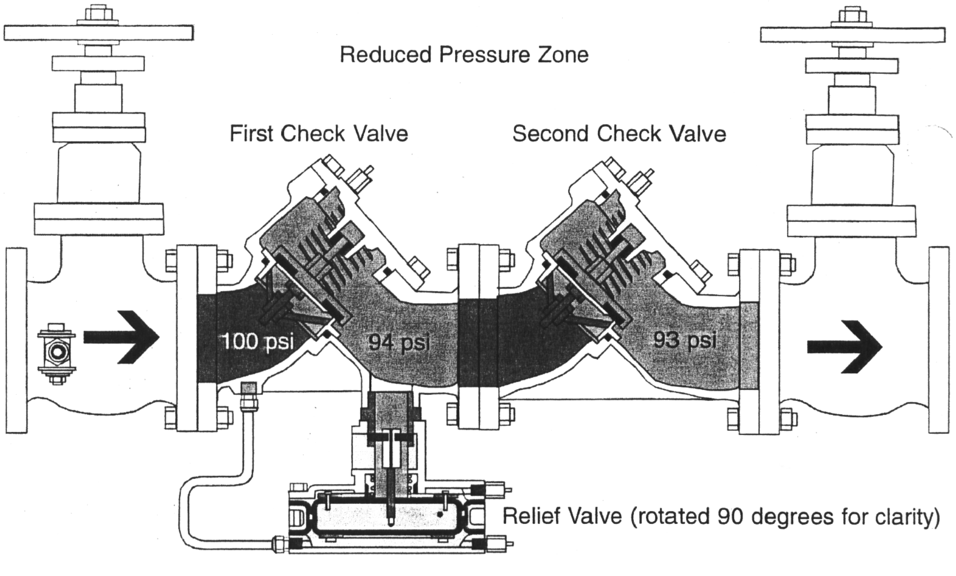

Figure 2. Reduced pressure principle backflow preventer. *Source*: U.S. Environmental Protection Agency. 2003. *Cross-Connection Control Manual*, Washington DC: EPA.

In case the valve leaks and the second check valve on the right does not close fully, water will leak back into the central chamber and increase the pressure in the chamber. The relief valve then opens and discharges water to the atmosphere. Keep in mind, if you see water coming from the relief valve on an RPBP, don't panic. It's actually working as designed. The valve assembly should be checked by a certified tester.

This type of device is usually installed on high hazard locations, such as hospitals, plating plants, and car washes.

Double Check Valve

The double check valve has two single check valves coupled within one body, and has test cocks (to determine if there's any leakage) and two closing gate valves (to isolate each section). It is essentially the same reduced pressure zone backflow-preventing (RPBP) device but without the relief valve (see Fig. 3).

The absence of the relief valve reduces the effectiveness of the device. Double check valves are used in low- to medium-level hazard installations. The check valves are spring-loaded and require one pound of pressure to open.

Vacuum Breakers

Vacuum breakers provide protection against back-siphonage. When the pressure in a service pipe is less than the atmospheric pressure, a vacuum can form in the pipe and cause contamination to be sucked into the system. Vacuum breakers have an element, such as a check valve, that glides on a supporting shaft and seals in the

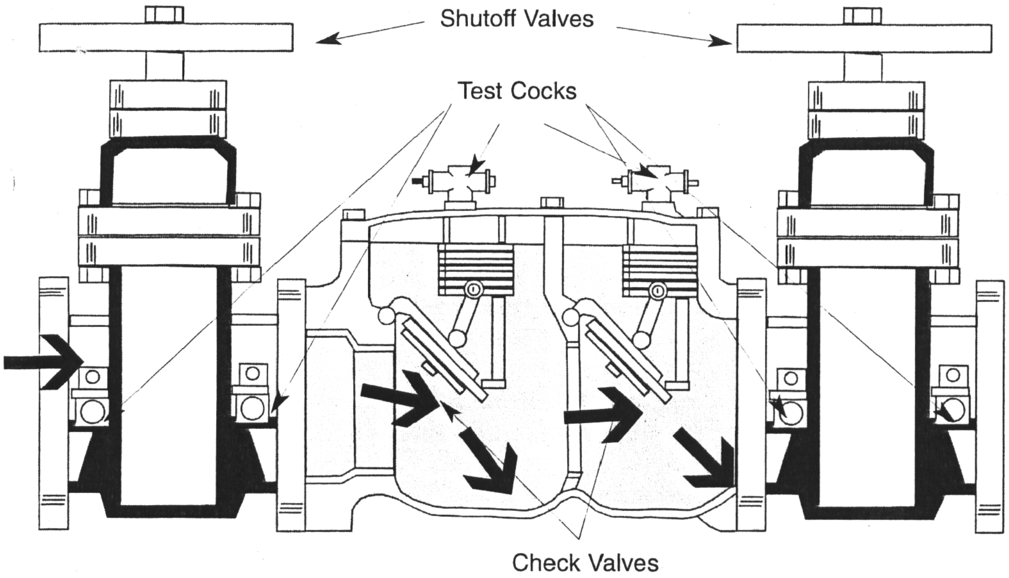

Figure 3. Double check valve. *Source*: AWWA, *Water Transmission and Distribution*, Second Edition.

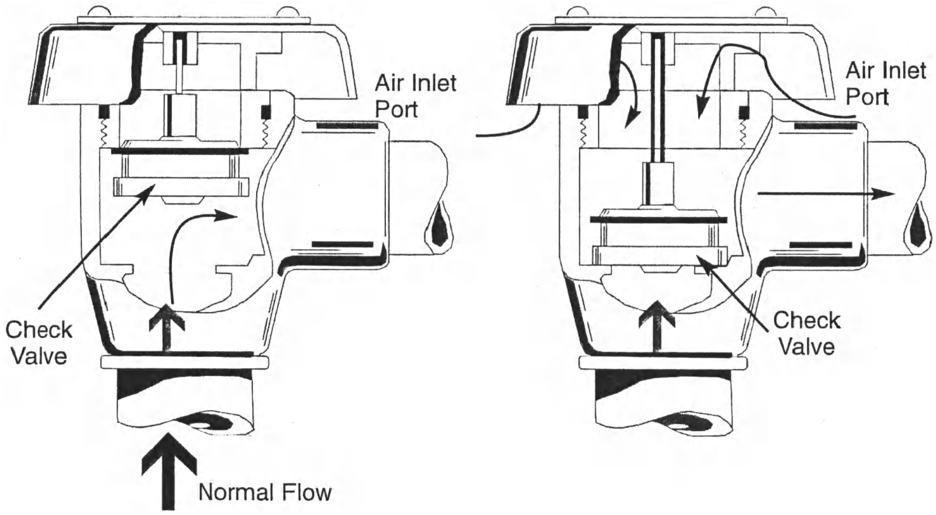

Figure 4. Vacuum breakers. *Source*: AWWA, *Water Transmission and Distribution*, Second Edition.

uppermost position from the push of water pressure (see Fig. 4).

If the flow in the pipe is stopped, the valve drops down, closes the water supply entry, and opens an air vent. This opens up the downstream piping to atmospheric pressure and prevents backsiphonage. Vacuum breakers do not protect against backpressure.

Barometric Loop

A barometric loop is formed by having a section of the pipe in the shape of an inverted "U" upstream of a cross connection (see Fig. 5). Based on a physics principle, the height of a water column open to the atmosphere at the bottom will not be greater than 33.9 feet at sea level pressure.

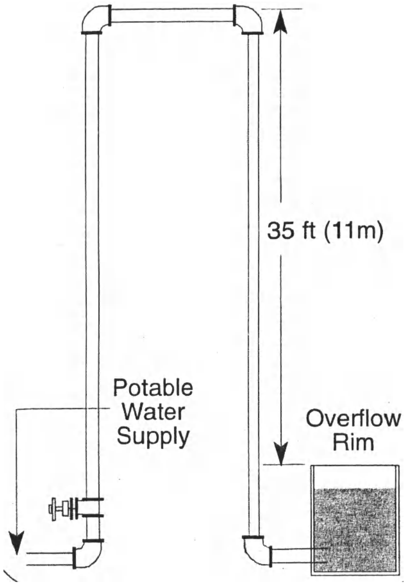

Figure 5. Barometric loop. *Source*: AWWA, *Water Transmission and Distribution*, Second Edition.

If the loop is greater than that height, backsiphonage cannot occur through it. However, the barometric loop is not effective against backpressure.

"YELLOW GUSHY STUFF" FROM FAUCETS

A small town in Maryland provides a dramatic example of what can happen because of a cross connection. One fateful day, yellow gushy stuff poured from some faucets there and the state warned residents from using the water for cooking, drinking, or bathing. The incident drew widespread attention and was a big story in the local media.

An investigation revealed that water pressure in the town mains was reduced temporarily due to a water pump failure in the distribution system. A gate valve between a herbicide chemical holding tank and the town water supply mains had been left open. A lethal cross connection was created that allowed the herbicide to flow into the water supply. When the normal water supply pressure returned, water containing the herbicide was pumped into many faucets.

Door to door public notification, extensive flushing, sampling, and other measures were taken to get the situation under control. Fortunately, no one was seriously injured in this incident.

Source: U.S. Environmental Protection Agency. 2003. *Cross-Connection Control Manual*. Washington DC: EPA.

CROSS CONNECTION CONTROL PROGRAMS

Numerous, well-documented cases about illnesses and other hazards posed by cross connections have been documented. (See the sidebar above.) More information about the health risks cross connections may present and methods to prevent them is needed. Water utility personnel (managers, operators, local officials), plumbers, public health officials, and consumers need to be aware of the risks and understand prevention methods.

As mandated by the Safe Drinking Water Act, water suppliers are responsible for ensuring that the water they supply meets federal primary drinking water regulations and is delivered to consumers without compromising water quality due to its distribution system. Water utilities may want to implement a cross connection program to stave off any problems that could occur. Such a program would include informing consumers, conducting inspections of the distribution system, analyzing and recognizing potential cross connections, and installing backflow prevention devices where needed.

WHAT ABOUT TERRORISM AND WATER SECURITY?

Concern that U.S. water supplies could be vulnerable to terrorist attacks has increased in the post-9/11 era. Because they are a place where lethal substances could be introduced into the water distribution system, cross connections should be identified and corrected.

The Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (Section 1433) requires systems that serve more than 3,300 people to assess their vulnerability to a terrorist attack. (See the article "Security and Emergency Planning: Community-Wide Efforts Require Preparation" in the Winter 2003 *On Tap*.)

The act states that the vulnerability assessment shall include but not be limited to "a review of pipes and constructed conveyances, water collection, pretreatment, storage and distribution facilities, electronic, computer or other automated systems."

WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1996. *Water Transmission and Distribution, Principles and Practices of Water Supply Operations*, 2nd Edn. Denver: AWWA.

U.S. Environmental Protection Agency. 2003. *Cross-Connection Control Manual*. Washington, DC: EPA. (Available as a product from NDWC, item #DWBLDM03)

Montana Water Center. 2002. *Sanitary Survey Fundamentals Preparation Course CD*. Bozeman, MT: Montana Water Center. (Available as a product from NDWC, item #DWCDTR19)

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Tech Brief: **Valves**, item #DWFSOM21
Tech Brief: **Water Quality in Distribution Systems**, item #DWFSOM25
Tech Brief: **Water Treatment Plant Residuals Management**, item #DWBLPE65

MOLECULAR-BASED DETECTION OF *CRYPTOSPORIDIUM PARVUM* IN WATER

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INTRODUCTION

Cryptosporidium is an apicomplexan protozoan parasite that is becoming increasingly recognized as an important infectious pathogen in water. The parasite is transmitted by the fecal–oral route, usually by ingestion of oocyst-contaminated water or food (1–3). A *C. parvum* oocyst is small, averaging 5 μm × 4.5 μm, and its coat is bilayered and highly proteinaceous, allowing it to resist chlorine-based disinfection in water treatment facilities (4). Within the oocyst are four motile sporozoites (Fig. 1), which are the infectious forms of *Cryptosporidium*. After passing through the stomach, the oocyst releases the infectious sporozoites, which attach to epithelial cells of the small intestine. Asexual and sexual reproduction of *Cryptosporidium* within the infected host results in autoinfection and self-perpetuation of the disease. Sexual reproduction also results in the production of infectious oocysts that are excreted along with fecal matter into the environment.

Cryptosporidiosis, the globally occurring disease caused by *Cryptosporidium* infection, can result in gastrointestinal distress with copious amounts of diarrhea, abdominal cramping, and fever. In healthy individuals, infection is an acute but self-limiting illness that generally lasts 1 to 2 weeks. However, in immunocompromised individuals, symptoms are more severe, and the illness may become chronic and can result in death. It has been recognized that two distinct *C. parvum* genotypes, referred to as the human genotype (genotype I or genotype H) and the cattle genotype (genotype II or genotype C), are responsible for human cryptosporidiosis. Morgan-Ryan et al. (5) proposed a new species, *Cryptosporidium hominis*, to denote the human genotype. *Cryptosporidium hominis* infects humans primarily, whereas *C. parvum* infects both humans and numerous other mammalian hosts such as mice, dogs, cattle, sheep, goats, and pigs. There is no cure therapy currently available for *Cryptosporidium* infection, so prevention is the key to containing and managing this disease. Prevention requires accurate monitoring and detection of the parasites in water and food samples.

As intestinal parasites, *C. parvum* cannot be cultured *in vitro*. Therefore, traditional culture methods used in routine microbiology labs are not suitable to detect and enumerate *C. parvum* oocysts. Classical methods to detect *Cryptosporidium* are based on microscopy of clinical samples that can be combined with different stains for improved visualization. However, microscopy requires training and is subject to human error in both sample preparation and viewing. The use of fluorogenic dyes can make detection easier, but microscopy cannot indicate oocyst viability or infectivity. Rather than relying on the results of clinical samples to identify a *Cryptosporidium* outbreak, recent research has focused on analyzing water samples for oocysts. The U.S. EPA has developed a method that is recommended for detecting *Cryptosporidium* in raw and treated waters. This method requires the concentration of a water sample, immunomagnetic separation (IMS) of the oocysts from the concentrated debris, and determination of oocyst concentrations by immunofluorescence assay (IFA). Potential oocysts are further stained with vital dyes such as DAPI and propidium iodide, followed by differential interference contrast microscopy.

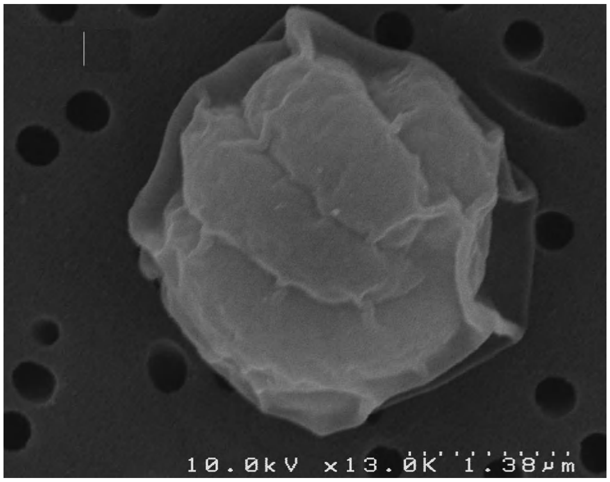

Figure 1. A scanning electron micrograph of a *C. parvum* oocyst. The four crescent-shaped sporozoites are visible within the oocyst. The deflated appearance of the oocyst is the result of dehydration required for sample preparation.

The number of oocysts within water sources is generally low and variable, so large volumes of water need to be concentrated for quantitative analysis. This can be accomplished by filtration, flocculation, or centrifugation. Oocysts are then purified from background detrital material by flotation, immunomagnetic separation, or flow cytometry. The concentrated water samples can be screened by molecular techniques to determine the presence of oocysts. A desired detection method should differentiate between dead or nonviable oocysts, which pose no threat to public health, and those oocysts that are viable and infective. Because only a few oocysts are needed to cause disease, efficient detection methods should be sensitive and amenable to quantification. Additionally, the detection method should differentiate between the *Cryptosporidium* species because not all species are harmful to humans. Molecular detection techniques have the advantage of being more specific, sensitive, reproducible, and often more rapid.

DETECTION OF *CRYPTOSPORIDIUM* INFECTIVITY

Although human infectivity assays are true representations of the disease, they are not practical for routine evaluations of oocyst infectivity. The most direct method for assessing oocyst viability and infectivity is to administer the oocysts experimentally to an animal (typically a neonatal mouse). Following a period of incubation, the intestine is sectioned longitudinally and the cells are examined for histological evidence of infection. Commonly used animal surrogates are neonatal or immunosuppressed rodents, typically CD-1 or BALB/c strains. In addition to ethical concerns, animal infectivity experiments are time-consuming, expensive, and not amenable to routine environmental testing.

Alternatively, *in vitro* infectivity involves exposing oocysts to excystation stimuli followed by inoculating them into a cultured adherent mammalian intestinal cell line, which supports infection and asexual development. Following a suitable infection period, samples are examined by fluorogenically labeled antibodies or nucleic acid sequences specific to *Cryptosporidium*. Based on the presence or absence of infection, the number of infective oocysts can be statistically determined according to a standardized most-probable number (MPN) table or MPN calculator (6).

The success of an *in vitro* cell culture assay depends on the type of cell line, the use of oocysts or sporozoites, preincubation excystation treatment, and centrifugation of the sample. Although cell culture requires intensive labor to grow and maintain the cell monolayer and a prolonged incubation period, the technique remains a good substitute for animal infectivity models. A number of cell lines can support the asexual development of *C. parvum*, but human ileocecal adenocarcinoma (HCT-8) cells that have been found superior in their ability to support parasite growth and represent a practical and accurate alternative to animal infectivity models, yield results similar to those with CD-1 mice in assessing *C. parvum* infectivity (7).

ANTIBODY TECHNOLOGY

Antibodies are produced by immune systems that bind to foreign antigens within the host organism. Strong target affinity, specificity, and sensitivity of antibodies make them ideal for targeting and identifying *Cryptosporidium*. Various types of antibodies can be used for molecular diagnostic methods: monoclonal antibodies (mAbs), polyclonal antibodies (pAbs), and recombinant antibodies (rAbs).

Monoclonal antibodies are identical because they were produced by one type of immune cell, all clones of a single parent cell. In contrast, pAbs are produced by different immune cells and differ from one another. Recombinant antibodies are constructed within a laboratory and are based on the artificial random recombination of antibody genes. This may yield antibodies that may not occur naturally.

Conjugation of antibodies to fluorophores or enzymes allow for the production of a visual signal. Many immunologic methods are available for detecting *C. parvum*, including flow cytometry, immunofluorescence assays (IFA), and enzyme-linked immunosorbent assays (ELISA).

Immunofluorescence Assay (IFA)

Routine detection of *Cryptosporidium* in environmental samples is most commonly performed using the IFA. In detecting the parasite, the characteristics used for identification include size, shape, and fluorescence. The cells become fluorescent via antibody staining, which is carried out either in suspension, on a microscope slide, or on a membrane prior to microscopic examination. Both fluorophore-conjugated pAbs and mAbs are used to identify purified oocysts. Nonspecific fluorescence is a problem with IFAs, along with background fluorescence of detritus, algae, and some freshwater diatoms and cyanobacteria.

Foci Detection Method (FDM)

An *in vitro* cell culture infectivity assay involves exposing oocysts to excystation stimuli followed by inoculating them into a cultured mammalian cell line, which supports infection and asexual development. An infectious focus is the site of infection of at least one sporozoite in the cell culture. After 24–48 h, samples are examined for the presence of infection. Foci are labeled with fluorophore-conjugated antibodies specific to the various life stages of *Cryptosporidium* and are visualized by epifluoresence microscopy.

Enzyme-Linked Immunosorbent Assay (ELISA)

ELISA has been developed to detect and evaluate the growth of *C. parvum* in culture systems using antibodies developed against its various life-cycle stages. ELISA can be used to test multiple samples simultaneously and does not require a high level of technical skill compared with that for identifying parasites based on morphological and staining characteristics by microscopic examination. Tests commonly use 96-well microtitration plates coated by antibodies specific for *Cryptosporidium*. Tests samples are then added to the plate. After washing away nonbinding materials, a second enzyme-conjugated antibody specific to *Cryptosporidium* is added to the sample wells. Addition of the enzyme substrate results in a color reaction to indicate the presence of the parasite. There may be problems of cross-reactivity with algae and turbidity interfering with results, but this can be overcome by the development and use of more specific antibodies.

Flow Cytometry

A flow cytometer analyzes particles in a suspension as they pass by a laser beam. The light scattering pattern is analyzed and correlated to size and internal complexity along with the fluorescent light emitted by each particle. Flow cytometer cell sorters can also sort particles of interest from unwanted particles by using the binding of a fluorescein-conjugated antibody to antigens present on *Cryptosporidium* oocysts. Particles within the sample that do not match the criteria for *Cryptosporidium* are filtered out.

POLYMERASE CHAIN REACTION (PCR) DETECTION METHODS

PCR involves using oligonucleotide primers to amplify a DNA fragment specific to the target organism. The desired fragment is identified by gel electrophoresis and can be subsequently sequenced. PCR is reproducible, cost-effective, sensitive and amenable to quantitation, and capable of differentiating among *Cryptosporidium* species that infect humans. Common gene targets for PCR detection include 18S ribosomal DNA, heat-shock proteins (i.e., *hsp*70), and oocyst wall proteins.

Real-Time PCR

Real-time PCR involves virtual real-time visualization of fluorescence emitted by a fluorogenic probe accumulated during PCR. Quantification of amplified DNA during the exponential phase of the reaction, when reagents are not limiting, allows precise determination of the initial quantity of the target sequences. Real-time PCR offers higher throughput, reduced turnaround time, and minimal amplicon contamination due to a closed-vessel system. The quantification range of real-time PCR methods is greater (5–6 log units) than conventional PCR (2–3 log units).

Cryptosporidium species and genotypes can be differentiated through melt curve analysis, which is based on melting temperature differences of PCR-probe complexes, and reflects the extent of complementation of the probes to the amplified PCR fragments. Real-time PCR investigations for environmental detection have demonstrated that the method is rapid, sensitive, and specific.

Reverse Transcription-PCR (RT-PCR)

Only viable organisms can produce messenger RNA (mRNA), so RT-PCR selectively detects viable organisms. In this method, a specific fragment of the complementary DNA (cDNA), which is produced from an mRNA template by reverse transcriptase, is amplified by PCR. Reverse transcriptase is extremely sensitive to chemical contamination, so the RT step is the source of greatest variability. Common gene targets for RT-PCR analysis of *C. parvum* viability include *hsp70*, amyloglucosidase, and *B*-tubulin.

Cell Culture-PCR (CC-PCR)

Comparable with FDM in detecting oocyst infectivity, a CC-PCR assay involves the extraction of genomic DNA from an infected cell culture and amplification of specific DNA fragments by PCR. A cell culture infectivity assay, coupled with either real-time PCR or an MPN assay, can be used to quantify infective oocysts. Alternatively, mRNA can be extracted from the infected cell culture and subjected to RT-PCR to detect infectious oocysts.

Most Probable Number-PCR (MPN-PCR)

In a standard MPN assay, replicate samples are serially diluted and evaluated by PCR for the presence of *Cryptosporidium*-specific nucleic acid sequences. Used in conjunction with a cell culture infectivity assay, MPN-PCR could provide a good alternative to using FDM alone for enumerating infective oocysts. Because MPN assays are costly, labor-intensive, and require a large volume of samples with multiple preparation steps, alternative detection strategies may be more suitable for quantitative analyses.

NUCLEIC ACID PROBES

Small nucleotide chains (oligonucleotides) can be constructed to a desired DNA sequence. The binding nature of DNA is such that complementary single-stranded DNA (ssDNA) fragments strongly bind to one another, whereas a single nucleotide mismatch drastically reduces the binding strength of the two fragments.

Fluorescent *In Situ* Hybridization (FISH)

FISH uses fluorescently labeled oligonucleotide probes targeted to *C. parvum*-specific sequences, such as ribosomal RNA (rRNA). Ribosomal RNA is used as a target because it should be present in high quantities in viable and potentially infective oocysts, but due to its short half-life, it would be degraded in nonviable oocysts. Oocysts are collected and made permeable to the labeled probes by the addition of organic solvents. Species-specific probes hybridize with target rRNA within the permeabilized oocysts and are detected by epifluorescence microscopy or flow cytometry.

Microarray (DNA Chip)

Microarray technology combines PCR with hybridization of oligonucleotide probes. An array of oligonucleotide probes is synthesized and fixed to a chip. Oocyst genomic DNA is extracted and highly specific, and conserved target genes, such as rRNA and *hsp70*, are amplified by PCR and then fluorescently labeled. For

Table 1. Summary of the Molecular Detection Methods That Can Be Used for Detecting *Cryptosporidium parvum* in Environmental Samples

Detection Method	Differentiate Among *Cryptosporidium* Species	Determine Infectivity	Quantifiable	Detection Limit[a]	Reference
IFA	−	−	+	10 oocysts	(8)
FDM—animal	−	+	+	60 oocysts	(10)
FDM—cell culture	−	+	+	5–10 oocysts	(10)
FDM-MPN	−	+	+	2–10 oocysts	(6,10)
PCR	+	−	−	1–10 oocysts	(18)
Real-time PCR	+	−	+	1–5 oocysts	(11)
Real-time CC-PCR	+	+	+	1 oocyst	(12)
RT-PCR	+	+	−	1 oocyst	(13)
CC-RT-PCR	+	+	−	10 oocysts	(14)
CC-PCR	+	+	−	10 oocysts	(15,16)
MPN-PCR	+	−	+	10 oocysts	(17)
Flow cytometry	−	−	+	10 oocysts	(18)
FISH	+	−	+	100 oocysts	(8)
Microarray	+	−	+	Not available	(19,20)

[a] Detection limits are not directly comparable as the conditions used by different researchers may not be similar.

identification at the species level, highly variable or species-specific genes are used. PCR products hybridize with their complementary probe sequences, and the presence or absence of *Cryptosporidium* can be determined by computerized detection of fluorescent emissions. The high throughout capability of microarrays can allow simultaneous detection of numerous different genera of pathogens or species within a genus.

A complete list of the methods described is presented in Table 1. The table indicates whether each method can distinguish among *Cryptosporidium* species, detect oocyst infectivity, quantify detected oocysts, and has a limitation on detection. A reference for each of the methods is also included in the table. A recent review article by Carey et al. (22) provides a more detailed description of *Cryptosporidium* detection methods.

Acknowledgment
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BIBLIOGRAPHY

1. Carreno, R.A. et al. (2001). Phenotypic and genotypic characterization of *Cryptosporidium* species and isolate. *J. Ind. Microbiol. Biotechnol.* **226**: 95–106.
2. Millard, P.S. et al. (1994). An outbreak of cryptosporidiosis from fresh-pressed apple cider. *JAMA* **272**(20): 1592–1596.
3. Smith, H.V. (1998). Detection of parasites in the environment. *Parasitology* **117**(7): S113–S141.
4. Korich, D.G. et al. (1990). Effects of ozone, chlorine dioxide, chlorine and monochloramine on *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* **56**(5): 1423–1428.
5. Morgan-Ryan et al.
6. Weir, S.C. et al. (2001). Improving the rate of infectivity of *Cryptosporidium parvum* oocysts in cell culture using centrifugation. *J. Parasitol.* **87**(6): 1502–1504.
7. Higgins, J.A. et al. (2003). Recovery and detection of *Cryptosporidium parvum* oocysts from water samples using continuous flow centrifugation. *Water Res.* **37**(15): 3551–3560.
8. Rochelle, P.A. et al. (2002). Comparison of *in vitro* cell culture and a mouse assay for measuring infectivity of *Cryptosporidium parvum*. *Appl. Environ. Microbiol.* **68**(8): 3809–3817.
9. U.S. Environmental Protection Agency. (1999). *Method 1622: Cryptosporidium in water by filtration/IMS/FA*. Office of Water EPA-821-R-99-061.
10. Slifko, T.R. et al. (2002). Comparison of tissue culture and animal models for assessment of *Cryptosporidium parvum* infection. *Exp. Parasitol.* **101**(2–3): 97–106.
11. Johnson, D.W. et al. (1995). Development of a PCR protocol for sensitive detection of *Cryptosporidium* oocysts in water samples. *Appl. Environ. Microbiol.* **61**(11): 3849–3855.
12. Limor, J.R., Lal, A.A., and Xiao, L. (2002). Detection and differentiation of *Cryptosporidium* parasites that are pathogenic for humans by real-time PCR. *J. Clin. Microbiol.* **40**(7): 2335–2338.
13. MacDonald, L.M. et al. (2002). The development of a real-time quantitative-PCR method for characterisation of a *Cryptosporidium parvum in vitro* culturing system and assessment of drug efficacy. *Mol. Biochem. Parasitol.* **121**: 279–282.
14. Stinear, T., Matusan, A., Hines, K., and Sandery, M. (1996). Detection of a single viable *Cryptosporidium parvum* oocyst in environmental water concentrates by reverse transcription-PCR. *Appl. Environ. Microbiol.* **62**(9): 3385–3390.
15. Rochelle, P.A., De Leon, R., Stewart, M.H., and Wolfe, R.L. (1997). Comparison of primers and optimization of PCR conditions for detection of *Cryptosporidium parvum* and *Giardia lamblia* in water. *Appl. Environ. Microbiol.* **63**(1): 106–114.
16. Di Giovanni, G.D. et al. (1999). Detection of infectious *Cryptosporidium parvum* oocysts in surface and filter backwash water samples by immunomagnetic separation and integrated cell culture-PCR. *Appl. Environ. Microbiol.* **65**(8): 3427–3432.
17. LeChevallier, M.W., Abbaszadegan, M., and Di Giovanni, G.D. (2000). Detection of infectious *Cryptosporidium parvum* oocysts in environmental water samples using an integrated cell culture-PCR (CC-PCR) system. *Water Air Soil Pollut.* **123**(1/4): 53–65.
18. Tsuchihashi, R., Loge, F.J., and Darby, J.L. (2003). Detection of *Cryptosporidium parvum* in secondary effluents using a most probable number-polymerase chain reaction assay. *Water Environ. Res.* **75**(4): 292–299.
19. Chung, J., Vesey, G., Gauci, M., and Ashbolt, N.J. (2004). Fluorescence resonance energy transfer (FRET)-based specific labeling of *Cryptosporidium* oocysts for detection in environmental samples. *Cytometry* **60**(A): 97–106.
20. Straub, T.M. et al. (2002). Genotyping *Cryptosporidium parvum* with an *hsp70* single-nucleotide polymorphism microarray. *Appl. Environ. Microbiol.* **68**(4): 1817–1826.
21. Wang, Z., Vora, G.J., and Stenger, D.A. (2004). Detection and genotyping of *Entamoeba histolytica, Entamoeba dispar, Giardia lamblia*, and *Cryptosporidium parvum* by oligonucleotide microarray. *J. Clin. Microbiol.* **42**(7): 3262–3271.
22. Carey, C.M., Lee, H., and Trevors, J.T. (2004). Biology, persistence and detection of *Cryptosporidium parvum* and *Cryptosporidium hominis* oocyst. *Water Res.* **38**: 818–862.

CRYPTOSPORIDIUM

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Cryptosporidia are small, spherical, obligate, intracellular sporozoan parasites that infect the intestinal tract of a wide range of mammals, including humans. *Cryptosporidium* oocysts range in size from 2 to 8 μm, depending on the species and the stage of the life cycle. Oocysts are commonly found in many of the lakes and rivers that supply public drinking water as a result of runoff from sewage and animal wastes applied to nearby fields and pastures or from areas of wildlife or livestock activity (4,7,10). Infection, resulting from ingesting oocysts, manifests as cryptosporidiosis. Although *Cryptosporidium* was first described in 1907, human infection was not reported until 1976. Today, *Cryptosporidium parvum* is well recognized as the cause of the disease cryptosporidiosis in humans and cattle and is one of the more opportunistic agents seen in patients with AIDS that occurs primarily in individuals with compromised immune systems. Currently, there is no totally effective therapy for cryptosporidiosis (3,8,11,12).

LIFE CYCLE AND MORPHOLOGY

Cryptosporidia undergo alternating life cycles of sexual and asexual reproduction that are completed within the gastrointestinal tract of a single host. The developmental stages of the life cycle occur intracellularly and extracytoplasmically and include schizogony, gametogony, fertilization, and sporogony (1). The developmental stages of the organism are contained within a host cell parasitophorous vacuole, located at the microvillous surface of the host cell. The cycle begins when infectious oocysts containing four sporozoites are discharged in the feces of a parasitized animal. These thick-walled oocysts remain viable for months unless exposed to extremes of temperature, desiccation, or concentrated disinfectants (1). Following ingestion by another animal, most likely from food or water that has become fecally contaminated, the oocyst excysts and releases sporozoites that attach to the microvilli of the small bowel epithelial cells, where they develop into trophozoites (2). Trophozoites divide asexually (schizogony) to form schizonts that contain eight daughter cells known as type I merozoites. Upon release from the schizont, these cells attach to another epithelial cell, and the schizogony cycle is repeated to produce schizonts that contain four type II merozoites. Type II merozoites develop into male (microgametocyte) and female (macrogametocyte) sexual forms. Fertilization results in a zygote (oocyte) that develops into an oocyst, which is ultimately shed into the lumen of the bowel. The oocysts undergo sporulation to the infective stage within the brush border of the enterocytes and are excreted as infectious oocysts in the stool (3–5).

The majority of oocysts generated possess a thick, protective cell wall that ensures their intact passage in the feces and survival in the environment; however, approximately 20% of the oocysts generated fail to develop the thick wall, and following release from a host cell, the thin cell membrane on these oocysts ruptures and releases four infectious sporozoites. These sporozoites penetrate the intestinal lumen and initiate a new autoinfective cycle within the original host. The presence of this thin-walled, autoinfective oocyst can lead to an overwhelming infection that creates a persistent, life-threatening infection in an immunocompromised individual (4).

CLINICAL DISEASE

The pathogenesis of *Cryptosporidia* is not completely understood; age and immune status at the time of primary exposure do not appear to influence susceptibility to infection. However, once the primary infection has been established, the immune status of the host plays an extremely important role in determining the length and severity of the illness (4).

Cryptosporidia undergo their life cycle in the enteric epithelial cells and also in the gallbladder, respiratory, and renal epithelium, especially in immunocompromised hosts (1). The symptom found in all reported cases is acute diarrhea (2). Clinical symptoms found in immunocompetent individuals include nausea; low-grade fever; abdominal cramps; anorexia; and profuse watery, frothy bowel movements that may be followed by constipation. Other individuals may be asymptomatic, particularly later in the course of the infection. In patients who have the typical watery diarrhea, the stool specimen will contain very little fecal material, consisting mainly of water and mucus flecks, and the organisms are trapped in the mucus. In most cases, a patient who has a normal immune system will have a self-limited infection lasting 1 to 2 weeks, whereas a patient who is immunocompromised may have a chronic infection with symptoms ranging from asymptomatic to severe (2,4). Studies to examine susceptibility and serologic responses to reinfection have demonstrated that previous exposure of immunocompetent adults to *Cryptosporidium* is not entirely protective but may decrease the severity of disease and the number of oocysts shed (6).

Cryptosporidium can generate life-threatening infections in immunocompromised individuals, particularly in human AIDS patients (1). In these individuals, the duration and severity of diarrheal illness will depend on the immune status of the patient. It is believed that cryptosporidiosis in AIDS patients causes malabsorption and intestinal injury in proportion to the number of organisms that infect the intestine. Most severely immunocompromised patients cannot overcome the infection; the illness becomes progressively worse with time and leads to death. The disease is prolonged; profuse, watery diarrhea persists from several weeks to months or years, as a result of the autoinfective nature of the organism, reportedly resulting in fluid losses as high as 25 L/day (7). In such patients, infections in areas other than the gastrointestinal tract may cause additional symptoms such as respiratory problems, cholecystitis, hepatitis, and pancreatitis (4).

Diagnosis

Oocysts recovered in clinical specimens usually represent the 80% that are thick-walled. The oocysts are difficult to visualize because of their small, colorless, transparent appearance, and may be confused with yeast cells. In the past, cryptosporidiosis has been diagnosed following examination of small or large bowel biopsy material, under both light and electron microscopy; however, in *Cryptosporidium* infections, the entire mucosa may not be infected uniformly; therefore, biopsy specimens may miss the infected area. As a result, cases have recently been diagnosed by recovering the oocysts from fecal material using flotation or fecal concentration techniques. Diagnosis is achieved by demonstrating the oocysts in feces, sputum, or possibly respiratory secretions (3). Special staining techniques such as the modified acid-fast, Kinyoun's, and Giemsa methods may be employed to enhance visualization, along with the direct fluorescent-antibody (FA) or enzyme-linked immunosorbent assay (ELISA) techniques that incorporate monoclonal antibody reagents (4).

Recently, the issues of water quality and water testing have become more important and controversial. Today, most water utilities have developed their own water quality testing laboratories or contracted with commercial water laboratories for the recovery and identification of *Cryptosporidium*. Currently, the most common methods for capturing and recovering oocysts from water employ polypropylene cartridge filters or membrane filtration. The oocysts are subsequently eluted and may be concentrated on a percoll-sucrose gradient by flotation or by immunomagnetic separation (IMS) and visualized with commercially available immunofluorescence assay kits. Oocysts are often present in small numbers in environmental samples; therefore, molecular techniques involving the polymerase chain reaction (PCR) may also be used to detect oocysts in water samples (2,8). Integrated cell culture-PCR infectivity assays address the drawbacks of alternative methods such as vital dye staining by allowing for both detection of organisms and the determination of viability and infectivity (9). Considering that, under favorable conditions of moisture and moderate temperature, oocysts can remain viable and infectious for a relatively long time and have been reported viable after storage for 12 months, a great need still exists for simple, efficient, and reliable procedures for capturing and recovering *Cryptosporidium* oocysts from water (10) (Fig. 1).

Treatment

There is no effective specific treatment for *Cryptosporidium* infection, despite testing of hundreds of compounds (1,6). Cryptosporidiosis tends to be self-limiting in patients who have an intact immune system; the clinical course of infection varies, depending on the immune status of the host. Treatment with antidiarrheal drugs along with rehydration therapy may reduce the severity of acute cryptosporidiosis but is less effective for chronic cryptosporidiosis that involves the colon and extraintestinal tissues (4). The antibiotic paromomycin, it has been shown, slightly reduces parasite numbers and stool frequency and may be combined with azithromycin as a course of treatment (6,11). The establishment of a parasitophorous vacuole within the host cell may somehow protect the parasite from antimicrobial drugs (6).

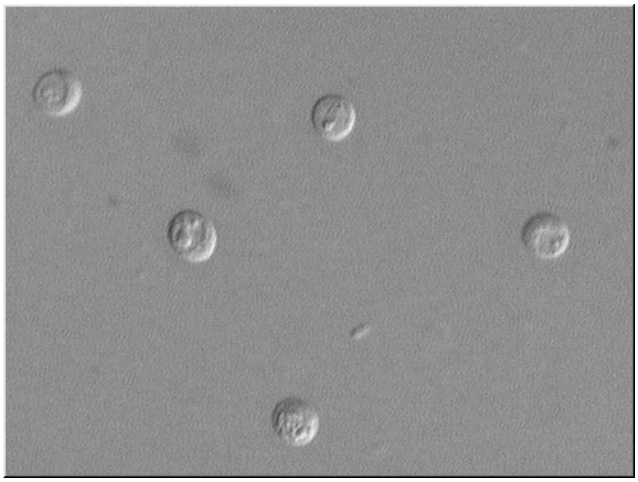

Figure 1. *Cryptosporidium parvum* oocysts viewed at 1000× magnification by Nomarski differential interference contrast (DIC) magnification.

Epidemiology and Prevention

Cryptosporidium is transmitted by oocysts that are usually fully sporulated and infective when they are passed in stool. The principal transmission route is direct fecal–oral spread and transmission by contaminated water. Calves and other animals such as livestock, dogs, cats, and wild mammals are potential sources of human infections, and contact with these animals or their feces may be an unrecognized cause of gastroenteritis in humans (1). Generally, young children tend to have higher infection rates, and there is a high prevalence of cryptosporidiosis in children in areas where sanitation and nutrition are poor (10). Direct person-to-person transmission is likely and may occur through direct or indirect contact with stool material. Outbreaks of human disease in day-care centers, hospitals, and urban family groups indicate that most human infections result from person-to-person contact (5). Indirect transmission may occur from exposure to positive specimens in a laboratory, from contaminated surfaces, or from consuming contaminated food or water. In healthy adults who have no serologic evidence of past infection by *Cryptosporidium parvum*, as few as thirty *Cryptosporidium parvum* oocysts is sufficient to cause infection, and in some cases, infection has occurred from just one oocyst (11). In the United States, the parasite has been identified in 15% of patients who have AIDS and diarrhea (5).

The potential contamination of water supplies by *Cryptosporidium* oocysts is a considerable issue for the drinking water industry. Oocysts can penetrate physical barriers and withstand the conventional disinfection processes used for drinking water treatment. Waterborne outbreaks of *Cryptosporidium* are an increasing public health problem and have resulted from untreated surface water, filtered public water supplies, and contaminated well water (3,12). Large-scale outbreaks of cryptosporidiosis in industrialized countries have been associated with contamination of community drinking water (9). Disease transmission through the waterborne route is especially important because of the capacity for affecting large communities of susceptible individuals. A massive waterborne outbreak was reported in Milwaukee, Wisconsin, where contamination of the public water supply during March and April of 1993 resulted in more than 400,000 infections and about 50 deaths (12,13). Additional outbreaks involving public swimming pools and wading pools demonstrate the ability of *Cryptosporidium* to cause infection even when ingested in small amounts of fully chlorinated water (11).

The increase in the number of reported waterborne disease outbreaks associated with the *Cryptosporidium* species can be attributed to improved techniques for oocyst recovery and identification resulting in the demonstration of oocysts in surface and drinking water and in sewage effluents. It is very likely that cryptosporidiosis is underdiagnosed, especially in immunocompetent adults and children, as analysis for the oocysts is not normally included in a routine stool analysis (6). The importance of agricultural wastewater and runoff, particularly from lambs and calves, is also now recognized as a potential source of infective *Cryptosporidium* oocysts (4).

Prevention involves taking proper steps to reduce the likelihood of waterborne contamination. Properly drilled and maintained wells that tap into groundwater are unlikely to contain pathogens because of the natural filtration that takes place as water passes through the soil; however, contamination may still occur if surface water can move through coarse soils or fractured bedrock into groundwater aquifers. Shallow or poorly constructed wells and springs are at risk of contamination from surface water runoff; therefore, wells should be protected from surface contamination by an intact well casing, proper seals, and a cap above ground (14). Human and animal waste contamination are minimized by protecting the watershed, controlling land use, creating and enforcing septic system regulations, and best management practices in an effort to control runoff (14).

Cryptosporidium oocysts are susceptible to ammonia, 10% formalin in saline, freeze-drying, exposure to temperatures below freezing or above 65 °C for 30 minutes, and 50% commercial bleach (4). For individuals who wish to take extra measures to avoid waterborne cryptosporidiosis in their drinking water, according to the EPA and the CDC, boiling the water is the most effective way of killing the organism (15). In addition to boiling water, oocysts can be removed by certain types of filters to ensure that drinking water is safe (14).

BIBLIOGRAPHY

1. Bowman, D. (1999). *Cryptosporidium, Georgis' Parasitology for Veterinarians*, 7th Edn. W.B. Saunders Company, New York, pp. 99–100.
2. Leventhal, R. and Cheadle, R. (1989). *Protozoa, Medical Parasitology: A Self Instructional Text*, 3rd Edn. F.A. Davis Company, Philadelphia, PA, pp. 96–97.
3. Ash, L. and Orihel, T. (1997). *Cryptosporidium parvum*. In: *Atlas of Human Parasitology*, 4th Edn. American Society of Clinical Pathologists, Chicago, IL, pp. 124–125.
4. Garcia, L. and Bruckner, D. (1997). *Intestinal Protozoa (Coccidia and Microsporidia) and Algae*. In: *Diagnostic Medical Parasitology*, 3rd Edn. ASM Press, Washington, DC, pp. 54–66.
5. Ryan, K.J. (1994). *Cryptosporidia*. In: *Sherris Medical Microbiology: An Introduction to Infectious Diseases*, 3rd Edn. Appleton & Lange, Norwalk, CT, pp. 655–657.
6. Clark, D. (1999). New insights into human cryptosporidiosis. *Clin. Microbiol. Rev.* **12**(4): 554–563.
7. Balows, A., Hausler, W., Herrmann, Jr., K., Isenberg, H., and Shadomy, H. (1991). *Cryptosporidium* species. *Manual of Clinical Microbiology*, 5th Edn. ASM, Washington, DC, pp. 764–766.
8. Widmer, G., Orbacz, E., and Tzipori, S. (1999). β-Tubulin mRNA as a marker of *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* **65**(4): 1584–1588.
9. DiGiovanni, G. et al. (1999). Detection of infectious *Cryptosporidium parvum* oocysts in surface and filter backwash water samples by immunomagnetic separation and integrated cell culture-PCR. *Appl. Environ. Microbiol.* **65**(8): 3427–3432.
10. Dubey, J.P., Speer, C.A., and Fayer, R. (1990). *Cryptosporidiosis of Man and Animals*. CRC Press, Boca Raton, FL, pp. 1–82.
11. Guerrant, R. (1997). Cryptosporidiosis: an emerging, highly infectious threat. *Emerging Infect. Dis.* **3**(1): 51–57.
12. Sartory, D.P. et al. (1998). Recovery of *Cryptosporidium* oocysts from small and large volume water samples using a compressed foam filter system. *Lett. Appl. Microbiol.* **27**: 318–322.
13. Sreter, T. et al. (2000). Morphologic, host specificity, and molecular characterization of a Hungarian *Cryptosporidium meleagridis* isolate. *Appl. Environ. Microbiol.* **66**(2): 735–738.
14. Avery, B.K. and Lemley, A. (1996). *Cryptosporidium: A Waterborne Pathogen*. U.S. Department of Agriculture Water Quality Program. 329WQFS6.
15. *Guidance for people with severely weakened immune systems*, United States Environmental Protection Agency, Office of Water, 1999, EPA 816-F-99-005.

MEASURING *CRYPTOSPORIDIUM PARVUM* OOCYST INACTIVATION FOLLOWING DISINFECTION WITH ULTRAVIOLET LIGHT

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Historically, ultraviolet light inactivation of *Cryptosporidium parvum* oocysts was considered ineffective; however, recently it was demonstrated that the methods for measuring oocyst inactivation can yield erroneous results and that neonatal mouse infectivity assays, which indicated that very low UV doses are highly effective for oocyst inactivation, are needed for determining inactivation of UV-treated oocysts. The moral, ethical, and financial constraints of using mouse infectivity has generated the need for more user-friendly alternative methods for measuring oocyst inactivation. Cell culture infectivity assays are considered promising alternatives, and this article discusses a cell culture-immunofluorescence (IFA) procedure, which following optimization, yielded results similar to those expected from mouse infectivity assays. This cell culture-IFA procedure will be an invaluable analytical tool for control or bench scale studies using *C. parvum* oocysts and the same water matrices as those intended for use in UV reactor validation studies.

HISTORICAL PERSPECTIVE

A number of investigators have examined the effect of low-pressure UV light on viruses and bacteria (1,2) and found that MS2 bacteriophage requires approximately 70 mJ/cm^2 of UV light to render 4-log inactivation and that hepatitis A virus requires fourfold lower UV doses to yield similar levels of inactivation. From the studies of Wilson et al. (1), MS2 bacteriophage was approximately two times more resistant than viruses and three to ten times more resistant than bacteria. Protozoan parasites, which display greater resistance than bacteria or viruses to chemical disinfectants, were examined for their susceptibility to UV light by Karanis et al. (3). Reportedly delivery of 400 mJ/cm^2 yielded 3-log inactivation of *Trichomonas vaginalis*, and *Giardia lamblia* required 180 mJ/cm^2 to yield 2-log inactivation. In 1993, Lorenzo-Lorenzo et al. (4) examined the impact of UV light on *Cryptosporidium* oocysts; however, due to an inadequate description of their disinfection experiments, the effectiveness of UV light for *Cryptosporidium* oocyst inactivation was not recognized. Two years later, a unit known as the *Cryptosporidium* inactivation device (CID), which delivered a total UV dose of 8748 mJ/cm^2 from low-pressure lamps, was examined and 2- to 3-log inactivation of oocysts was reported using the fluorogenic vital dye assay (4′-6′-diamidino-2-phenylindole and propidium iodide) and *in vitro* excystation (5). Following this, Clancy et al. (6) confirmed the findings of Campbell et al. (5); however, the apparent requirement for high UV doses for significant oocyst inactivation continued to present an obstacle to the regulatory and water industry in supporting implementation of this technology.

From 1998 to 1999, comparative bench scale and demonstration scale (215 gpm) *Cryptosporidium* oocyst inactivation studies were performed that used medium-pressure UV lamps and examined oocyst inactivation using *in vitro* viability assays (DAPI/PI and *in vitro* excystation) as well as mouse infectivity assays (7). These studies conclusively demonstrated the effectiveness of low UV doses for inactivating *Cryptosporidium* in finished water. These data rapidly gained attention from both regulatory agencies and the water industry and instigated the revolution in the U.S. water industry for UV disinfection to inactivate *Cryptosporidium* oocysts effectively. In addition to demonstrating the effectiveness of low levels of UV light for oocyst inactivation, Bukhari et al. (7) also found that *in vitro* viability assays underestimated oocyst inactivation following their exposure to either UV light or ozonation (8) and that mouse infectivity assays, albeit cumbersome, needed to be the methods of choice for future studies of this nature. Following these initial studies, a number of investigators confirmed the effectiveness of UV light for inactivating *Cryptosporidium* oocysts as well as *Giardia* cysts (9) and Microsporidia spores (10).

MEASURING *C. PARVUM* OOCYST INACTIVATION FOLLOWING EXPOSURE TO UV LIGHT

In vitro assays for determining the viability of *C. parvum* oocysts offer several advantages over the traditional animal infectivity assays in that results can be generated in a short time. Although these assays are relatively simple to use and relatively inexpensive, recently it was shown that they do not accurately demonstrate whether oocysts are capable of infectivity in neonatal mice. For example, using fluorogenic vital dyes (i.e., DAPI/PI, SYTO-9, and SYTO-59) or *in vitro* excystation, the viability information for oocysts subjected to ultraviolet light (7) or ozone (8) disinfection was grossly overestimated compared with infectivity data using neonatal mice. Unfortunately the "gold" standard mouse infectivity assays have various limitations, which in addition to the moral, ethical, and financial constraints of animal experimentation, include the high degree of variability of using outbred strains of neonatal mice. As a result, the water industry has been seeking alternative, more user-friendly procedures for measuring oocyst viability/infectivity.

In vitro infectivity assays for determining *C. parvum* oocyst inactivation have the potential to fill this void. One such *in vitro* infectivity assay uses human ileocecal adenocarcinoma (HCT-8) cells in conjunction with quantitative polymerase chain reaction (q-PCR) and has been used previously to determine the infectivity of environmentally derived oocysts (11). This assay has the advantage of providing a direct indication of the amount of amplifiable DNA with a specific set of primers. Furthermore, this assay also can help avoid the high variability of using the most probable number format of mouse infectivity assays. Using this assay to measure inactivation of bench-scale, UV-treated *C. parvum* oocysts indicated log inactivation values of 1.16, 1.24, and 1.84 logs for 10, 20, and 40 mJ/cm^2, respectively. These inactivation values for *C. parvum* oocysts were considerably lower than those reported in previous studies using mouse infectivity assays (7,12). Previous research has indicated that oocysts exposed to UV doses ranging between 10 and 40 mJ/cm^2 continue to respond to excystation stimuli and release their sporozoites. This suggests that UV-treated oocysts inoculated onto cell monolayers could potentially excyst, and then released sporozoites could invade cell monolayers. Examination of HCT-8 monolayers confirmed the presence of pinpoints of invasion, which probably originated from invasive sporozoites (Fig. 1). A number of different oocyst pretreatment steps were used to promote differentiation between UV affected and unaffected sporozoites; however, these pretreatments did not nullify the background signal detected by the quantitative PCR procedures.

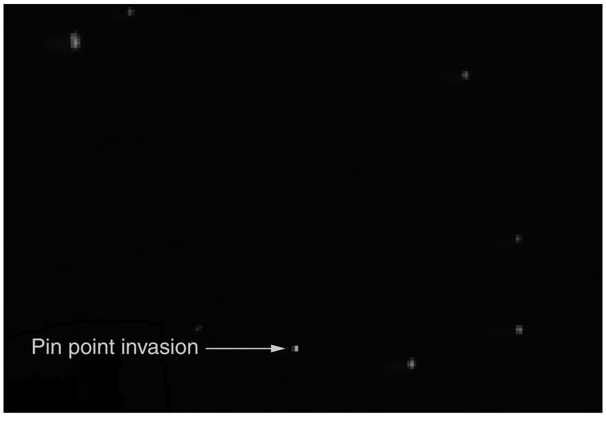

Figure 1. UV-treated oocysts yielding pinpoints of invasion.

CELL CULTURE-IFA FOR MEASURING INACTIVATION OF UV-TREATED *C. PARVUM* OOCYSTS

Bukhari and LeChevallier (13) used an infectivity-enhancing oocyst pretreatment step consisting of preacidification and 0.05% bile treatment followed by inoculation onto HCT-8 monolayers, incubation at 37 °C for 72 h, and quantitative detection of infection by immunofluorescence microscopy. The rationale behind this assay was that UV-treated oocysts would undergo excystation and subsequently invade HCT-8 cells, leading to discrete pinpoints of invasion. In contrast, untreated organisms would invade the HCT-8 cells but would continue to differentiate further to generate clusters of secondary infection (Fig. 2).

Enumerating secondary clusters of infection for various inocula of oocysts (i.e., 10,100, and 1000 oocysts) has enabled development of a dose response curve (Fig. 3). This curve, which was generated from multiple trials ($n = 75$ to 115) using predetermined oocyst inocula, was analyzed by linear regression to derive an equation for calculating the number of infectious organisms present in an inoculum of UV-treated oocysts after the number of clusters had been determined by immunofluorescence microscopy.

UV disinfection experiments using the Iowa isolate of *C. parvum* oocysts were conducted, and following cell culture infectivity, the infectious clusters were extrapolated from the dose response curve generated for the untreated oocysts to calculate levels of inactivation (Fig. 4). A UV dose of 1 mJ/cm^2 rendered 0.44 log inactivation of oocysts, and UV doses between 1 and 4 mJ/cm^2 yielded a linear decline in oocyst inactivation; 3 mJ/cm^2 rendered 2.79–2.84 log inactivation, and 4-log inactivation occurred at 4 mJ/cm^2. Between 4 and 20 mJ/cm^2, measurements by the cell culture procedure continued to indicate oocyst inactivation levels of 4 logs. It is highly probable that the actual levels of oocyst inactivation after UV doses between 4 and 20 mJ/cm^2 were in excess of 4 logs; however, as the determinable oocyst inactivation by the cell culture procedure is a factor of the highest original inoculum of UV-treated oocysts applied onto the monolayers (i.e., 1×10^5 oocysts), the maximum measurable levels of inactivation by this cell culture procedure were limited to 4 logs or lower in these experiments. Although theoretically it would be possible to use higher oocyst inocula (i.e., 1×10^6–1×10^8 oocysts per monolayer) to accurately determine the levels of oocyst inactivation at individual UV doses between 4 and 20 mJ/cm^2, this would be of little empirical value from the perspective of the disinfection needs of the water industry or the logistics of conducting experiments with adequate quantities of infectious oocysts.

As a result of the investigations by Bukhari and LeChevallier (13), it has been demonstrated that UV-treated *C. parvum* oocysts can undergo excystation and that the sporozoites from these inactivated oocysts can invade monolayers of HCT-8 cells to generate pinpoints of invasion. Optimization of excystation triggers and cell culture incubation periods led to development of a cell culture-IFA procedure that enabled detecting as few as 10 infectious oocysts. Using this cell culture-IFA allowed discriminating pinpoints (generated from noninfectious but invasive sporozoites) from secondary structures (generated from infectious sporozoites). This phenomenon is the primary reason that the cell culture quantitative PCR procedure described by DiGiovanni et al. (11) cannot be used to measure inactivation of UV-treated oocystes because the assay cannot discriminate between DNA originating from invasive sporozoites and that from infectious sporozoites.

Using the optimized cell culture-IFA procedure, it was confirmed that low UV doses (i.e., 2–5 mJ/cm^2) can be very effective for inactivating *C. parvum* oocysts. Comparison of data from this current study with previously published reports, using either tissue culture infectivity or mouse

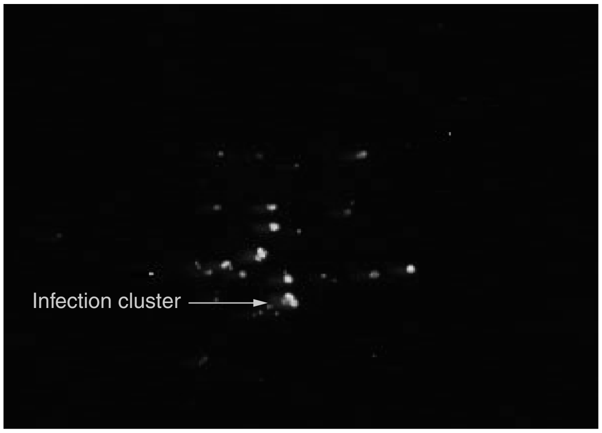

Figure 2. Infection clusters from infectious oocysts.

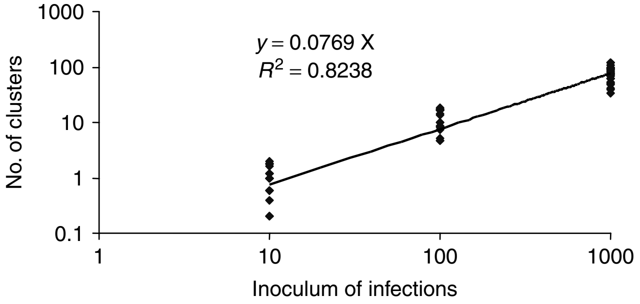

Figure 3. *Cryptosporidium parvum* oocyst infectivity in HCT-8 monolayers, as detected by immunofluorescence microscopy.

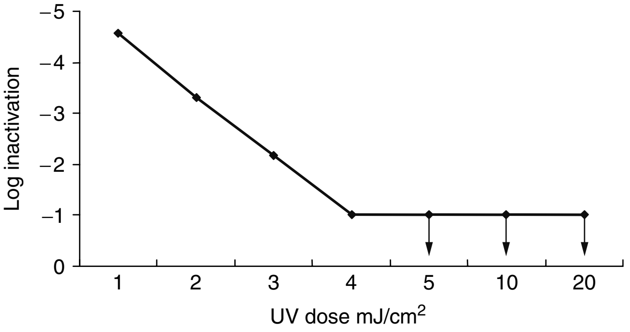

Figure 4. Inactivation of *C. parvum* oocysts by UV light, as determined by the cell culture-IFA procedure.

infectivity assays, also demonstrates excellent agreement. Numerous studies (9,12,14,15) have assessed levels of oocyst inactivation from UV doses ranging between 1 and <40 mJ/cm^2. Not surprisingly, there is wide variability in the data generated from these various studies, which may result from differences in oocyst preparation, disinfection conditions, and methods for infectivity measurements. Nonetheless, using UV doses between 1 and 3 mJ/cm^2, the oocyst inactivation data generated in our current study were within the range of inactivation data generated in the studies cited (Fig. 5).

Data from the previous disinfection studies have also been used in the USEPA's Ultraviolet Disinfection Guidance Manual, to predict the probable levels of oocyst inactivation for a given UV dose. According to these probability tables, the UV dose required for 0.5-log inactivation of oocysts ranged from 0.7 to 3.0 mJ/cm^2, whereas in our current study, 0.44-log inactivation of *C. parvum* oocysts was noted at delivery of 1 mJ/cm^2. The probability tables also predicted 50% likelihood that a UV dose of 2.9 mJ/cm^2 would lead to 2.5-log oocyst inactivation, whereas in our study, delivery of 3 mJ/cm^2 led to approximately 2.8-log inactivation. Although our data indicated 3- and 4-log oocyst inactivation from UV doses as low as 4 mJ/cm^2 and consistently >4-log inactivation of oocysts from UV doses ranging between 5 and 20 mJ/cm^2, >4-log oocyst inactivation was noted only when UV doses exceeded 10 mJ/cm^2 in the previous studies cited. At 5 mJ/cm^2, although our data indicated >4-log inactivation, the previous studies indicated >1-log and approximately 3-log inactivation of oocysts. These differences need to be interpreted with caution and do not necessarily imply differences in susceptibility between the isolates of *C. parvum* used. As an example, it is known that the oocyst inactivation levels can be censored as a result of the original oocyst inoculum administered in the infectivity assay, which in turn influences the outcome of the calculated levels of oocyst inactivation. In (Fig. 5), examining the inactivation data at 5 mJ/cm^2 suggests that a single oocyst inactivation value (>1 log) may be an outlier. Perhaps this inactivation level was derived from administering a lower inoculum of oocysts (i.e., 1×10^3 oocysts) than the inoculum size (i.e., 1×10^5 oocysts) used in our study. Should this be the case, then it would argue that our data provide a more robust indication of the levels of oocyst inactivation than those generated from censored data. Furthermore, examining the general oocyst inactivation patterns for increasing UV doses in (Fig. 5) adds further credibility to the previous discussion, as data accrued during the course of our study both overlap and extend the general trend in oocyst inactivation provided by previous UV disinfection studies. This would further support the finding that oocyst inactivation levels at 5 mJ/cm^2 are more likely to be greater than 3 or 4 logs.

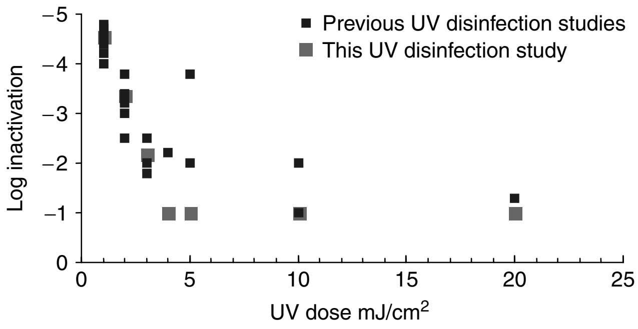

Figure 5. *Cryptosporidium parvum* oocyst inactivation in various UV disinfection studies.

In conclusion, UV disinfection is a promising technology for rapid and effective inactivation of waterborne *C. parvum* oocysts. Numerous manufacturers can supply equipment using medium-pressure, low-pressure, or low-pressure, high-output lamps within their UV reactors. For water utilities to select the appropriate UV reactors for their disinfection requirements, it is imperative that reactors are validated on-site or off-site using the matrices intended for disinfection. Although the validation studies are likely to be conducted using surrogate organisms such as the MS2 bacteriophage, it is imperative to do control- or bench-scale studies also using the same matrix and *C. parvum* oocysts. For the latter, the cell culture-IFA procedure described in this article is an invaluable analytical tool.

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BIBLIOGRAPHY

1. Wilson, B.R., Roessler, P.F., Van Dellen, E., Abbaszadegan, M., and Gerba, C.P. (1992). Coliphage MS 2 as a UV water disinfection efficacy test surrogate for bacterial and viral pathogens. *Proc. Water Qual. Technol. Conf.*, Nov. 15–19, Toronto.
2. Wiedenmann, A. et al. (1993). Disinfection of hepatitis A virus and MS 2 coliphage in water by ultraviolet irradiation: Comparison of UV susceptibility. *Water Sci. Technol.* **27**: 335–338.
3. Karanis, P. (1992). UV sensitivity of protozoan parasites. *J. Water Supply Res. Technol. Aqua* **41**: 95.
4. Lorenzo-Lorenzo, M.J., Ares-Mazas, M.E., Villacorta-Martinez de Maturana, I., and Duran-Oreiro, D. (1993). Effect of ultraviolet disinfection of drinking water on the viability of *Cryptosporidium parvum* oocysts. *J. Parasitol.* **79**: 67–70.
5. Campbell, A.T., Robertson, L.J., Snowball, M.R., and Smith, H.V. (1995). Inactivation of oocysts of *Cryptosporidium parvum* by ultraviolet irradiation. *Water Res.* **29**: 2583–2586.
6. Clancy, J.L., Hargy, T.M., Marshall, M.M., and Dyksen, J.E. (1998). Inactivation of *Cryptosporidium parvum* oocysts in water using ultraviolet light. *J. Am. Water Works Assoc.* **90**: 92–102.
7. Bukhari, Z., Hargy, T.M., Bolton, J.R., Dussert, B., and Clancy, J.L. (1999). Inactivation of *Cryptosporidium parvum* oocysts using medium-pressure ultraviolet Light. *J. Am. Water Works Assoc.* **91**: 86–94.
8. Bukhari, Z. et al. (2000). Comparison of *Cryptosporidium parvum* viability and infectivity assays following ozone treatment of oocysts. *Appl. Environ. Microbiol.* **66**: 2972–2980.

9. Craik, S.A., Finch, G.R., Bolton, J.R., and Belosevic, M. (2000). Inactivation of *Giardia muris* cysts using medium pressure ultraviolet radiation in filtered drinking water. *Water Res.* **34**: 4325–4332.
10. John, D.E., Nwachuku, N., Pepper, I.L., and Gerba, C.P. (2003). Development and optimization of a quantitative cell culture infectivity assay for the microsporidium *Encephalitozoon intestinalis* and application to ultraviolet light inactivation. *J. Microbiological Methods* **52**: 183–196.
11. Di Giovanni, D.D., Hashemi, F.H., Shaw, N.J., Abrams, F.A., LeChevallier, M.W., and Abbaszadegan, M. (1999). Detection of infectious *Cryptosporidium parvum* oocysts in surface and filter backwash water samples by immunomagnetic separation and integrated cell culture-PCR. *Appl. Environ. Microbiol.* **65**: 3427–3432.
12. Clancy, J.L., Bukhari, Z., Hargy, T.M., Bolton, J.R., Dussert, B., and Marshall, M.M. (2000). Using UV to inactivate *Cryptosporidium*. *J. Am. Water Works Assoc.* **92**: 97–104.
13. Bukhari, Z. and LeChevallier, M.W. (2004). Finished water disinfection with UV light: Overview of validation studies at American Water. *IUVA News* **6**: 15–20.
14. Landis, H.E., Thompson, J.E., Robinson, J.P., Blatchley, E.R. (2000). Inactivation responses of Cryptosporidium parvum to UV radiation and gamma radiation. *Proceedings of the Water Quality Technology Conference*, Salt lake City, November 5–9.
15. Shin, G.A., Linden, K.G., Arrowood, M., and Sobsey, M. (2001). Low pressure UV inactivation and subsequent repair potential of Cryptosporidium parvum oocysts. *Appl. Environ. Microbiol.* **67**: 3029–3032.

DECHLORINATION

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Dechlorination is the practice of removing all or a specified fraction of total residual chlorine. In potable water practice, dechlorination is used to reduce the residual chlorine to a specified level at a point where the water enters the distribution system. Dechlorination has been beneficial for waters that are burdened with high concentrations of ammonia nitrogen and organic nitrogen. In some cases where taste and odor control is a severe problem, control is achieved by complete dechlorination, followed by rechlorination. This removes the taste-producing nuisance residuals and prevents the formation of nitrogen trichloride (NCl_3) in the distribution systems. Dechlorination of wastewater and power plant cooling water is required to eliminate residual chlorine toxicity, which is harmful to the aquatic life in the receiving waters. Other special applications requiring dechlorination are ahead of demineralizers, boiler makeup water, certain food plant operations, bottled water, and the beverage industry. In these cases, the dechlorination process is arranged to remove all residual chlorine.

The most practical method of dechlorination is by sulfur dioxide and/or aqueous solutions of sulfite compounds. Among sulfur/sulfite compounds, sulfur dioxide (SO_2) is the most widely used chemical for dechlorination. Other compounds such as sodium bisulfite ($NaHSO_3$) and sodium metabisulfite ($Na_2S_2O_5$) can be used as practical alternatives to sulfur dioxide. Sodium thiosulfate ($Na_2S_2O_3$) is another chemical that is used entirely as a laboratory dechlorinating chemical. Other methods used for dechlorination are granular-activated carbon and aeration.

Free and combined residual chlorine can be effectively reduced by sulfur dioxide and sulfite salts. Free chlorine is the amount of chlorine available as dissolved chlorine gas (Cl_2), hypochlorous acid (HOCl), and hypochlorite ion (OCl^-) that is not combined with ammonia (NH_3) or any other compounds in water. Combined chlorine is the sum of species composed of free chlorine and ammonia, including monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine or nitrogen trichloride (NCl_3). The sulfite ion is the active agent when sulfur dioxide or sulfite salts are dissolved in water. Their dechlorination reactions are identical. Sulfite reacts instantaneously with free and combined chlorine. Reactions yield small amounts of acidity, which is neutralized by the alkalinity of water (2.8 milligrams of alkalinity as calcium carbonate is consumed per milligram of chlorine reduced). Most potable waters and wastewaters have sufficient alkalinity buffering power that there is no cause for concern about lowering the pH by sulfur dioxide addition. The amount of sulfur dioxide required per part of chlorine is 0.9, but in actual practice, this ratio can be as high as 1.05. Owing to the low vapor pressure of sulfur dioxide, special precaution must be taken when using ton containers to prevent reliquefication. Unlike chlorination, dechlorination with sulfur dioxide does not require any contact chamber as the reaction occurs in a matter of seconds, probably 15–20 s at the most. There has been some apprehension about the possibility that excess sulfur dioxide might consume a significant amount of dissolved oxygen in the receiving waters downstream from a dechlorinated water discharge. In properly controlled systems, this reaction does not have sufficient time for completion. Hence, little effect on dissolved oxygen concentration has been reported.

Granular and powdered carbon may be used to dechlorinate free, and some combined, chlorine residuals. The carbon requirements for dechlorination are typically determined by on-site pilot testing. The parameters of significance include mean particle diameter of carbon (pressure drop within the carbon contactor) and influent quality (pH, organics, and colloids). Carbon doses in the range of 30 to 40 mg/L have been reported. Granular-activated carbon (GAC) has proved effective and reliable as a dechlorination agent in potable water treatment. In addition, carbon provides filtration that removes other undesirable materials. In wastewater treatment, however, GAC has not been successful as a dechlorinating agent, possibly, because GAC is poor at removing organochloramines that form when significant concentrations of organic nitrogen are present. Because of the higher cost of carbon systems, their use is typically limited to specific sites or effluent with special discharge limitations. An aeration process can be used for dechlorination. Chlorine, hypochlorous acid, chlorine dioxide, and nitrogen trichloride are sufficiently volatile to be removed by aeration.

READING LIST

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, New York.

Fair, G.M., Geyer, J.C., and Okun, D.A. (1968). *Waste and Wastewater Engineering*. John Wiley & Sons, New York.

WEF. (2002). *Chlorination/Dechlorination Handbook*. Water Environment Federation, Alexandria, VA.

WEF/ASCE. (1998). *Design of Municipal Wastewater Treatment Plants*, 4th Edn. Water Environment Federation, Alexandria, VA.

White, G.C. (1999). *Handbook of Chlorination and Alternative Disinfectants*, 4th Edn. John Wiley & Sons, New York.

DESALINATION

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INTRODUCTION

Desalination is the production of fresh, low-salinity potable water from a saline water source (seawater or brackish water) via membrane separation or evaporation. The mineral/salt content of the water is usually measured by the water quality parameter, total dissolved solids (TDS), in milligrams per liter (mg/L) or parts per thousand (ppt). The World Health Organization and the United Sates Environmental Protection Agency (EPA), under the Safe Drinking Water Act, have established a maximum TDS concentration of 500 mg/L as a potable water standard. This TDS level can be used as a classification limit to define potable (fresh) water. Typically, water of TDS concentration higher than 500 mg/L and lower or equal to 15,000 mg/L is classified as brackish. Natural water sources such as sea, bay, and ocean waters that usually have TDS concentrations higher than 15,000 mg/L are generally classified as seawater. For example, Pacific Ocean seawater along the U.S. West Coast has a TDS concentration of 35,000 mg/L, of which approximately 75% is sodium chloride. Approximately 97.5% of the water on our planet is located in the oceans and therefore is classified as seawater. Of the 2.5% of the planet's fresh water, approximately 70% is polar ice and snow, and 30% is groundwater, river and lake water, and air moisture. So even though the volume of the earth's water is vast, less than 10 million of the 1400 million cubic meters of water on the planet are of low salinity and are suitable for use after using only conventional water treatment. Desalination provides a means for tapping the world's main water resource—the ocean.

During the past 30 years, desalination technology has made great strides in many arid regions of the world such as the Middle East and the Mediterranean. Today, desalination plants operate in more than 120 countries worldwide, and some desert states, such as Saudi Arabia and the United Arab Emirates, rely on desalinated water for more than 70% of their water supply. According to the 2003 desalination plant inventory report prepared by the International Desalination Association (1), by the end of 2001, worldwide there were 15,233 desalination plants whose total installed treatment capacity is 32.4 million cubic meters per day (8560 MGD).

Seawater or brackish waters are typically desalinated using two general types of water treatment technologies—thermal evaporation (distillation) and membrane separation. Currently, approximately 43.5% of the world's desalination systems use thermal evaporation technologies. This percentage has been decreasing steadily during the past 10 years due to the increasing popularity of membrane desalination, which is driven by remarkable advances in membrane separation and energy recovery technologies and associated reduction of overall water production costs.

THERMAL DESALINATION

All thermal desalination technologies use distillation (heating of source water) to produce water vapor that is then condensed into low-salinity potable water. Thermal desalination is most popular in the Middle East, where seawater desalination is typically combined with power generation, which provides low-cost steam for distillation. Thermal desalination requires a large quantity of steam. The ratio of the mass of potable water produced to the mass of heating steam used to produce this water is commonly referred to as a gain output ratio (GOR) or performance ratio. Depending on the thermal desalination technology used, site-specific conditions, and the source water quality, the GOR varies between 2 and 24. The thermal desalination technologies most widely used today are multistage flash distillation (MSF), multiple effect distillation (MED), and vapor compression (VC).

Multistage Flash Distillation

In the MSF evaporator vessels (flash stages or effects), high-salinity source water is heated, whereas the vessel pressure is reduced to a level at which the water vapor "flashes" into steam. Each flash stage (effect) has a condenser to turn the steam into distillate. The condenser is equipped with heat exchanger tubes that are cooled by the source water fed to the condensers. An entrainment separator removes high-salinity mist from the low-salinity rising steam. This steam condenses into pure water (distillate) on the heat exchanger tubes and is collected in distillate trays from where it is conveyed to a product water tank. Historically, MSF is the first commercially available thermal desalination technology used to produce potable water on a large scale, which explains its popularity. More than 80% of the thermally desalinated water today is produced in MSF plants. The GOR for the MSF systems is typically between 2 and 8. The pumping power required to operate MSF systems is 2.0 to 3.5 kWh per cubic meter of product water.

Multiple Effect Distillation

In the MED process, the source water passes through a number of evaporators (effects or chambers) connected in series and operating at progressively lower pressures. In MED systems, the steam vapor from one evaporator (effect) is used to evaporate water from the next effect. MED desalination systems typically operate at lower temperatures than MSF plants (maximum brine concentrate temperature of 75 °C vs. 115 °C) and yield higher GORs. The newest MED technologies, which include vertically positioned effects (vertical tube evaporators or VTEs), may yield GORs up to 24 kilograms of potable water per kilogram of steam. The pumping power required to operate MED systems is also lower than that typically needed for MSF plants (0.8 to 1.4 kWh per cubic meter of product water). Therefore, MED is now increasingly gaining ground over MSF desalination, especially in the Middle East where thermal desalination is still the predominant method for potable water production from seawater.

Vacuum Compression

The heat source for VC systems is compressed vapor produced by a mechanical compressor or a steam jet ejector rather than a direct exchange of heat from steam. In these systems, the source water is evaporated and the vapor is conveyed to a compressor. The vapor is then compressed to increase its temperature to a point adequate to evaporate source water sprayed over a tube bundle through which the vapor is conveyed. As the compressed vapor exchanges its heat with the new source water that is being evaporated, it condenses into pure water. VC desalination has been used mostly for small municipal and resort water supply systems and industrial applications. The power required to operate mechanical VC systems is typically between 10 and 20 kWh per cubic meter of product water. Further discussion of the applicability of the thermal desalination technologies described is presented elsewhere (2,3).

MEMBRANE DESALINATION

Membrane desalination is a process of separating minerals from source water using semipermeable membranes. Two general types of technologies are currently used for membrane desalination—reverse osmosis (RO) and electrodialysis (ED). In reverse osmosis, the product water (permeate) is separated from the salts in the source water by pressure-driven transport through a membrane. By the RO process, desalinated water is transported under pressure through the membrane while the minerals of the source water are concentrated and retained by the membrane. Applying high pressure for desalination is mainly needed to overcome the naturally occurring process of osmosis, which drives the desalinated water back through the membrane into the water of more concentrated mineral content. Nanofiltration (NF) is a process similar to RO, where membranes whose order-of-magnitude larger pore size is used to remove high-molecular-weight compounds that make water hard (i.e., calcium and magnesium).

Desalination by Electrodialysis

In ED-based treatment systems, the mineral–product water separation is achieved by applying electrical direct current (DC) to the source water, which drives the mineral ions in the source water through membranes to a pair of electrodes of opposite charge. A commonly used desalination technology that applies the ED principle is electrodialysis reversal (EDR). In EDR systems, the polarity of the electrodes is reversed periodically during the treatment process.

The energy for ED desalination is proportional to the amount of salt removed from the source water. TDS concentration and source water quality determine to a great extent which of the two membrane separation technologies (RO or ED) is more suitable and cost-effective for a given application. Typically, ED membrane separation is cost-competitive for source waters whose TDS concentration is lower than 2000 mg/L. The TDS removal efficiency of ED desalination systems is not affected by nonionized compounds or objects of weak ion charge (i.e., solids particles, organics, and microorganisms). Therefore, the ED membrane desalination process can treat source waters of higher turbidity, biofouling, and scaling potential than RO systems. However, the TDS removal efficiency of ED systems is typically lower than that of RO systems (15 to 90% vs. 99.0% to 99.8%), which is one key reason why they are used mainly for brackish water desalination.

Reverse Osmosis Desalination

Reverse osmosis desalination is the most widely used membrane separation process today. Currently, there are more than 2000 RO membrane seawater desalination plants worldwide whose total production capacity is in excess of 3 million cubic meters per day (800 MGD). For comparison, the number of ED plants in operation is less than 300, and their total production capacity is approximately 0.15 million cubic meters per day (40 MGD).

RO membrane desalination plants include the following key components: a source water intake system, pretreatment facilities, high-pressure feed pumps, RO membrane trains, and a desalinated water conditioning system. The source water intake system could be an open surface water intake or a series of seawater beach wells or brackish groundwater wells. Depending on the source water quality, the pretreatment system may include one or more of the following processes: screening, chemical conditioning, sedimentation, and filtration. Figure 1 shows a typical configuration of a seawater RO membrane system. The filtered water produced by the plant's pretreatment system is conveyed by transfer pumps from a filtrate water storage tank through cartridge filters and into the suction pipe of the high-pressure RO feed pumps. The cartridge filters are designed to retain particles of 1 to 20 microns that have remained in the source water after pretreatment. The main purpose of the cartridge filters is to protect the RO membranes from damage. The high-pressure feed pumps are designed to deliver the source water to the RO membranes at a pressure required for membrane separation of the freshwater from the salts, typically 15 to 35 bars (200 to 500 psi) for brackish source water and 55 to 70 bars (800 to 1,000 psi) for seawater. The feed pressure required is site-specific and is mainly determined by the source water salinity and the configuration of the RO system.

The "engine" of every desalination plant that turns seawater into fresh potable water is the RO membrane element (Fig. 2). The most widely used RO membrane element consists of two membrane sheets glued together

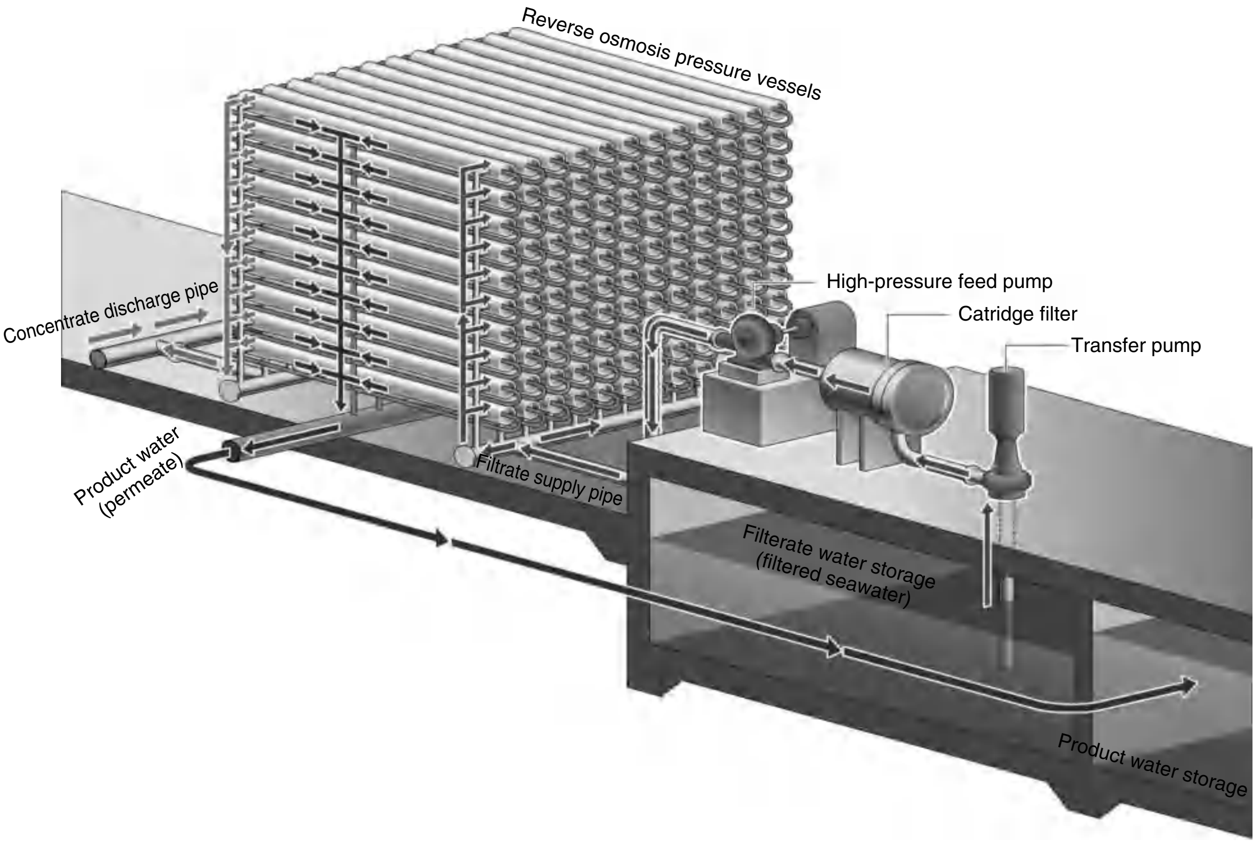

Figure 1. RO membrane train.

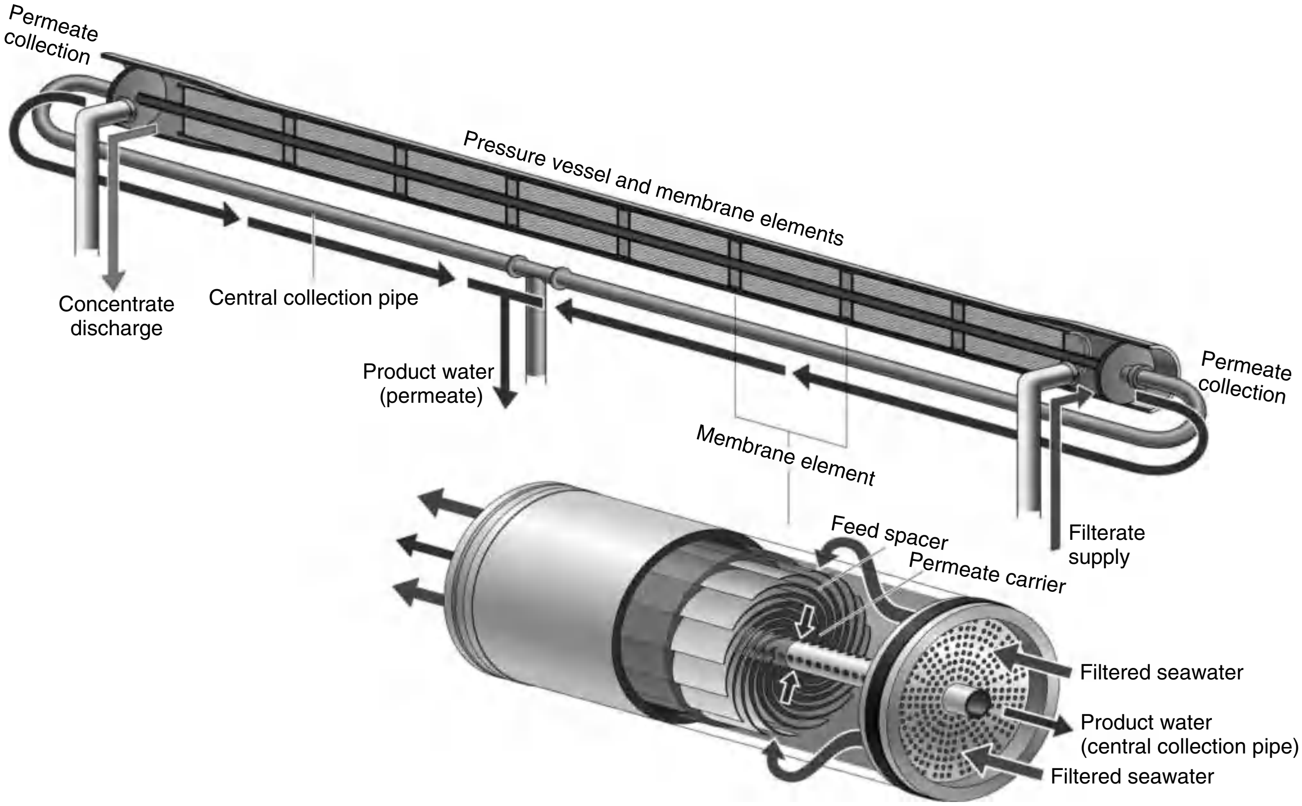

Figure 2. RO membrane vessel.

and spirally wound around a perforated central tube through which the desalinated water exits the membrane element. The first membrane sheet, which actually retains the source water minerals on one side of the membrane surface, is typically made of thin-film composite polyamide and has microscopic pores that can retain compounds smaller than 200 daltons. This sheet, however, is usually less than 0.2 microns thick, and to withstand the high pressure required for salt separation, it is supported by a second thicker membrane sheet, which is typically made of higher porosity polysulfone that has several orders-of-magnitude larger pore openings. The commercially available membrane RO elements today are of standardized diameter, length, and salt rejection efficiency. For example, the RO membrane elements most commonly used for potable water production in large-scale plants are 8 in. in diameter, 40 in. long, and can reject 99.5% or more of the TDS in the source water. Standard membrane elements have limitations with respect to a number of performance parameters such as feed water temperature (45 °C), pH (minimum of 2 and maximum of 10), silt density index (less than 4), chlorine content (not tolerant to chlorine in measurable amounts), and feed water pressure [maximum of 80 to 100 bars (1100 to 1400 psi)].

During reverse osmosis, the water molecules move through the RO membranes at a rate commonly referred to as flux. Membrane flux is expressed in cubic meters per second per square meter (m^3/sm^2) or gallons per day per square foot (gfd) of active membrane surface area. For example, a typical seawater membrane RO element is operated at 8 to 10 gfd.

Membrane performance tends to deteriorate over time due to a combination of wear and tear and irreversible fouling of the membrane elements. Typically, membrane elements have to be replaced every 3 to 5 years to maintain their performance in water quality and power demand for salt separation. Improvements in membrane element polymer chemistry and production processes have made the membranes more durable and have extended their useful life. Elaborate conventional media pretreatment technologies and ultra- and microfiltration membrane pretreatment systems prior to RO desalination are expected to extend membrane useful life to 7 years and beyond, thereby reducing the costs for their replacement and the overall cost of water.

RO membrane elements are installed in pressure vessels that usually house six to eight elements per vessel (see Fig. 2). Multiple pressure vessels are arranged on support structures (racks) that form RO trains. Each RO train is typically designed to produce between 10% and 20% of the total amount of the membrane desalination product water flow. Figure 1 depicts one RO train.

After the RO salt/water separation is complete, a great portion of the feed water energy applied through the high-pressure RO pumps stays with the more concentrated seawater and can be recovered and reused to minimize the overall energy cost of seawater desalination. Dramatic improvements in membrane elements and energy recovery equipment during the last 20 years coupled with enhancements in the efficiency of RO feed pumps and reduction of the pressure losses through the membrane elements have allowed reducing the power to desalinate seawater to less than 3.5 kWh/m^3 (13.5 kWh/1000 gallons) of freshwater produced today. Considering that the cost of power is typically 20% to 30% of the total cost of desalinated water, these technological innovations have contributed greatly to reducing the overall cost of seawater desalination. Novel energy recovery systems working on the pressure exchange principle (pressure exchangers) are currently available in the market, and use of these systems is expected to reduce further desalination power costs by approximately 10% to 15%. The pressure exchangers transfer the high pressure of the concentrated seawater directly into the RO feed water at an efficiency exceeding 95%. Future lower energy RO membrane elements are expected to operate at even lower pressures and to continue to yield further reduction in the cost of desalinated water.

The ratio between the volume of the product water produced by the membrane desalination system and the volume of the source water used for its production is commonly called recovery and is presented as a percentage of the plant RO system feed water volume. The maximum recovery that can be achieved by a given pressure-driven membrane desalination system depends mainly on the source water salinity and is limited by the magnitude of the osmotic pressure to be overcome by the RO system high-pressure feed pumps and by the scaling potential of the source water. Scaling occurs when the minerals left behind on the rejection side of the RO membrane are concentrated to a level at which they begin to form precipitates (crystalline compounds), which in turn plug the membrane pores and interfere with fresh water transport through the membrane. Typically, desalination plants using brackish source water can achieve 65% to 85% recovery. Seawater desalination plants can turn only 40% to 60% of source water into potable water because seawater typically has an order of magnitude higher salinity than brackish water. Detailed guidelines for designing membrane desalination plants are provided elsewhere (4,5).

DESALINATED WATER QUALITY

When membrane desalination is used to produce potable water, the product water quality depends mainly on the concentration of salts in the source water, the salt-rejection capability of the RO membranes, and the applied membrane feed pressure. In thermal desalination, the product water quality depends mostly on the heating system and temperature, the pressure applied, and the type of distillation technology. The product water quality of thermal desalination systems is significantly less dependent on source water salinity than that produced by a membrane system. This makes thermal distillation processes an attractive alternative for parts of the world, such as the Middle East, where source water TDS is very high (40,000 to 46,000 mg/L) and low-cost steam is readily available.

Typically, thermal desalination processes produce water of very low TDS concentration (1 to 60 mg/L). A single-stage, reverse osmosis system for seawater desalination produces permeate of 250 to 350 mg/L. More elaborate RO systems can produce water of quality matching that of a thermal desalination plant. Usually, the temperature of thermally desalinated water is 2 °C to 5 °C higher than the temperature of water produced by membrane separation.

Desalinated water (permeate) produced by both thermal and membrane desalination is highly corrosive and has to be chemically conditioned (typically by lime addition) to increase product water alkalinity and to adjust pH (usually by addition of chlorine dioxide and/or acid to the lime conditioned permeate) to meet potable water quality regulations.

CONCENTRATE MANAGEMENT

The two main streams produced by every desalination plant are low-salinity freshwater and high-salinity concentrate. The results of a recent study completed by the U.S. Bureau of Reclamation (6) on the concentrate disposal methods most widely used in the United States (in order of decreasing frequency) are shown in Table 1.

Sanitary sewer and surface water discharge are the two most popular and cost-effective methods for concentrate disposal. Depending on the site-specific conditions, deep well injection, evaporation ponds, and spray irrigation can also be competitive concentrate disposal alternatives. The zero liquid discharge system typically has the highest construction and operating costs. However, under specific circumstances, such as cold climate, low evaporation and soil uptake rates, high land costs, and low power costs, the zero liquid discharge system can be cost-competitive with evaporation pond and spray irrigation disposal.

Table 1. Concentrate Disposal Methods and Their Frequency of Use in the United States

Concentrate Disposal Method	Frequency of Use, % of Plants Surveyed
Surface water discharge	45
Sanitary sewer discharge	42
Deep well injection	9
Evaporation ponds	2
Spray irrigation	2
Zero liquid discharge	0

COST OF DESALINATED WATER

Desalination water costs depend on many factors, including the type of treatment technology; the source water quality; the target product water quality; the size of the desalination plant; and the costs of energy, chemicals, labor, and membranes. The all-inclusive cost of potable water produced using a brackish water source treated by membrane separation usually varies between US\$0.25 and \$0.65/m^3 (US\$1.0 to \$2.5/1000 gallons) of product water. Seawater desalination cost is estimated at US\$0.65 to \$1.20/m^3 (US\$2.5 to \$4.5/1000 gallons). For very small plants located in isolated areas, this cost could be significantly higher. For comparison, the cost of water produced from fresh natural water sources (i.e., low-salinity groundwater, lake, and river water) is typically between US\$0.15 and \$0.40/m^3 (\$0.6 and \$1.5/1000 gallons). This cost is driven mainly by the source water quality, the type of treatment technologies used, and the size of the water treatment plant. Developments in seawater desalination technology during the past two decades combined with the transition to construction of large capacity plants, colocation with power plant generation facilities, and enhanced competition by using the build-own-operate-transfer (BOOT) method of project delivery have resulted in a dramatic decrease in the cost of desalinated water (7). These factors are expected to continue to play a key role in further reducing the production cost of desalinated water.

BIBLIOGRAPHY

1. Wagnick Consulting. (2002). IDA *Worldwide Desalination Plant Inventory*. International Desalination Association, pp. 5–1.
2. Water Desalting Committee of AWWA. (2004). *Water Desalting—Planning Guide for Water Utilities*. John Wiley & Sons, New York, p. 14.
3. Pankratz, T. and Tonner, J. (2003). *Desalination.com—An Environmental Primer*, Lone Oak, Houston, TX, p. 29.
4. AWWA. (1999). *Manual of Water Supply Practices—M46. Reverse Osmosis and Nanofiltration*, 1st Edn. American Water Works Association, Denver, CO, p. 21.
5. Watson, I.C. et al. (2003). *Desalting Handbook for Planners*. 3rd ed. Desalination and Water Purification Research Program Report No. 72, U.S. Bureau of Reclamation, p. 85.
6. Mickley, M.C. (2001). *Membrane concentrate disposal: Practices and regulation*. Desalination and Water Purification Research Program Report, U.S. Bureau of Reclamation, p. 229.
7. Voutchkov, N. (2004). The ocean—a new resource for drinking water. *Public Works*, June: 30.

DIATOMACEOUS EARTH FILTRATION FOR DRINKING WATER

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Diatomaceous Earth (DE) filtration is a process that uses diatoms or diatomaceous earth—the skeletal remains of small, single-celled organisms—as the filter media. DE filtration relies upon a layer of diatomaceous earth placed on a filter element or septum and is frequently referred to as pre-coat filtration. DE filters are simple to operate and are effective in removing cysts, algae, and asbestos from water. DE has been employed in many food and beverage applications for more than 70 years and was used specifically to filter potable water during WWII. Since then, it has been used to produce high-quality, low-cost drinking water. DE filtration is currently one of the

U.S. Environmental Protection Agency's (EPA) approved technologies for meeting the requirements of the Surface Water Treatment Rule (SWTR) and is most suitable for small communities that need to comply with the rule.

WHAT IS DE FILTRATION?

DE contains fossil-like skeletons of microscopic water plants called diatoms, which are a type of algae. These diatoms range in size from less than 5 micrometers to more than 100 micrometers, and have a unique capability of extracting silica from water to produce their skeletal structure. When diatoms die, their skeletons form a diatomite deposit. In its natural state, diatomite is 85 percent inert silica. The soluble portion of diatomite is extremely low (less than 1 percent). The odorless, tasteless, and chemically inert characteristics make DE safe for filtering water or other liquids intended for human consumption.

APPLICATION AND HISTORICAL BACKGROUND

During WWII, the U.S. Army needed a new type of water filter suitable for rapid, mobile military operations. The U.S. Army Engineer Research and Development Laboratories (ERDL) developed a DE filter unit that was lightweight, easily transported, and able to produce pure drinking water. Later, DE filtration technology was applied to filtering swimming pool water and more gradually to producing drinking water.

The earliest municipal DE filter installation was a 75,000 gallons per day (gpd) system in Campbell Hills, Illinois, that began operating in 1948. By 1977, municipalities had constructed more than 145 plants. Today, nearly 200 DE plants are successfully operating.

HOW DOES DE FILTRATION WORK?

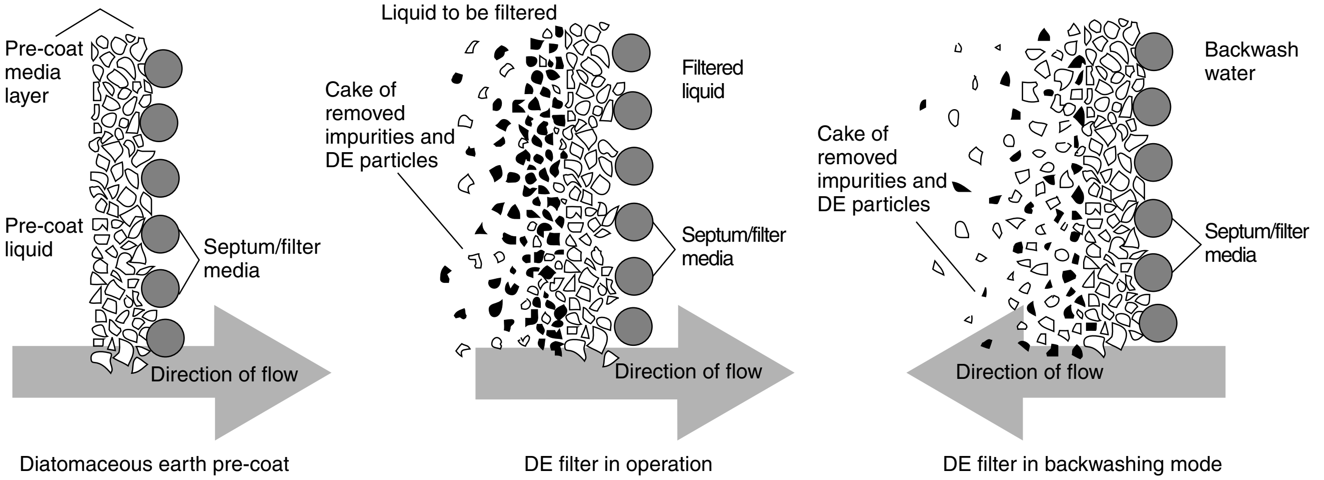
DE filtration strains particulate matter from water, and the process rarely uses coagulant chemicals. First, a cake of DE is placed on filter leaves. A thin protective layer of diatomaceous earth builds up, or accumulates, on a porous filter septum (a permeable cover over interior collection channels) or membrane. Recirculating DE slurry through the filter septum establishes this layer. The septum is most often plastic or metallic cloth mounted on a wire mesh-covered steel frame. The DE process is also called pre-coat filtration because the solids separation at the start of a run takes place on the built-up pre-coat layer of DE.

After the pre-coat forms on the filter leaves (usually 1/8 inch thick) raw water containing a low dose of DE, which is called body feed, is fed through the filter. Particulate solids in the product flow are separated on the pre-coat surface. With such separation, the unwanted particulate matter actually becomes part of the filter media. During a filter run, removing particulate matter from raw water causes head loss to gradually build up in the filter. The accumulation of DE body feed on the filter reduces the rate of head loss. When maximum head loss is reached, the flow of water into the filter is stopped and the filter cake is cleaned.

High-pressure sprays, directed at the accumulated cake, detach the cake and provide dilution for draining the slurry suspension from the filter vessel. When cleaned, the filtration operation is repeated, beginning with the pre-coat cycle (see Fig. 1). Operators typically discard the DE removed from the filter leaves.

APPROPRIATE FEED WATER QUALITY AND PERFORMANCE CAPABILITIES

The use of DE filters is limited to treating source waters with an upper limit of turbidity at 10 NTU. Also, filtration rates range from 0.5 to 2 gallons per minute per square foot (gpm/ft^2). The particle size that DE filtration removes relies upon the size distribution of the DE particles used for the pre-coat and body feed. DE filters are very effective for removing *Giardia* and *Cryptosporidium* cysts. In some cases, studies have reported up to a 6-log reduction of these cysts under routine operating conditions. Because DE filtration usually does not involve coagulation, its potential for removing dissolved constituents, such as color, is low. Therefore, the utility or its engineer must determine raw water quality before considering DE filteration.



Diatomaceous earth pre-coat

DE filter in operation

DE filter in backwashing mode

Figure 1. Diatomaceous earth filter. *Source*: Fulton, George P. 2000. *Diatomaceous Earth Filtration for Safe Drinking Water*.

WHAT ARE THE MONITORING AND OPERATING REQUIREMENTS?

Monitoring requirements for DE filtration are simpler than requirements for coagulation and filtration because operators rarely ever use coagulant chemicals for DE filtration. However, operators must continuously monitor raw and filtered water turbidity. Operators also must monitor filter head loss so that they can determine when to backwash the filter.

In general, DE filter plant operators need mechanical skills to operate the body feed pumps, pre-coat pumps, mixers, pipes, and valves. They also must be skilled in preparing the body feed and precoat slurries. Also, keeping DE filter leaves clean is of primary importance. A leaf filter that is not properly cleaned at the end of a filter run can accumulate dirt and slime on the filter cloth, which prevents a uniform pre-coat from forming when the filter is restored to service.

ELEMENTS OF A DE FILTER

Figure 2 shows the common elements in the manufacture of any flat leaf filter used in treating drinking water. The principal elements of a DE filter include the following:

- containment vessel,
- baffled inlet,
- filter leaves mounted on an effluent manifold,
- a method of cleaning the filter leaves at the end of a run,
- a drain to receive the backwash water,
- open top or access mode, and
- DE slurry preparation tank and pump feed.

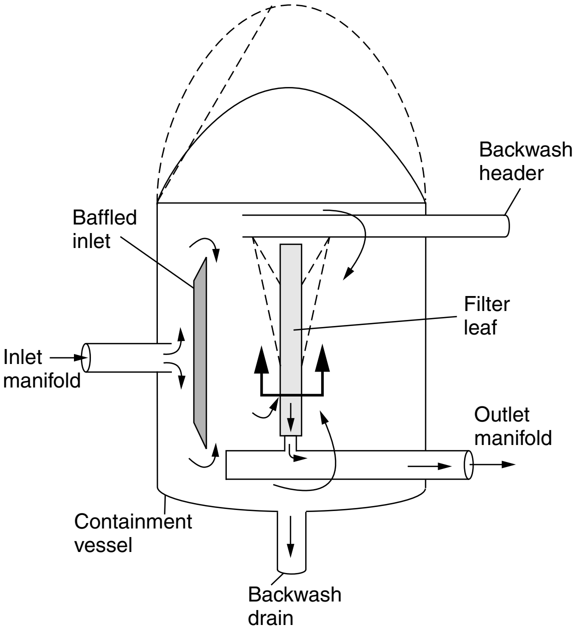


Figure 2. Elements of a flat leaf filter. *Source*: Fulton, George P. 2000. *Diatomaceous Earth Filtration for Safe Drinking Water*.

TYPES OF DE FILTRATION

Two types of DE filters exist: (1) *pressure filters*, which have a pump or high-pressure water source on the influent side and (2) *vacuum filters*, which have a pump on the effluent side. Vacuum filters are open to the atmosphere. Pressure filters are enclosed within pressure vessels.

The two basic groupings of DE filter designs are essentially defined by the hydraulic mode of operation, and are shown in (Fig. 3a and 3b).

The principal advantages of pressure filters over the vacuum filters are related to the significantly higher differential head available.

Table 1. Pressure and Vacuum Filters

Pressure Filters	Vacuum Filters
• Operates at higher flowrates, resulting in smaller, more compact filter units.	• Lower capital fabrication cost.
• Longer filter runs, reducing the use of pre-coat material and backwash water because of less frequent cleaning cycles.	• Lower maintenance costs.
• Less likelihood that gas bubbles will disrupt the media.	• Tanks are open at the top, making access and observation easy.

Source: Mel J. Mirliss, Vipin Bhardwaj, and the National Drinking Water Clearinghouse.

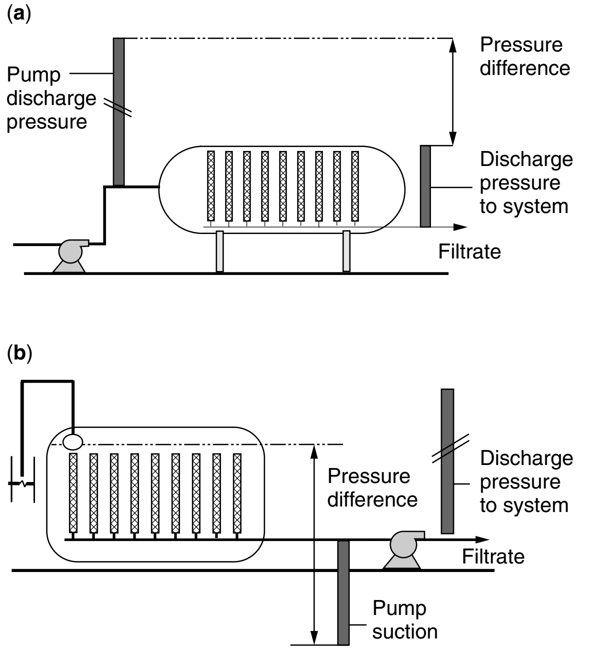


Figure 3. (**a**) Pressure filter. (**b**) Vacuum filter. *Source*: Fulton, George P. 2000. *Diatomaceous Earth Filtration for Safe Drinking Water*.

IS DE SUITABLE FOR SMALL SYSTEMS?

DE filtration is well-suited to small systems, because it does not require chemical coagulation, so operators do not need to learn about this complex aspect of water treatment. In addition, installation costs for DE systems are less than those for other technologies, such as membranes. DE filtration is currently one of the EPA's approved technologies for meeting SWTR requirements.

An ideal, cost-effective DE filtration application is for well water supplies under the influence of surface waters, but that are otherwise acceptable in quality. Superior cyst removal capability makes the DE filter more advantageous than other alternatives. However, there is a potential difficulty in maintaining complete and uniform thickness of DE on the filter septum.

WHERE CAN I FIND MORE INFORMATION?

- Fulton, George P., P.E. (2000). *Diatomaceous Earth Filtration for Safe Drinking Water*. American Society of Civil Engineers, Reston, VA.
- "Precoat Filtration." 1988. AWWA M30, *Manual of Water Supply Practices*. American Water Works Association, Denver, CO.
- *Technologies for Upgrading or Designing New Drinking Water Treatment Facilities*, EPA/625/4-89/023. (Available from the EPA) or contact the National Drinking Water Clearinghouse.

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READING LIST

Fulton, George P. 2000. *Diatomaceous Earth Filtration for Safe Drinking Water*. American Society of Civil Engineers, Reston, VA.

Safe Water from Every Tap, 1997. *Improving water service to small communities.* National Research Council, National Academy Press, Washington, DC.

Schuler, P.F., Gosh M.M., and Boutros S.N. 1988. *Comparing the removal of Giardia and Cryptosporidium using slow sand and diatomaceous earth filtration.* pp. 789–805, *Proceedings of 1988 AWWA Conference*, Denver, CO.

Ongerth, J.E., Hutton, PE December 1997. DE filtration to remove *Cryptosporidium*. *Journal of American Water Works Association*. American Water Works Association, Denver, CO.

Small System Compliance Technology List for the Surface Water Treatment Rule and Total Coliform Rule, 1998. U.S. Environmental Protection Agency, 815-R-98-001.

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EMERGING WATERBORNE INFECTIOUS DISEASES

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Humanity is plagued at present by at least 1709 different infectious diseases. These diseases are caused by pathogens, which are microscopic and parasitic organisms of diverse natures, including infectious proteins (prions), viruses, bacteria, fungi, and protozoa. Compared to diseases like cancer and metabolic diseases that have genotypic roots, including heart disease, diabetes, and the like, progress in the fight against infectious diseases has been rapid during the last half century. Whereas infectious diseases such as smallpox, measles, polio, rabies, plague and numerous other bacterial diseases have once been a global scourge, many of these diseases have now become controllable due to spectacular advances in public health practices, including improvements in the quality of water and sanitation and by immunization, education, early diagnosis, and the use of antibiotics/antimicrobials and other drug therapies. However, globally, 45% of all deaths and 63% of early childhood deaths are still caused by infectious diseases.

INFECTIOUS DISEASES, EMERGING DISEASES, AND ZOONOSES

New, emerging, reemerging, and resurgent infections contribute significantly to the infectious disease problems that the world is experiencing now. At least 156 such diseases have now been identified. Taken from a report by the Institute of Medicine (1), emerging infections may be defined as follows: "emerging infections are those whose incidence in humans has increased within the past two decades or threatens to increase in the near future. Emergence may be due to the spread of a new agent, to the recognition of an infection that has been present in the population but has gone undetected, or to the realization that an established disease has an infectious origin. Emergence may also be used to describe the reappearance (or "reemergence") of a known infection after a decline in incidence." Generally, new diseases are synonymous with emerging diseases and can be regarded as diseases first described in the last 10 to 30 years. Most of these diseases are caused by specific modifications (mutation/evolution, species jump, etc.) of agents that are already in the environment. Reemerging diseases are those that have persisted at a subdued level in the population and recur as a result of antimicrobial drug resistance or other changes that might favor marked increases in disease incidence. Reemerging diseases can also be described as resurgent, pertinently referring to an abrupt increase in incidence or geographic distribution of the particular disease. The emergence and reemergence of diseases are clearly related to changes in the infectious pathogen, the vector or transmission system, and the host population. Such epidemiologically important changes may include drug resistance and mutations resulting in increased virulence, changes in the distribution or activity of vectors, globalization and increased travel, war, population explosions, climatic and ecological changes, geographical displacement of species, movement into previously uninhabited areas, poverty and breakdown of health care systems, and changes in agriculture and industrialization. Six infectious diseases can be identified as current, leading, high mortality rate diseases, and all of them conform to the criteria for emergence described before: AIDS, acute respiratory infection, diarrheal diseases, malaria, measles, and tuberculosis.

A great many infectious diseases are zoonoses: These are diseases that are naturally transmitted between vertebrate animals and man—49% or 832 of all known infectious diseases can be considered zoonoses. A fair number of infectious diseases of man started out as zoonotic events but have since established a much more important human-to-human epidemiological cycle (e.g., HIV-AIDS, dengue hemorrhagic fever). Strikingly, however, 73% of all the emerging diseases considered (114 of 156) are zoonoses. Infectious diseases are typically transmitted through direct contact, insect vectors, sexual contact, respiratory tract (aerosolized microbes), and by contaminated food and water. Here we are concerned with waterborne infection, with pathogen entry through the mouth and alimentary track or, in some instances, through epithelial cells of the respiratory system.

WATERBORNE INFECTIOUS DISEASES: THE SPECTRUM OF PATHOGENS

Human and animal fecal pollution of water sources is the leading cause of waterborne infections. This fecal–oral route of infection contributes to hundreds of millions of cases of diarrhea and millions of deaths (particularly among children) every year. Clearly, improved water sanitation that leads to safe drinking water for all of humanity would be the ultimate solution. Some emerging waterborne infections do not enter through the oral route but through the respiratory route. These infections are attributed to specific pathogens that have been made airborne through water spraying in nurseries, flower and vegetable markets, personal showers, and the like.

Viral Agents

Many waterborne diseases are caused by viruses, which include adenoviruses (types 40 and 41), astroviruses, caliciviruses (including Norwalk and hepatitis E viruses), Enteroviruses (picornaviruses), and reoviruses (including rotaviruses). By far the most common medical condition associated with waterborne viral infection is diarrhea. The medical and economic importance of viral diarrhea should not be underestimated, millions of deaths (particularly, of children) are caused by these infections. At present, only a handful of these viral diseases is considered emerging and the most important of them, astrovirus enteritis, calicivirus enteritis, and hepatitis (E), are specifically discussed here.

Bacterial Agents

Increased resistance to antibiotics is a major factor in the resurgence of common bacterial infectious diseases and epidemic bacterial diarrhea such as those caused by waterborne *Escherichia coli, Shigella*, and *Vibrio*. The use of antimicrobials in agriculture has significantly contributed to this phenomenon, although evolution and adaptation of organisms have also led to converting nonpathogens into pathogens by adding of toxin producing capability. In addition, new bacterial zoonoses emerge, and some human pathogens are newly recognized, thanks to rapidly improving diagnostic techniques. This, as well as the reemergence of pathogens due to immune deficiencies related to HIV/AIDS, applies to the whole spectrum of infectious disease agents.

Protozoal Agents

These parasites typically are contaminants of potable water supplies. Whereas inadequate sanitation and chlorination of water supplies should prevent most of the waterborne bacterial diseases, large outbreaks of protozoan enteritis are usually associated with surface water supplies that are inadequately flocculated and filtered or not treated at all (many of these pathogens are chlorine resistant). In the last decade, enteric protozoa have become the leading cause of waterborne disease outbreaks for which an etiologic agent could be identified. The most common of these infections are caused by *Cryptosporidium* and *Giardia*, *Cyclospora* has also recently emerged as an enteric protozoan.

SPECIFIC EMERGING WATERBORNE INFECTIOUS DISEASES

Aseptic Meningitis and Various Other Syndromes

These diseases are caused by enteroviruses, viruses that—as their name suggests, replicate in the intestinal tract. Enteroviral infection is one of the most common types of viral infections in humans, but they do not often result in serious disease, although some serotypes of enteroviruses may cause serious clinical syndromes. Such syndromes may include acute paralysis, encephalitis, meningitis, myocarditis, hepatitis, and chronic infection (particularly in immunocompromised individuals). Enteroviruses belong to the *Enterovirus* genus of the *Picornaviridae* family and include the polioviruses, group A Coxsackieviruses, group B Coxsackieviruses, echoviruses, and (newer) enteroviruses. There are 3 different polioviruses, 61 nonpolio enteroviruses, 23 Coxsackie A viruses, 6 Coxsackie B viruses, 28 echoviruses, and 4 other enteroviruses. Enteroviruses evolve rapidly and emerge as new strains, but others are of emerging importance due to drug resistance. Some enterovirus serotypes have been responsible for serious, large epidemics throughout the world in recent years. Echovirus infections have been responsible for several large epidemics of aseptic meningitis in Japan, Europe, and the Middle East in the past years. These epidemics involved different highly infectious serotypes of the virus, types 4, 9, and 30, but also of new genetic variants of these viral serotypes. Enterovirus 71 (EV71) has caused major disease outbreaks in North America, Europe, Malaysia, Japan, and Australia since 1995. In 1998, this virus infected at least a million individuals in Taiwan and caused a 20% case fatality among children under 5 years of age.

Astrovirus Enteritis

Today, astroviruses are considered much more prevalent than previously thought (e.g., 75% of 5 to 10-year-old children in Britain demonstrate antibodies against astroviruses). These are small, round viruses that have a starlike appearance under the electron microscope. Following a 1 to 4-day incubation period, the clinical symptoms present as watery diarrhea that lasts 2–3 days. These gastrointestinal disorders are usually not serious, but astroviruses are a leading cause of childhood diarrhea, and dehydration may be especially severe in immunocompromised individuals.

Calicivirus Enteritis

This disease, caused by a group of small cuplike viruses, is very common—serological evidence indicates that most people are infected by age 12. The symptoms are diarrhea with nausea and vomiting. Fever and respiratory infection occur in a small number of cases. It is thought that these viruses emerged from ocean reservoirs, with subsequent zoonotic and interspecies movement. Among the known calicivirus pathogens of humans are the Norwalk and Norwalk-like viruses and the Sapporo and Sapporo-like viruses. Although it is thought that pathogenic caliciviruses are likely to continue emerging from the world's oceans in various forms, only the Norwalk-like viruses are now and from a public health point of view, of emerging importance. Norwalk-like viruses cause sporadic and epidemic gastroenteritis in all age groups of humans, but losses of fluids and electrolytes are particularly serious in the very young and elderly. Transmission is by the fecal–oral route, and shellfish-related outbreaks frequently occur where appropriate standards for proper disposal of human sewage are not applied. Contaminated water, ice, eggs, salad ingredients, and ready-to-eat foods are other sources of infection.

Campylobacteriosis

This diarrheal disease, caused by *Campylobacter jejuni*, occurs worldwide. Infection by *Campylobacter* species has been known in livestock for many decades, but it has also been recognized as an important pathogen in humans since the middle 1970s. The development of selective media contributed to this recognition, and drug resistance and the emergence of toxin producing strains have recently become of considerable importance. Although this disease is usually self-limiting, treatment with antibiotics may reduce bacterial numbers and the duration of the infection and may be of particular value in cases involving immunocompromised individuals or where complications are evident. From this perspective, the emergence of antibiotic resistant strains of *Campylobacter* all over the world is disconcerting. *Campylobacter jejuni* infections, it is thought are more common than infections by other enteric bacteria such as *Shigella, Salmonella* and *Escherichia coli* O157:H7. Whereas other *Campylobacter* species (e.g., *C. laridis, C. hyointestinalis*) may also be involved in disease, *C. jejuni* is responsible for 99% of the cases. The bacterium is gram-negative, has a curved rod-shaped morphology and is motile. It is highly infectious and symptoms are diarrhea, fever, abdominal pain, nausea, headache, and myalgia. Complications are rare, but the infection may progress toward reactive arthritis, hemolytic uremic syndrome, and septicemia. Guillain-Barre syndrome is also recognized as a rare (1 per 1000 infected individuals) complication leading to disease of the peripheral nervous system.

Cholera

Cholera is caused by the gram-negative, motile, rod-shaped bacterium, *Vibrio cholerae*. The disease, essentially an acute and serious infection of the small intestine with diarrhea that can be severe and is accompanied by dehydration and shock, occurs worldwide. The symptoms associated with cholera are caused by the enterotoxins produced by V*ibrio cholerae* during the infection. Accurate records of cholera date back almost a century, but cholera may have been known in India and elsewhere for thousands of years. This disease may be considered emerging due to new pandemics (serotype O1) and the appearance of pathogenic strains that have evolved by genetic recombination (serotype 0139). The emerging serotype O139 appeared in 1992 and has as yet only been reported from Southeast Asia where it causes epidemics in populations that were previously exposed to other serotypes of the same pathogen. In similar evolutionary fashion, *Vibrio cholerae* can become resistant to antibiotics by acquiring a transposon element and/or a plasmid that confers resistance to multiple antibiotics.

Vibrio cholerae O1, however, caused a pandemic spread over six continents during the past 40 years. The bacterium initially (1960s) spread from Indonesia to Eastern Asia, India, the former USSR, Iran, and Iraq.

Thereafter, in 1970, serotype O1 took hold in West Africa and then became endemic in most of the African continent. In 1991, it spread throughout South and Central America, and involved more than a million known cases at a mortality rate of about 1%. Much higher mortality rates (33%) were observed in 1994 in a large epidemic among Rwandan refugees in Zaire (33%). In recent times, Africa continued to host large cholera epidemics. These included a 1997 outbreak in Kenya, Tanzania, and Mozambique, a 1998 outbreak in Congo and Zaire, and in 2000/2001, a large epidemic in South Africa.

Cryptosporidiosis

The etiological agent of this persistent diarrheal disease is the protozoal parasite *Cryptosporidium parvum*. Together with the AIDS epidemic, cryptosporidiosis emerged in the early 1980s as a zoonosis, after having been known as a veterinareal disease for more than a century. Apart from persistent diarrhea, symptoms may include abdominal pain, nausea, and low-grade fever, and significant weight loss. Infectious oocysts may still be excreted long after diarrheal disease has ended (up to 5 weeks). In the growing number of immunocompromised individuals worldwide, this has become a life-threatening and highly infectious enteric disease. Compounding the threat of this disease is the fact that the pathogen is difficult to filter from water resources, is resistant to chlorine, is ubiquitous in many animals, can survive in infected water for long periods of time, and is highly infectious. It is therefore not surprising that *C. parvum* has now become the major protozoan pathogen of humans. A wide spectrum of water supplies has been implicated and these include contaminated and inefficiently treated/flocculated/filtered drinking water such as from water plants and boreholes or from swimming pools, wading pools, hot tubs, jacuzzis, fountains, lakes, rivers, springs, ponds, and streams. A high rate of secondary person-to-person transmissions in households and institutions has also been documented.

Cyclosporiasis

This protracted, relapsing gastroenteritic disease is similar to cryptosporidiosis and is also caused by a coccidian parasite, in this case, *Cyclospora cayetanensis.* This organism is food- and waterborne, and it emerged in the 1990s as a serious and widespread gastrointestinal parasite. In contrast to the zoonotic *C. parvum*, *C. cayetanensis* is specific to human hosts and is not a known pathogen of vertebrate animals. Cyclosporiasis is most common in tropical and subtropical regions and endemic in Central and South America, Southeast Asia, the Caribbean islands, and parts of Eastern Europe, but large outbreaks have recently been reported in the United States and Canada, reports also came from the United Kingdom and various African countries. Apart from fecally contaminated water, various types of fresh produce such as raspberries, basil, field greens, and salad mixes have been indicated as sources of the pathogen. Although *Cyclospora* oocysts, like *Cryptosporidium* oocysts, are resistant to chlorine, they are double the size of *Cryptosporidium* oocysts and may be more easily removed by flocculation and filtration methods used in water plants. Further, due to the noninfectious nature of newly formed oocysts, secondary person-to-person spread of *Cyclospora cayetanensis* is a much less likely route of transmission than that for cryptosporidiosis.

Dermatitis

This is an inflammation of the skin marked by redness, pain, and itching (skin rashes) that is caused by the gram-negative and rod-shaped bacterium, *Pseudomonas aeruginosa*. Until the recent recognition of waterborne dermatitis caused by *Pseudomonas aeruginosa*, this organism was rarely implicated in disease. The bacterium typically survives in biofilms and antibiotic resistant strains are also appearing, but effective control should be possible by proper water treatment.

Gastritis

Helicobacter pylori, a spiral gram-negative bacterium was first recognized in 1982 as a cause of gastritis. It appears that the human stomach is the only recognized reservoir for this bacterium and infection is common in the general population. Although most infected individuals are asymptomatic and are unlikely to develop a serious medical problem from the infection, *H. pylori* causes 90% of duodenal ulcers and up to 80% of gastric ulcers, and infected persons have a twofold to sixfold increased risk of developing gastric cancer. In fact, *H. pylori* is classified as a group I (or definite) carcinogen by the World Health Organization's International Agency for Research on Cancer. It is not known why some patients become symptomatic and others do not. The transmission of *H. pylori* also remains unclear, although the bacteria are most likely to spread from person to person through fecal–oral or oral–oral routes.

Giardiosis

This disease, one of the most common diarheal diseases spread by drinking and recreational water in the United States and probably worldwide, is caused by the intestinal protozoan parasite *Giardia intestinalis*, also known as *G. lamblia* or *G. duodenalis*. This agent also infects domestic and wild animals (e.g., cats, dogs, cattle, deer, and beavers). Emerging as a widespread and common disease during the past two decades, giardiasis has been traced back to contaminated swimming pools, hot tubs, fountains, lakes, rivers, springs, streams and ponds. As for the other parasitic diseases discussed here, the life cycle begins when cysts are ingested through person-to-person transmission or ingestion of fecally contaminated food or water. The ingested cysts release trophozoites in the duodenum where they attach to the surface of the intestinal epithelium. *Giardia* cysts can be excreted in fecal stools intermittently for weeks or months, and infection of a new host can result from ingestion of as few as 10 cysts.

Hemorrhagic Colitis and Complications

Enterohemorrhagic *Escherichia coli* (EHEC) is another bacterial pathogen that has recently emerged as a major waterborne enteric pathogen. After recognition of waterborne infection by this agent in 1985, the disease has been reported worldwide, and case numbers are ever increasing. Whereas *E. coli* bacteria are usually symbiotic as part of the normal intestinal flora of animals and humans, some strains of the organism can cause disease by producing large quantities of Vero toxins. It is a bacterial virus (or bacteriophage) that carries the toxin gene. When infecting the bacteria, the bacteriophage, integrates into the bacterial genome and from there provides the toxin producing capability. Today, a large number of *E. coli* serotypes that can produce Vero toxins are recognized, but the serotype O157:H7 is the predominant pathogen that is most frequently associated with hemorrhagic colitis in humans. The disease is serious, usually characterized by bloody diarrhea, abdominal cramps and nausea, but more severe complications, known as hemolytic uremic syndrome (HUS)—leading to complete renal failure, may follow. Case fatality rates for *E. coli* O157:H7 range from 3–36%, the fate of patients depends on age and immunocompetence.

Waterborne transmissibility through both drinking and recreational waters together with antibiotic and chlorine resistance and an ability to survive in water for long periods of time, are major factors in the widespread emergence of EHEC. In addition, these organisms are highly infectious and are often spread to humans as zoonoses, EHEC has a very wide host range among domestic animals and wildlife. Outbreaks continue to be recognized worldwide in the United States, Japan (1996—6000 cases), United Kingdom, Australia, Europe, Argentina, Chile, and throughout Africa (e.g., South Africa, Swaziland, Kenya, Nigeria, Cote d'Ivoire, Central Africa Republic, and Egypt). In recent years, a number of efficient diagnostic techniques have been developed for accurate detection of isolate *E. coli* O157:H7, which also allows for distinction from other bacterial enteropathogens (e.g., *Shigella*) with which it may easily be confused due to clinical similarities of disease manifestation.

Hepatitis (Hepatitis E-Like Viruses)

Hepatis virus E (HEV) was isolated for the first time in 1988. This virus was then characterized in subsequent years, and it has recently been placed in its own taxonomic group, "hepatitis E-like viruses", within the class IV (+) sense RNA viruses. The disease is found most frequently in the developing world (e.g., South East Asia, India, Middle East, Africa, and Central America) and is transmitted primarily through the fecal–oral route in contaminated drinking water. Person-to-person transmission of HEV may occur during large epidemics, but this route of transmission appears to be uncommon. The incubation period following exposure to HEV is, on average a lengthy 40 days but may range from 15 to 60 days (mean, 40 days). Diarrhea is a less common symptom in this case, malaise, anorexia, abdominal pain, arthralgia, fever, anorexia, hepatomegaly, jaundice, nausea, and vomiting are more common. The disease is most often seen in young to middle-aged adults (15–40 years old) where the fatality rate is relatively low at 0.1–1%. However, pregnant women appear to be exceptionally susceptible to severe disease, and excessive mortality has been reported in this group (up to 30%). Recent genetic and serological evidence suggests frequent transmission of HEV between animals and humans, and zoonoses may explain the mechanism of HEV maintenance in populations during the periods between epidemic outbreaks.

Legionnaires' Disease

Legionnaires' disease, or legionnellosis, is an acute pneumonia caused by the bacterium *Legionnella pneumophila*. This is a flu-like illness, typically occurring 3 days after exposure and followed within a week by high fever, chills, dry cough, muscle aches and headache. The disease is usually self-limited but can lead to higher mortality in the presence of various risk factors such as immunodeficiency, cigarette smoking, chronic lung diseases, lung malignancies, heart disease, and old age. When this disease was first recognized in the late 1970s, the associated etiological agent was hard to isolate, given that *Legionnella* is a particularly fastidious organism that does not grow on typical culture media. The importance of these waterborne gram-negative, rod-shaped bacilli has since become clear, following the development of suitable diagnostic techniques. Of importance is the fact that these bacteria are parasites of protozoa (e.g., *Amoeba* sp.) that are common in rivers, lakes, and streams. Within these hosts, *Legionnella* will proliferate and be protected from environmental hazards, including chlorination. In addition, following intracellular replication in protozoal cells, *L. pneumophila* converts to a virulent form and expresses a number of traits (including enhanced motility) that will assist in extracellular survival and transmission to new cells. This phenomenonant is thought, explains the virulence of *L. pneumophila* for the macrophages in the human lung, given the similarities in cell biology of these cells and protozoal cells. If the virulent form of the bacteria is inhaled, replication may occur within the alveolar macrophages, and disease will ensue. This transmission occurs most easily in the presence of airborne water droplets, so Legionnellosis has become particularly important and common following the various practices leading to aerosolization of water (e.g., showers, spraying of produce in large markets, and air conditioning).

Shigellosis Colitis

Shigella is a highly infectious, gram-negative, rod-shaped bacterium, most species are implicated in waterborne infections. Although not new, it is the virulence and ability to develop drug resistance through plasmids that confers resistance to a large spectrum of antibiotics, which characterize a resurgence of shigellosis colitis. Disease symptoms include abdominal pains, fever, and rectal pain, and complications may include sepsis, seizure, renal failure, and hemolytic uremia syndrome. *Shigella dysenteriae type 1* (Sd1) is the cause of epidemic dysentery that usually originates from water polluted with human feces. This type is a major cause of dysentery in Asia and Central and South America and has only recently arrived in Africa. After major pandemics in southern Africa in the early and middle 1990s, *Shigella dysenteriae type 1* has now become endemic in many countries in Africa. Other species of *Shigella* that are frequently responsible for waterborne infections are *Shigella sonnei* and *Shigella flexneri*.

Toxoplasmosis

This infection, which is symptomless in most cases, is caused by the coccidian protozoan *Toxoplasma gondii*. However, the parasite is considered an important emerging pathogen in the AIDS patient group worldwide, where infection can cause lymphadenopathy, central nervous system disorders, myocarditis, pneumonitis, and cranial lesions. Domestic cats are the definitive host for *Toxoplasma* but, apart from humans, there are numerous additional intermediate hosts in the animal kingdom. Infection takes place by ingesting contaminated food and water or by inhaling airborne *Toxoplasma* oocysts.

Tuberculosis (TB)

Although most individuals infected with *Mycobacterium tuberculosis* are asymptomatic carriers of TB, this should be considered a serious long-term pulmonary disease. In symptomatic cases, listlessness, chest pain, loss of appetite, fever, and weight loss are early symptoms of pulmonary tuberculosis. This may progress into night sweats, bleeding in the lungs, coughing up of sputum with pus, and shortness of breath. Exposure usually occurs through inhalation of infected droplets and thus, similar to legionnellosis, the aerosolization of water contributes to the transmissibility of *Mycobacterium* where water supplies are contaminated with the organism (often in hospitals). Tuberculosis is not a new infection, but multidrug-resistant tuberculosis (MDRTB) has become a major public health problem during the last 10 years, particularly as an opportunistic infection in concert with the AIDS epidemic.

CONCLUDING REMARKS

In considering the reasons for the emergence of the specific waterborne infectious diseases described, it is easy to identify a number of common and very specific causal elements. These include (1) the rising incidence of diseases or other factors that affect immune competence in groups or populations, including HIV/AIDS, malnutrition, and the like; (2) genetic adaptation of pathogens, including the acquisition of resistance plasmids, toxin genes, and other virulent factors; (3) overcrowding combined with poor sanitation and deteriorating or inadequate public health infrastructure; (4) increased exposure to animal reservoirs (as a result of geographical expansion, overpopulation, and competition for dwindling water resources) and continual zoonoses. Based on these factors, the potential for the continued emergence and reemergence of infectious diseases seems inexhaustible. Advances in vaccination, therapeutic intervention, and surveillance are crucial elements in the fight against these diseases, but even so, much may be achieved through education, improved hygiene, and proper water sanitation.

BIBLIOGRAPHY

1. Ackelsberg, J., Sivapalasingam, S., Olsen, S.J. et al. (1999). *A Large Waterborne Outbreak of* Escherichia coli *O157:H7 and* Campylobacter *Infections in County Fair Attendees*. NY. Presented at the 37th Annual meeting of the Infectious Disease Society of America, Philadelphia, PA, November 18–21, 1999. Abstract 728.
2. Allos, B.M. (2001). *Campylobacter jejuni* infections: update on emerging issues and trends. *CID* **32**: 1201–1206.
3. Barrett, T.J. et al. (1994). Laboratory investigation of a multistate food-borne outbreak of *Escherichia coli* O157:H7 by using pulsed Field gel electrophoresis and phage typing. *J. Clin. Microbiol.* **32**: 3013–3017.
4. Basu, A. et al. (2000). *Vibrio cholerae* O139 in Calcutta, 1992—1998. *Emerging Infect. Dis.* **6**(2): 139–147.
5. Berke, T. et al. (1997). Phylogenetic analysis of the Caliciviruses. *J. Med. Virol.* **52**: 419–424.
6. Chalmers, R.M., Aird, H., and Bolton, F.J. (2000). Waterborne *Escherichia coli* 0157. *J. Appl. Microbiol. Symp. Supple.* **86**: 124S–132S.
7. Colwell, R.R. (1996). Global Climate and infectious disease: The Cholera paradigm. *Science* **274**: 2025–2031.
8. DaSilva, E. and Iaccarino, M. (1999). Emerging diseases: A global threat. *Biotechnol. Adv.* **17**: 363–384.
9. Emmerson, A.M. (2001). Emerging waterborne infections in health-care settings. *Emerging Infect. Dis.* **7**(2): 272–276.
10. Enserink, M. (2000). Malaysian Researchers trace Nipah virus outbreaks to bats. *Science* **289**: 518–519.
11. Ewald, P.W. (1991). Waterborne transmission and the evolution of virulence among gastrointestinal bacteria. *Epidemiol. Infect.* **106**: 83–119.
12. Ewald, P.W. (1998). The evolution of virulence and emerging diseases. *J. Urban Health* **75**(3): 480–492.
13. Farmer, J.J. and Davis, B.R. (1985). H7 antiserum-sorbitol fermentation medium: A single-tube screening medium for detecting *Escherichia coli* O157:H7 associated with hemorrhagic colitis. *J. Clin. Microbiol.* **22**: 620–625.
14. Feng, P. (1995). *Escherichia coli* serotype O157:H7: Novel vehicles of infection and emergence of phenotypic variants. *Emerging Infect. Dis.* **1**(2): 47–52.
15. Fields, P.I. et al. (1997). Molecular characterization of the gene encoding H antigen in *Escherichia coli* and development of a PCR restriction fragment length polymorphism test for identification of *E. coli* O157:H7 and O157: NM. *J. Clin. Microbiol.* **35**: 1066–1070.
16. Fratamico, P.M., Buchanan, R.L., and Cooke, P.H. (1993). Virulence of an *Escherichia coli* O157:H7 sorbitol positive mutant. *Appl. Environ. Microbiol.* **59**: 4245–52.
17. Goma Epidemiology Group. (1995). Public health impact of Rwanda refugee crisis: what happened in Goma, Zaire, in July 1994, *Lancet* **345**: 339–344.
18. Gomez-Lus, R., Clavel, A., Castillo, J., Seral, C., and Rubio, C. (2000). Emerging and re-emerging pathogens. *Int. J. Antimicrobial Agents* **16**: 335–339.
19. Beckett, G. et al. (2000). Pseudomonas Dermatitis/Folliculitis Associated with Pools and Hot Tubs—Colorado and Maine, 1999—2000. Morbidity and Mortality Weekly Report. *Centres for Disease Control and Prevention MMWR* **49**(48): 1087–1091.
20. Besser, R.E., Griffin, P.M., and Slutsker, L. (1999). *Escherichia coli* 0157:H7 gastroenteritis and the haemolytic uremic syndrome: An emerging infectious disease. *Annu. Rev. Med.* **50**: 355–367.
21. Herwaldt, B.L. (2000). *Cyclospora cayatanensis*: A review, focusing on the outbreaks of Cyclosporiasis in the 1990s. *Clin. Infect. Dis.* **31**: 1040–57.

22. Hunter, P.R. et al. (2001). Waterborne diseases. *Emerging Infect. Dis. Supple.* **7**(3): 544–545.
23. International Agency for Cancer Research. (1994). *Shistosomes, liver flukes and Helicobacter pylori. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*. IARC, Lyon, 61.
24. Iverson, E.R. et al. (1998). Epidemic *Shigella dysenteriae* in Mumiao, western Kenya. *Trans. Roy. Soc. Trop. Med. Hyg.* **92**: 30–31.
25. Jaykus, L. (1997). Epidemiology and detection as options for control of viral and parasitic foodborne disease. *Emerging Infect. Dis.* **3**(4): 529–539.
26. Karas, J.A., Pillay, D.G., Naicker, T., and Storm, A.W. (1999). Laboratory surveillance of *Shigella dysenteriae* type 1 in Kwa Zulu-Natal. *S. Afr. Med. J.* **89**: 59–63.
27. Karmali, M.A. (1989). Infection by Verocytotoxin-producing *Escherichia coli*. *Clin. Microbiol. Rev.* **2**: 15–38
28. Keene, W.E. et al. (1994). A swimming associated outbreak of hemorrhagic colitis caused by *Escherichia coli* O157:H7 and *Shigella sonnei*. *N. Engl. J. Med.* **331**: 579–84.
29. Lederberg, J. (1997). Infectious disease as evolutionary paradigm. *Emerging Infect. Dis.* **3**(4): 417–423.
30. Minshew, P. et al. (2000). Outbreak of gastroenteritis associated with an interactive water fountain at a Beachside Park—Florida, 1999. Morbidity and Mortality Weekly Report. *Centres for Disease Control and Prevention MMWR* **49**(25): 565–568.
31. Morse, S.S. (1995). Factors in the emergence of infectious diseases. *Emerging Infect. Dis.* **1**(1): 7–15.
32. Olsvik, O. et al. (1991). A nested PCR followed by magnetic separation of amplified fragments for detection of *Escherichia coli* Shiga like toxins genes. *Mol. Cell Probes* **5**: 429–35.
33. Pollard, A.J. and Dobson, S.R. (2000). Emerging infectious diseases in the 21st century. *Curr. Opin. Infect. Dis.* **13**: 265–275.
34. Satcher, D. (1995). Emerging infections: getting ahead of the curve. *Emerging Infect. Dis.* **1**(1): 2–6.
35. Shears, P. (2000). Emerging and re-emerging infections in Africa: the need for improved laboratory services and disease surveillance. *Microbes Infection* **2**: 489–495.
36. Smith, A.W. et al. (1998). Calicivirus emergence from ocean reservoirs: zoonotic and interspecies movements. *Emerging Infect. Dis.* **4**(1): 13–20.
37. Stehr-Green, J. et al. (1991). International notes campylobacter enteritis—New Zealand, 1990. Morbidity and Mortality Weekly Report. *Centres for Disease Control and Prevention MMWR* **40**(7): 116–117.
38. Swanson, M.S. and Hammer, B.K. (2000). *Legionella pneumophila* pathogenesis: fateful journey from Amoebae to macrophages. *Annu. Rev. Microbiol.* **54**: 567–613.
39. Swerdlow, D.L. et al. (1992). A waterborne outbreak in Missouri of *Escherichia coli* O157:H7 associated with bloody diarrhoea and death. *Ann. Intern. Med.* **117**: 812–819.
40. Szewzyk, U., Szewzyk, R., Manz, W., and Schleifer, K.H. (2000). Microbiological safety of drinking water. *Annu. Rev. Microbiol.* **54**: 81–127.
41. Vogt, R.L. et al. (1982). *Campylobacter enteritis* associated with contaminated water. *Ann. Intern. Med.* **96**: 292–296.
42. Walford, D. and Noah, N. (1999). Emerging infectious diseases—United Kingdom. *Emerging Infect. Dis.* **5**(2): 189–194.
43. Willshaw, G.A. et al. (1993). Examination of raw beef products for the presence of Vero cytotoxin producing *Escherichia coli*, particularly those of serogroup O157. *J. Appl. Bacteriol.* **75**: 420–426.
44. World Health Organisation. (1995). *Guidelines for the Control of Epidemics Due to* Shigella dysenteriae *Type 1 (WHO/CDR/95.4)*. Pp. 1–47.
45. Yamai, S., Okitsu, T., Shimada, T., and Katsube, Y. (1997). Distribution of serogroups of *Vibrio cholera* non O1 non O139 with specific reference to their ability to produce cholera toxin and addition of novel serogroups. *J. Japanese Assoc. Infect. Dis.* **71**: 1037–1045.
46. Yamasaki, S. et al. (1997). Cryptic appearance of a new clone of *Vibrio cholerae* O1 biotype El Tor in Calcutta, India. *Microbiol. Immunol.* **41**: 1–6.
47. http://www.cdc.gov/.
48. http://www.who.int/.
49. http://www.cfsan.fda.gov/.
50. http://www.fsis.usda.gov/.
51. http://www.fas.org/.
52. http://www.doh.gov/.
53. http://www.pedianet.com/.
54. http://www.ncbi.nlm.nih.gov/ICTV/.

IMPROVING WATERBORNE DISEASE SURVEILLANCE

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INTRODUCTION

Public health surveillance has played a key role in controlling the spread of communicable disease and identifying the need for specific public health practices, such as the filtration and chlorination of drinking water supplies. However, the characteristics of waterborne outbreaks since the early 1990s have raised questions about whether current water treatment practices can prevent transmission of some enteric pathogens (1–5). In addition, one analysis suggested that a significant fraction of all enteric disease in the United States may be due to drinking water (3). Another study found evidence that consuming surface-derived drinking water which meets current U.S. Environmental Protection Agency (USEPA) drinking water standards may significantly increase the risk of enteric illness (6). These concerns have motivated the U.S. Congress to require USEPA to prepare a report on the magnitude of epidemic and endemic waterborne disease in the United States.

Even as the needs increase for better information about waterborne disease occurrence and causes, some have suggested that our disease surveillance system is in a state of crisis and may possibly collapse (7). Another study revealed that state health departments often cannot dedicate any staff to enteric disease surveillance (8). Current concerns over the preparedness for detecting and controlling bioterrorism attacks have also motivated interest in the adequacy of waterborne disease surveillance. In this chapter, issues relating to disease surveillance and outbreak investigations are presented to assist readers in understanding the strengths and weaknesses of current waterborne disease surveillance and outbreak detection programs and to suggest additional steps to strengthen the system. With limited public health resources available, it is important to carefully consider the goals and approaches to waterborne disease surveillance. In addition to addressing the information needs of governmental disease control programs, it is essential to ensure that the information needs of the drinking water industry, the regulatory agencies, and the public are best served. It may also be essential for drinking water utilities to participate in and, perhaps, help fund these surveillance systems.

BACKGROUND

It is increasingly accepted that additional information is needed about the occurrence and causes of waterborne disease, both epidemic and endemic. The Centers for Disease Control (CDC) funded “emerging pathogen” surveillance projects in selected state health departments, in part to improve surveillance for several important waterborne agents. In New York City (NYC), the Department of the Environment (DEP), responsible for drinking water treatment and delivery, convened a panel of public health experts in 1994 to evaluate current health department disease surveillance programs. The panel recommended specific waterborne disease surveillance activities and epidemiologic studies to determine endemic waterborne disease risks associated with use of unfiltered surface water sources (Table 1) (9). Efforts to improve NYC waterborne disease surveillance are funded by the NYC DEP, the first time this has occurred for a drinking water utility in the United States.

Table 1. New York City Panel Recommendations on Waterborne Disease Surveillance

Designate an individual who is specifically responsible for coordinating waterborne disease surveillance
Conduct special surveillance studies of nursing and retirement home populations
Conduct surveillance in managed care populations
Monitor visits to emergency rooms
Conduct surveillance of high-risk populations
Monitor sales of prescription and nonprescription medications

An option for improving waterborne disease surveillance is to build on the current surveillance programs in place in most state and local health departments. This system is based on voluntary disease reporting by healthcare providers and clinical laboratories. However, a number of limitations of the system have been identified, and other factors may have already significantly reduced the effectiveness of traditional disease surveillance programs. Some pathogens, such as *Cryptosporidium*, are often difficult to diagnose, and other pathogens may exist for which there are no known diagnostic tests or no tests available for routine use. Changes in healthcare access and delivery practices may reduce the number of patients seeking healthcare and, also, the chances that medically attended diseases are confirmed by laboratory tests.

An outbreak resulting in many medically attended illnesses in a large city could be unrecognized, as almost happened in the Milwaukee outbreak. In that outbreak, a large increase in the occurrence of diarrheal illness occurred around March 30–31, 1993. On Thursday, April 1, 1993 a pharmacist noted a dramatic increase in sales of over-the-counter antidiarrheal and anticramping medications. Normally his pharmacy sold $30 a day of such medications. Starting that Thursday, drug sales increased to approximately $500–$600 a day, or 17–20 times the normal sales. The increased sales continued on Friday, as a result of which the pharmacy sold most of its supply of antidiarrheal medications. The pharmacist called the health department to inquire about excessive reports of diarrhea or intestinal illness. The health department was unaware of any outbreak. On Saturday the increased sales continued so the pharmacist contacted the three local television stations to report what he believed to be a major occurrence of diarrheal disease in the city. On Sunday night his report was carried on the evening news for one station and by Wednesday, April, 7, the outbreak was confirmed by the Milwaukee Health Department.

In the case of the Milwaukee outbreak, few of the people sought medical care for their diarrhea. However, even in situations where care was sought, it is possible that no one physician would notice an outbreak. For example, if many different healthcare providers treated the patients, it is possible that no one provider would recognize excess occurrences of illness. In addition, the existence of health effects in a small but extremely susceptible subpopulation might be difficult to detect because of the small number of people at risk.

As some changes have made it more difficult to detect outbreaks, other changes present new disease surveillance opportunities. Computerization of patient records, healthcare and laboratory workloads, prescription and nonprescription pharmaceutical sales, and calls to nurse hotlines are potential new tools for more effective and less costly disease surveillance. Technological advancements, such as detection of antigen or antibodies specific to a pathogen in sera, stools, and other secretions, may improve detection of etiological agents. These may also allow detection of infections in the absence of disease.

To better evaluate the current and alternative surveillance opportunities, five questions have been selected for discussion in this chapter:

1. What are the limitations of our current disease surveillance systems?
2. Should the early detection of outbreaks be the primary goal of a surveillance system and, if so, how can it be best achieved?
3. What is meant by endemic or background rates of disease, can some of this endemic disease be attributable to drinking water, and what should water utilities do to better understand these risks?
4. Can findings from outbreak investigations be used to estimate the unreported burden of enteric disease attributable to drinking water?
5. Since only a fraction of infected persons become ill from most enteric infections, should expanded surveillance programs monitor infection rather than illness?

LIMITATIONS OF THE CURRENT DISEASE SURVEILLANCE SYSTEMS

What are the limitations of our current disease surveillance systems? Detection of waterborne disease outbreaks depends, in part, on a state-federal system of notifiable or reportable diseases. Disease reporting is primarily the responsibility of healthcare providers and diagnostic laboratories. State or local laws require the reporting of certain diseases. Primary responsibility for disease surveillance rests with the state or local public health authorities. Most state surveillance systems are "passive," in that reports are sent to the state or local health department by cooperative health care providers or laboratories. Providers and laboratories usually receive little encouragement from the health department to report illnesses. Government enforcement of reporting requirements is minimal. An "active" system will routinely contact some or all healthcare providers and laboratories, asking for illness reports (Table 2) (10).

It has long been recognized that both passive and active disease reporting incompletely ascertain the level of disease in the community. The level of completeness varies by disease, by state, and by areas or populations within a state (11). For example, reporting is likely to be more complete for severe diseases such as hemorrhagic *E. coli* than for milder infections, such as Norwalk virus gastroenteritis. Laboratories tend to be much better at reporting their findings than are physicians (10). Even within an area, there can be great variations in reporting, depending on the interest of clinical laboratories and the dedication of diagnosing physicians (11). For example, for pathogens that are new or where there are questions about the mode of transmission, reporting may be more complete than for agents that are common, where the mode of transmission is well known and where public health intervention is less necessary.

Table 2. Surveillance System Definitions

Mandatory reporting	A diagnosed case of disease is required, by law, to be reported; for example, in the case of cryptosporidiosis, all diagnosed cases are to be reported
Passive	Disease reports are submitted by providers and/or laboratories without specific follow-up by the health department
Active	Providers and/or laboratories are contacted to encourage diseases reporting; because of resource requirements, this is usually done as a special project for a limited duration of time
Enhanced	Special additional efforts are made to encourage disease reporting; this might include news releases, posters at strategic locations, presentation to special populations, or health surveys in communities with water quality problems

In addition to incomplete reporting of diagnosed illnesses, only a portion of all infections will ever be medically attended. As illustrated in (Fig. 1), only a fraction of infections will lead to illness. These infected persons may be unaware of their infection. In other cases, such as sometimes occurs as a result of childhood *Giardia* infection, the child fails to thrive but experiences none of the classic symptoms of giardiasis. When symptoms occur, they may be mild and/or may resolve in a short period of time. In this case, the person may not seek medical care or may simply visit a pharmacy to obtain medication to alleviate their symptoms. In the case of Milwaukee, despite the large number of reported cases of cryptosporidiosis, very few people visited their physician and few stool specimens were positive for *Cryptosporidium* oocysts.

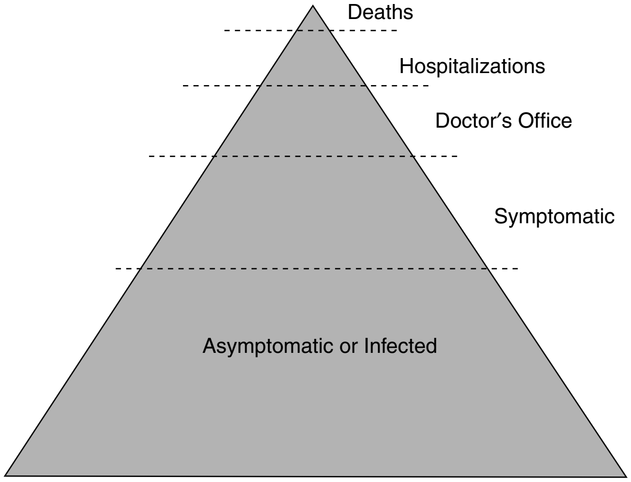

Figure 1. Disease pyramid.

If the person seeks healthcare, the physician may fail to correctly diagnose the infection, since in many cases symptoms are not sufficiently specific to accurately identify the pathogen. If misdiagnosed and the infection resolves itself, the patient may not seek additional healthcare and no report of an infection will be generated. Even when the physician correctly diagnoses the illness and prescribes the appropriate medication, a confirmatory laboratory test may not be ordered. If ordered, the patient may not submit the sample to the laboratory, since many patients are unwilling to submit stool specimens for laboratory analysis. Since laboratories are the primary source of disease reports for surveillance systems, without a laboratory-confirmed diagnosis, a report may never be filed. When a stool or blood sample is submitted for laboratory analysis, it can also test negative because of analytical or specimen collection error, untimely collection or because the material submitted was, by chance, free of the pathogen (12). Laboratory proficiency can vary considerably. This may be more of a problem for laboratories that run only a small number of the ordered test. For persons infected with enteric parasites, single stools may often be free of the parasite or have insufficient numbers of parasites to assure laboratory detection. In some cases, even multiple stools may be pathogen-negative.

If a sufficient number of cases of illness from the same pathogen are reported to the health department at about the same time and if the epidemiologist is alert to an increase in case reports, an outbreak may be identified. Because of the time required to perform the diagnostic tests and to report the results, outbreak recognitions may occur weeks after the onset of the actual outbreak.

Many outbreaks are first detected by an alert clinician. For example, in 1976, a Camas, Washington physician's son had returned from Russia with giardiasis. The physician later recognized that several of his patients had similar symptoms. This lead to the identification of a waterborne giardiasis outbreak (13). As mentioned earlier, in Milwaukee, Wisconsin a pharmacist noted a dramatic increase in sales of antidiarrheal medication. In California and Arizona, diarrheal illnesses reported to health agencies by 65 campers who had visited an Arizona park initiated an investigation that implicated contaminated water as the source of an outbreak that affected 1850 people (14). The fortuitous circumstances surrounding the detection of many outbreaks raises concerns about how many medium to large outbreaks are never detected. Small outbreaks may seldom be detected, especially among travelers who consume water from noncommunity systems or who swim in multiple locations.

Limitations of the current disease surveillance systems prompted a series of studies in the early 1980s to evaluate potential improvements in disease reporting and to evaluate the efficacy of active surveillance programs. A three state study of various approaches to active disease surveillance, funded by USEPA, detected no additional waterborne disease outbreaks in two states (Washington and Vermont) (15). However, in one state (Colorado) a greater than threefold increase in the number of detected waterborne outbreaks occurred (16). The reasons why Colorado was able to identify so many more outbreaks than either Washington State or Vermont are unclear. An intense effort was made to increase disease reporting in all states and dramatic increases in reports of enteric diseases were observed in all three states. It is possible that a combination of poor quality water supplies plus an exposed tourist population, without protective immunity, may have allowed Colorado to identify more outbreaks than the other two states.

In summary, active disease reporting can increase reporting of diagnosed illnesses only from providers and laboratories. All the other barriers to disease identification and reporting will still remain (Fig. 1). If healthcare access declines over time or, to reduce healthcare costs, physicians use fewer laboratory diagnostic services, then the number of diagnosed reportable illnesses will decline. This will occur despite the efforts of health departments to insure that most diagnosed illnesses are reported.

EARLY DETECTION OF OUTBREAKS

Should the early detection of outbreaks be the primary goal of a surveillance system, and, if so, how can it be best achieved? The occurrence of a waterborne disease outbreak is an exciting, newsworthy, and politically important event. Affected populations may experience severe illness and a large number of people may become ill. As a result of the investigation, much is often learned about the cause of major failures in water treatment or distribution. However, when the excitement has subsided, water system deficiencies have been corrected and the outbreak is officially said to be over, has the problem been solved or is disease continuing to occur but at a reduced level, below what is detectable by traditional surveillance activities?

For example, a waterborne disease outbreak investigation detected major problems with the filtration system of an anonymous small community water supply. The system was, at the time of its installation, considered adequate. However, high turbidity levels were observed in treated water at the time of the outbreak, suggesting poor operation of the filtration facility. Optimization of treatment by consulting engineers allowed the plant to dramatically improve pathogen removal. This improvement reduced the number of new cases of disease, and the outbreak officially ended. However, 2 years later a serological survey of the town's residents revealed the continued occurrence of infection by the same etiologic agent responsible for the earlier outbreak. These new data presented both philosophical and technical problems. Should all outbreaks be followed by such a survey? Is evidence of continuing infection sufficient reason for further intervention? If the serological survey were not conducted, there would be no evidence of increase risk of infection. If the plant was already optimized, what are the remaining intervention options without new filtration or disinfection technology?

This scenario assumes that the continued high serological levels resulted from waterborne transmission. In fact, without a follow-up epidemiologic investigation, it is not possible to distinguish waterborne from other routes of transmission. In addition, without improved surveillance activities, we know little about the absence of symptomatic disease. Low levels of disease from exposure to waterborne microbes over a period of many years can result in a much larger health burden for a community than the number of disease cases that might occur during a detected outbreak. However, exposure to some waterborne pathogens at levels that boost the immune response may prevent symptomatic illness. These concerns must all be considered when developing a surveillance system. Without clear goals and a commitment to conduct epidemiologic investigations and take appropriate actions, a better surveillance system will not improve public health.

Failure to detect low levels of disease transmission may provide a false sense of security. For example, why should an outbreak such as occurred in Milwaukee not have been preceded by many smaller outbreaks? Is it possible that in each of the cities experiencing a large waterborne cryptosporidiosis outbreak, prior undetected smaller outbreaks occurred? In fact, is it possible that lower levels of waterborne *Cryptosporidium* infection had occurred years prior to the outbreak? At the time of the detected outbreak, a higher number of oocysts may have passed through the treatment system or a more virulent strain of the pathogen emerged. If so, relying on disease surveillance systems that can only detect large outbreaks will seldom provide public health officials and the industry early warnings of emerging new diseases. This may be equivalent to basing the science of meteorology only on the study of hurricanes.

The detection of an outbreak can also affect future disease reports in an area. For example, it is possible that overreporting of symptoms consistent with the disease of interest could occur. If so, similar outbreaks may be detected in neighboring areas. Given the increased popularity of bottled water use, it is possible that the at-risk population could change following an outbreak if a significant fraction of the population discontinued drinking tapwater. Therefore, decreases in the occurrence of reported waterborne disease may not reflect better control of the contamination but a reduction in the number of exposed individuals.

ENDEMIC DISEASE

What is meant by endemic or background rates of disease and can some of this endemic disease be attributed to drinking water? Endemic level of disease is defined by the CDC as a persistent low to moderate level of disease occurrence. A persistently high level of occurrence is called *hyperendemic* while an irregular pattern of occurrence is called *sporadic* (Fig. 2). For most enteric infections, endemic disease results from a statistical averaging of small to moderate-sized undetected outbreaks or clusters of infection. There is little information to suggest that endemic levels of disease remain constant over time or across geographic areas, nor is there reason to believe the endemic level of disease is unimportant.

Over the past century, the importance of endemic disease has become increasingly recognized. Following World War I, an attempt was made to estimate the prevalence of parasite infections in both the returning British soldiers and the British population who remained at home (17). To the surprise of the researchers, a high prevalence of asymptomatic infection was found among persons who had never left Britain. Later, a survey of Wise County, Virginia in 1930 revealed that half of the population carried *Entamoeba histolytica* and that 38% carried *Giardia lamblia* (18). A study to determine the incidence of *Cryptosporidium* infection among Peace Corp workers to be sent overseas revealed that almost 30% had possibly experienced infection prior to leaving the United States (19). More recent work we conducted suggests that endemic rates of *Cryptosporidium* infection may be very high, but that rates of cryptosporidiosis may be low (20,21).

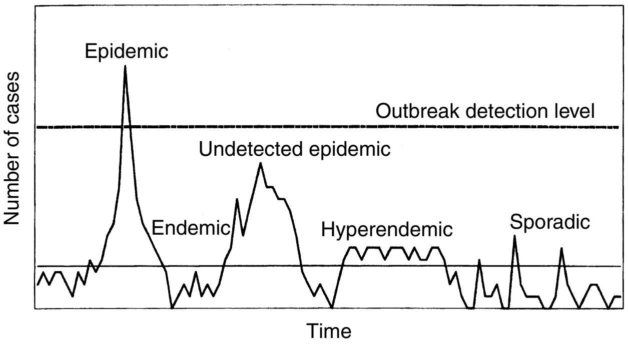

Figure 2. Epidemic versus endemic disease.

Data derived from disease surveillance systems cannot be used to compare endemic disease levels between areas or populations with different water systems. Whether observed differences in disease reports are due to the differences in the completeness of reporting or to differences in the occurrence of the disease or the infection cannot be answered, even with improved surveillance systems. In addition, it has become increasingly recognized that populations can develop protective immunity to infectious agents. If so, rates of infection may remain high while rates of illness remain low (21). The absence of disease in a population may, therefore, not mean that there is an absence of infections. Epidemiologic studies must be specifically designed and conducted to address the association of endemic disease with water system type or quality.

Several epidemiologic studies have reported waterborne disease associated with public water systems in the absence of a reported waterborne outbreak. In New Zealand, the incidence of laboratory-confirmed giardiasis was found to be higher in a part of the city receiving chlorinated, unfiltered surface water compared to the part where surface water was treated by coagulation, flocculation, granular filtration, and chlorination (22). In Vermont, a higher incidence of endemic giardiasis was found in municipalities using unfiltered surface water or wells than in municipalities with filtered surface water (23). A Canadian study attempted to estimate how much endemic enteric illness was due to drinking water (6). The fraction of illness attributable to drinking water was estimated by comparing rates of reports of “highly credible gastrointestinal illnesses” among persons drinking tapwater with rates among people drinking water from reverse osmosis filtration units. Although different rates of illness could have resulted from reporting biases, if the findings are confirmed by future studies, then drinking water may significantly contribute endemic disease in at least one community. Unfortunately, a study using a similar design conducted in Melbourne, Australia, did not provide evidence of endemic waterborne disease (24).

A variety of approaches have been proposed for estimating the burden of endemic diarrheal disease from drinking water sources. In addition to the Australian replication of the Payment design, a small pilot household intervention study in California has recently been completed (25). That study concluded that it was possible to blind families as to the type of treatment device they had, and although the study was not powered to examine illness rates, the families with true home treatment devices reported a lower rate of illness. A larger randomized household intervention study is under way in the United States. The advantage of the randomized household interventions is that the design precludes reporting biases and assignment biases, assuming that people do not know whether they are in the intervention or the control group. A major disadvantage of this approach is that only household drinking water quality is altered. Drinking water from other sources, such as work or at restaurants, is not altered. Another limitation is that long-term healthy residents are usually recruited and these people may have the lowest risk of suffering illness from waterborne infections. Therefore, negative results are difficult to interpret. Household intervention studies are limited in generalizability because they are conducted in single communities, although the study design would be amenable to national randomized trial.

Another proposed approach is to relate variations in the occurrence of health events, such as emergency room visits and hospitalization, with variation in drinking water turbidity levels (26,27). This approach has some merit; however, the results are difficult to interpret since no causal agents are identified. There are also concerns that the optimized statistical modeling cannot be statistically evaluated. Therefore, many of the claimed associations may be spurious.

Another approach uses planned changes in drinking water treatment and then evaluates the occurrence of potentially waterborne disease before and after intervention. The advantage of this approach is that most or all drinking water from an area is changed. This avoids one of the problems with household interventions. One disadvantage of this approach is that the sites receiving new water treatment technologies are not randomly assigned. For example, most unfiltered drinking water systems in the United States use high-quality source water. Adding filtration may not dramatically change the health risks from the drinking water. Another is that the community intervention looks at only one city or one pair of cities, so the sample size is restricted.

APPLICABILITY OF OUTBREAK INVESTIGATIONS

Can findings from outbreak investigations be used to estimate the burden of enteric disease attributable to drinking water? Epidemic disease is defined as an unusual occurrence or clustering of a specific illness. Between 1971 and 1994 there were 737 documented waterborne disease outbreaks (28–30). Almost half of these were due to unknown etiological agents that caused acute gastrointestinal illness. Among these outbreaks, the relative importance of different etiologic agents (viruses, bacteria, protozoa, and chemicals) can be estimated. For example, the etiologic agents most commonly associated with waterborne disease in the United States include, in descending order, undefined gastroenteritis, giardiasis, shigellosis, viral gastroenteritis, and hepatitis A. This ranking is based on outbreaks and may or may not reflect the relative importance of these etiologic agents for all waterborne disease.

For diseases where outbreaks account for the majority of illnesses, the outbreak is of primary interest. However, for many waterborne pathogens, outbreaks account for only a small fraction of all illnesses. For example, in a 1.5-year period during the late 1970s in Washington State, 1347 laboratory confirmed cases of giardiasis were reported to the state health department (31). Extensive follow-up of these cases (Table 3) revealed that clusters or possible small outbreaks accounted for only 16% of all cases of giardiasis reported during this time period. These data suggest that “endemic giardiasis” was overwhelmingly more abundant than “epidemic giardiasis” in Washington State during this time period.

There are a number of problems with extrapolating the characteristics of cases involved in outbreaks to revise all cases of illness, including the following:

1. If there is variation in the virulence of a pathogen, then detected outbreaks may predominantly be caused by the more virulent strains of the pathogen. This may overestimate the severe morbidity or mortality associated with the pathogen.
2. By examining only detected outbreaks, one may overestimate the importance of drinking water as a

Table 3. Case Clusters of Giardiasis in Washington State 1977–1978

Number of Cases	Etiology
10	Untreated streamwater consumption
14	Untreated water consumption at a work camp
11	One small community water system
12	Tourists returning from a resort in Mexico
17	One-daycare center outbreak
8	One-daycare center outbreak
24	Among 10 different daycare centers
73	Multiple cases among 21 families
51	Nonfamily association with another case
220	Total in all clusters

route of transmission. Because of the large number of cases often involved, waterborne outbreaks may be more detectable than outbreaks from other routes of transmission. Even a severe day care outbreak would involve only a few cases. Within family clusters usually involve too few cases to be a detectable outbreak.

3. Outbreak detection is often more difficult for common or endemic diseases than for uncommon diseases. For example, two cases of cholera anywhere in the United States might be considered an outbreak whereas 50 cases of cryptosporidiosis widely dispersed in a large U.S. city during a week might easily be absorbed as expected background cases of diarrhea and not recognized as an outbreak (9).

Outbreaks of short duration of illnesses (e.g., some viruses) are more difficult to detect and study than are outbreaks of long duration illnesses (e.g., giardiasis, shigellosis, hepatitis A). Therefore the importance of acute, self-limited gastrointestinal illness of undetermined etiology and short duration may be underestimated relative to outbreaks of parasitic infections and some bacterial or viral pathogens with a longer duration of symptoms.

Pathogens with long incubation periods are difficult to investigate since the conditions that allowed transmission of the pathogen may have changed between the time of infection and the time when the outbreak was detected. Underascertaining waterborne sources for disease outbreaks caused by these agents is likely.

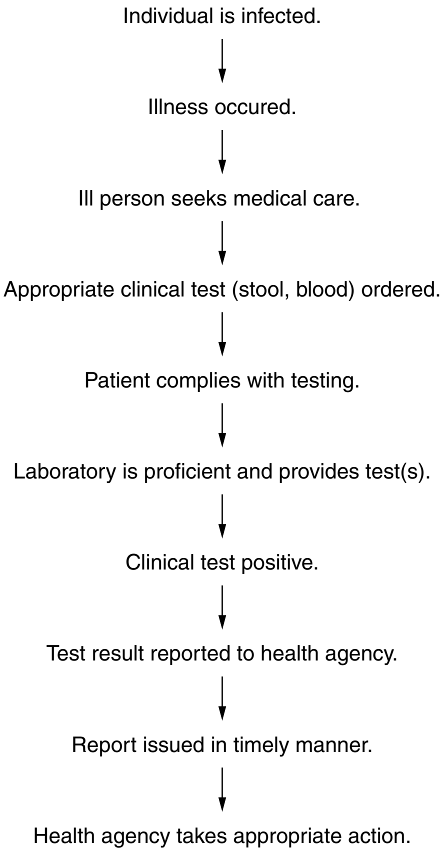

Figure 3. Events in reporting an individual infection.

MONITORING INFECTION VERSUS DISEASE

Only a fraction of infected persons become ill from the most commonly occurring enteric infections. Of the people that become ill, only a fraction of cases will be reposted (Fig. 3). Should expanded surveillance programs attempt to monitor infection rather than disease? The existence of asymptomatic carriers of infections has been known for some time (e.g., Typhoid Mary). However, the number of asymptomatic carriers for many infections has only relatively recently been appreciated. The parasite prevalence surveys in Britain (17) and in Virginia (18) found more asymptomatic infected persons than expected. Even as late as 1952, in New Hope, Tennessee, 10.6% of the general population was infected with *Giardia lamblia* (32). Following a 1966 giardiasis outbreak in Aspen, Colorado, a stool survey found that 5% of the population was infected with *Giardia* (33). A survey of Boulder, Colorado, also conducted following an outbreak, found a prevalence of 5% (34). Most of the individuals participating in these surveys were asymptomatic. A stool survey of one to 3-year-old Washington State children was conducted in 1980 (35). This survey found that 7% of the children were infected with *Giardia lamblia*. All participating children were reported as healthy at the time of the survey. The Seattle Virus Watch program, conducted during the 1960s and early 1970s monitored virus infections among a sample of people in selected U.S. cities. This study found that illness was reported in less than half of all enterovirus infections (36).

New serological tools have been developed since the early 1980s to better monitor the prevalence of prior infections among the population. Even though infection may not result in moderate or severe illness, there are several reasons for considering infection rather than disease, including the following:

1. Information on infections can provide a much expanded understanding of the relative importance of various routes of transmission and provide an early warning for risks of outbreaks.
2. Serological epidemiologic studies of infection can better estimate the extent of endemic waterborne disease. These studies are statistically more powerful to detect low risks in moderate-size populations.
3. Just as the occurrence of a coliform test indicates the potential of disease risk for a drinking water source, the waterborne transmission of pathogens, even when infection is predominantly asymptomatic, can provide critical information for evaluating water treatment systems and may help identify correctable problems in water source protection and/or treatment.
4. Widespread, unrecognized transmission of infection in the general population may indicate a devastating outbreak for a susceptible subpopulation.

Another advantage of serological surveillance occurs during an outbreak. An outbreak of cryptosporidiosis was detected in Las Vegas, Nevada in Spring 1994. Although this was clearly a cryptosporidiosis outbreak, the inability to detect problems with the water treatment system and publicity prior to the investigation that suggested the outbreak was waterborne raised questions over whether the outbreak could be classified as waterborne (37–39). Since the majority of the diagnosed cases also suffered from HIV or AIDS, the extent of the outbreak was unclear. Had asymptomatic infected persons been identified serologically, the effects of reporting bias would be reduced since asymptomatic cases would have no motivation to explain an asymptomatic infection.

IMPROVING DISEASE SURVEILLANCE

Several options are available for enhanced waterborne disease surveillance. The option or combination of options selected will depend on the specific goals for disease surveillance. The currently used national system of surveillance, based on diagnosed illness, has a long-established record of both performance and nonperformance for detecting outbreaks (Table 4). Because the current system is both inexpensive to maintain and currently operational, it has considerable appeal among public health practitioners. However, monitoring pharmaceutical sales, nurse hotline calls, or physician visits is a potential enhancement to the traditional disease surveillance programs (Table 5) (39,40).

The goal of our current disease surveillance system is outbreak detection. Unfortunately, there is little rigorous evaluation of its capability to detect outbreaks. Furthermore, the common occurrence of fortuitous situations that lead to the outbreak detection raise questions about the sensitivity of the system. To improve the sensitivity to detect small to medium-size outbreaks or to provide early information on the occurrence of an outbreak, these alternative approaches mentioned have promise. Over-the-counter pharmaceutical sales may be useful, but it has some significant limitations (40). The use of nurse hotline calls to continuously monitor the occurrence of infectious disease has tremendous promise, but no efforts have been made to use this surveillance tool (39). Better linkages with infectious disease specialists in healthcare organizations may also improve disease surveillance.

Table 4. Advantages and Disadvantages of the Current Waterborne Disease Surveillance System

Advantages
In-place and operational across the nation
Extensive health department experience using the system
Inexpensive to maintain
An operational nationwide network, operated by the Centers for Disease Control (CDC), for summarizing and reporting findings
Methodological development of algorithms for detecting excess occurrences of disease
Disadvantages
Inability to detect outbreaks when diagnosed cases are not reported to the health department
Delays in detecting outbreaks due to the time required for laboratory testing and for reporting of findings
Undetected outbreaks where health problems are not medically treated or where infection results in only mild or no illness
Limited opportunities for system improvement
Possible long-term trend in healthcare delivery that may reduce its efficacy

Table 5. Advantages and Disadvantages of New Waterborne Surveillance Systems

Advantages
They may detect outbreaks where few patients seek healthcare or where the illness is of sufficiently short duration that healthcare is unimportant
They are relatively fast in reporting outbreaks since the time delay between the onset of symptoms and the purchase of drugs or calls to nurses is likely to be short
They are relatively inexpensive to maintain, especially if nationwide retail pharmacies are involved or common nurse hotline software is programmed for reporting
Disadvantages
Since only symptoms are ascertained, they will not usually identify an etiologic agent
Although inexpensive to maintain, initial computer programming and establishing data sharing agreements would require some investment
The specificity of the system for outbreak detection (e.g., number of false leads) is untested

None of the traditional or enhanced surveillance tools will provide much useful information on low-level or endemic risk of enteric pathogen infection. However, new serological tests have increased the feasibility of studies to estimate the incidence of new infections or the prevalence of antibody response to pathogens and to relate this information with modes of transmission. In the early 1970s, the Seattle Virus Watch program examined occurrences of viral infections among volunteers in selected communities (33). Similar approaches to monitoring the occurrence of *Giardia* (41) and *Cryptosporidium* (42) infections have been developed since then. More work is needed to evaluate these new tools as well as to develop other tests. We also need to design cost-effective approaches to their widespread implementation. These tools may give us an opportunity to greatly improve our understanding of the importance of various modes of transmission and identify reasons why one population group has a higher endemic level of disease than another. It is likely that as more is known about the modes of transmission, a better understanding will emerge of both drinking water and nondrinking water routes of pathogen transmission.

Healthcare reforms may reduce the use of diagnostic laboratory services, reducing the value of laboratory-based disease surveillance. However, new opportunities for improved disease surveillance, including both individual and community disease reporting and surveillance of endemic infections, may also result. To fully exploit these opportunities, a new public health partnership with distributed responsibilities may be needed between healthcare providers, health maintenance organizations (HMOs), pharmacies, and the traditional public health agencies.

The increasing age of our population has resulted in increases in the number of immunosuppressed persons. Some of this immunosuppression may result from chronic diseases, while some may result from medically induced immunosuppression following treatment for other conditions. For example, many cancer patients have temporary periods of immunosuppression following treatment. These populations may be at especially high risk of adverse consequences of infection. Since diarrheal disease in this population is also relatively common, many infections may not be detected.

Infectious disease surveillance systems are operated by state and local public health agencies with little or no direct contact with healthcare providers. To improve disease surveillance system, it will likely be necessary to better integrate healthcare delivery systems with those disease surveillance programs. This integration can only occur if both the state public health agencies and the healthcare providers recognize benefits from this cooperation and barriers to data sharing are reduced.

DISCLAIMER

The views expressed in this chapter are those of the individual authors and do not necessarily reflect the views and policies of the USEPA. The chapter has been subject to the Agency's peer and administrative review and approved for publication.

BIBLIOGRAPHY

1. D'Antonio, R.G., Winn, R.E., Taylor, J.P., Gustafson, T.L., G.W. Gray, Current, W.L., Zajac, R.A., and Rhodes, M.M. (1985). A waterborne outbreak of cryptosporidiosis in normal hosts. *Annals Int. Med.* **103**: 886–888.
2. Bennett J.V., Holmberg, S.D., and Rogers, M.F. (1987). Infectious and parasitic diseases. *Closing the Gap: The Burden of Unnecessary Illness*. R.W. Amler and H.B. Dull (Eds.). Oxford University Press, New York.
3. Hayes, E.P. et al. (1989). Large community outbreak of cryptosporidiosis due to contamination of a filtered public water supply. *New Engl. J. Med.* **320**: 372–376.
4. Leland, D., McAnulty, J., Keene, W., and Terens, G. (1993). A cryptosporidiosis outbreak in a filtered water supply. *J. Am. Water Works Assoc.* **85**: 34–42.
5. MacKenzie, W.R. et al. (1994). A massive outbreak in Milwaukee of *Cryptosporidium* infection transmitted through the public drinking water supply. *New Engl. J. Med.* **331**(3): 161–167.
6. Payment, P., Richardson, L., Siemiatycki, J., et al. (1991). A randomized trial to evaluate the risk of gastrointestinal disease due to consumption of drinking water meeting current microbiologic standards. *Am. J. Public Health* **81**(6): 703–708.
7. Berkelman, R.L., Bryan, R.T., Osterholm, M.T., LeDuc, J.W., and Hughes, J.M.. (1994). Infectious disease surveillance: A crumbling foundation. *Science* **264**: 368–370.
8. Frost, F.J., Calderon, R.L., R. L., and Craun, G.L. (1995). Waterborne disease surveillance: Findings of a survey of state and territorial epidemiology programs. *J. Environ. Health.* **58**(5): 6–11.
9. Craun, C.L., Birkhead, G., Erlandsen, S., et al. (1994). *Report of New York City's Advisory Panel on Waterborne Disease Assessment*. The New York City Department of Environmental Protection, New York.
10. Foster, L.R. (1990). Surveillance for waterborne illness and disease reporting: State and local responsibilities. In: *Methods for Investigation and Prevention of Waterborne Disease Outbreaks*. G.F. Craun (Ed.). EPA/600/1-90/005a. USEPA Office of Research and Development, Cincinnati.
11. Chorba, T.L., Berkelman, R.L., Safford, S.K., Gibbs, N.P., and Hull, P.E. (1989). Mandatory reporting of infectious diseases by clinicians. *J. Am. Med. Assoc.* **262**: 3018–3026.
12. Chappell, C.L., Okhuysen, P.C., Sterling, C.R., and DuPont, H.L. (1996). *Cryptosporidium parvum*: Intensity of infection and oocyst excretion patterns in healthy volunteers. *J. Infect. Diseases* **173**: 232–236.
13. Kirner, J.C., Littler, J.D., and Angelo, L.A. (1978). A waterborne outbreak of giardiasis in Camas. *J. Am. Water Works Assoc.* **70**: 35–40.
14. Starko, K.M., Lippy, E.C., Dominguez, L.B., Haley, C.E. and Fisher, H.J. (1986). Campers' diarrhea traced to water-sewage link. *Public Health Reports* **101**: 527–531.
15. Harter, L., Frost, F., Vogt, R., Little, A., Hopkins, R., Gaspard, B., and Lippy, E. (1985). A three-state study of waterborne disease surveillance techniques. *Am. J. Public Health* **75**: 1327–1328.
16. Hopkins, R.S., Shillam, P., Gaspard, B., Eisnach, L., and Karlin, R.S. (1985). Waterborne disease in Colorado: three years surveillance and 18 waterborne outbreaks. *Am. J. Public Health* **75**: 254–257.
17. Smith, A.M. and Matthews, J.R. (1917). The intestinal protozoa of non-dysenteric cases. *Annals Trop. Med. Parasitol.* **10**: 361–390.
18. Faust, E.C. (1930). A study of the intestinal protozoa of a representative sampling of the population of Wise County, southwestern Virginia. *Am. J. Hygiene* **11**: 371–384.
19. Ungar, B.L., Milligan, M., and Nutman, T.B. (1989). Serologic evidence of *Cryptosporidium* infection in U.S. volunteers before and during Peace Corps service in Africa. *Arch. Int. Med.* **149**: 894–897.
20. Frost, F. (1998). Two-city *Cryptosporidium* study. *Am. Water Works Assoc. Research Found.—Drink. Water Research* **8**(6): 2–5.
21. Frost, F.J., Muller, T., Craun, G.F., Calderon, R.L., and P.A. Roeffer. (2001). Paired city *Cryptosporidium* serosurvey in the southwest USA. *Epidemiol. Infect.* **126**: 301–307.
22. Frasher, G.G. and Cooke, K.R. (1989). Endemic giardiasis and municipal water supply. *Am. J. Public Health* **79**: 39–41.
23. Birkhead, G. and Vogt, R.L. (1989). Epidemiologic surveillance for endemic *Giardia lamblia* infection in Vermont. *Am. J. Epidemiol.* **129**: 762–768.
24. Hellard, M.E., Sinclair, M.I., Forbes, A.B., and Fairley, C.K. (2001). A randomized blinded controlled trial investigating the gastrointestinal health effects of drinking water quality. *Environ. Health Perspect.* **109**: 773–778.

25. Colford, J.M., Rees, J.R., Wade, T.J., Khalakdina, A., Hilton, J.F., Ergas, I.J., Burns, S., Benker, A., Ma, C., Bowen, C., Mills, D.C., Vugia, D.J., Juranek, D.D., and Levy, D.A. (2001). Participant blinding and gastrointestinal illness in a randomized, controlled trial of an in-home drinking water intervention. *Emerging Infect. Diseases* **8**(1): 29–36.
26. Schwarz, J., Levin, R., and Hodge, K. (1997). Drinking water turbidity and pediatric hospital use for gastrointestinal illness in Philadelphia. *Epidemiology* **8**: 615–620.
27. Morris, R.D.F., Naumova, E.N., and Griffiths, J.K. (1998). Did Milwaukee experience waterborne cryptosporidiosis before the large documented outbreak in 1993? *Epidemiology* **9**: 264–270.
28. Craun, G.F. (1992). Waterborne disease outbreaks in the United States of America: Causes and prevention. *World Health Statistics Quart.* **45**: 192–196.
29. Moore, A.C., Herwaldt, B.L., Craun, G.F., Calderon, R.L., Highsmith, A.K., and Juranek, D.D. (1994). Waterborne disease in the United States, 1991 and 1992. *J. Am. Water Works Assoc.* **84**(2): 87–99.
30. Kramer, M.H., Herwaldt, B.L., Craun, G.F., Calderon, R.L., and Juranek, D.D. (1996). Surveillance for waterborne disease outbreaks—United States, 1993–1994. *J. Am. Water Works Assoc.* **88**: 66–80.
31. Frost, F., Harter, L., Plan, B., Fukutaki, K., and Holman, B. (1983). *Giardiasis in Washington State*. USEPA Report 83-134-882. National Technical Information Service, Springfield, VA.
32. Eyles, D.E., Jones, F.E., and Smith, S.C. (1953). A study of *Entamoeba histolytica* and other intestinal parasites in a rural west Tennessee community. *Am. J. Trop. Med.* **2**: 173–190.
33. Gleason, N.N., Horwitz, M.S., Newton, L.H., and Moore, G.T. (1970). A stool survey for enteric organisms in Aspen, Colorado. *Am. J. Trop. Med. Hygiene* **19**: 480–484.
34. Wright, R.A., Spender, H.C., Brodsky, R.E., and Vernon, T.M. (1977). Giardiasis in Colorado: An epidemiologic study. *Am. J. Epidemiol.* **105**: 330–336.
35. Harter, L., Frost, F., and Jakubowski, W. (1982). *Giardia* Prevalence among 1-to-3 year-old children in two Washington State counties. *Am. J. Public Health* **72**: 386–388.
36. Elveback, L.R., Fox, J.P., Ketler, A., Brandt, C.D., F.E. Wassermann, and Hall, C.E. (1966). The Virus Watch program; a continuing surveillance of viral infections in metropolitan New York families. 3. Preliminary report on association of infections with disease. *Am. J. Epidemiol.* **83**: 436–454.
37. Craun, G.F. and Frost, F.J. (2002). Possible information bias in a waterborne outbreak investigation. *Int. J. Environ. Health Research* **12**: 5–15.
38. Craun, G.F., Frost, F.J., Calderon, R.L., Hilborne, H., Fox, K.R., Reasoner, D.J., Poole, C., Rexing, D.J., Hubbs, S.A., and A.P. Dufour. (2001). Improving waterborne disease outbreak investigations. *Int. J. Environ. Health Research* **11**: 229–243.
39. Rodman, J.S., Frost, F.J., and Jakubowski, W. (1998). Using nurse hot line calls for disease surveillance. *Emerg. Infect. Diseases* **4**: 1–4.
40. Rodman, J.S., Frost, F., Burchat, I.D., Fraser, D., Langer, J., and Jakubowski, W. (1997). Pharmacy sales—a method of disease surveillance. *J. Environ. Health* **60**(4): 8–14.
41. Nulsen, M.F., Tilley, P.G., Lewis, L., Zhang, H.Z., and Isaac-Renton, J.L. (1994). The humeral and cellular host immune responses in an outbreak of giardiasis. *Immunol. Infect. Diseases* **4**: 100–105.
42. Moss, D.M. and Lammie, P.J. (1993). *J. Am. Soc. Trop. Med. Hygiene* **49**: 393.

DISINFECTANTS

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Disinfection of drinking water was instituted at a time when waterborne infectious diseases were the primary focus in public health. The use of disinfectants such as chlorine, chloramine, chlorine dioxide, ozone, and ultraviolet radiation has resulted in a reduction in the outbreak of diseases such as cholera and polio in many parts of the world. The choice of disinfectant is dependent on their availability, ease of use, cost, and their efficacy in disinfecting water. Some disinfectants commonly used in water treatment plants are not stable in water for long periods of time, which reduces their disinfection efficacy. Current practices to control pathogens in drinking water include using a combination of disinfectants, coagulation, and filtration. A main disadvantage of using disinfectants in drinking water is their ability to react with organic and inorganic matter in water to form disinfection byproducts that may be of health concern. The disinfectants can also be hazardous at high concentrations, but toxicological studies suggest that their toxicity is likely not relevant at the low concentrations encountered in drinking water.

PURPOSE

Contaminated, untreated, or inadequately treated water is known to transmit disease-causing pathogens such as bacteria, viruses, fungi, and protozoa (1). The size of these pathogens varies from a few hundred microns for bacterial clusters to around 0.01 μm for viruses (2). Although physical water treatment processes such as sedimentation and filtration may remove pathogens that are greater than 10 μm in size, ultra- or nanofiltration may be required to remove disease-causing pathogens (3). Conventional filtration is usually not practical for smaller systems, and, ultrafiltration may not be economically viable to treat large quantities of water; therefore, chemical treatment may have to be employed to treat water. The process of reducing the number of pathogenic microorganisms through the addition of chemicals (i.e., disinfectants) into water is called disinfection.

A variety of disinfectants may be used in water treatment plants, with the choice dependent on the location and size of the plant, the cost effectiveness, the pathogen(s) of concern, the water source, the characteristics of the pretreated water, and the disinfectant characteristics (e.g., solubility, stability, disinfecting and deodorizing ability, corrosiveness, and the time required to disinfect). Other factors that are considered include the effectiveness of the disinfectant in killing a range of microorganisms, the potential to form disinfection byproducts (DBPs) that may cause health effects in humans and animals, and the ability of the disinfecting agents to remain effective in water throughout the water distribution system.

HISTORY

Prior to A.D. 1600, civilizations consumed water based on visual clarity, or after treatments such as exposing the water to sunlight, dipping heated copper or other metals in water, boiling, and filtering water through a cloth (4). Other types of water treatment such as exposure to germicidal metals (e.g., silver and copper), sand filtration, distillation, coagulation, and adsorption with alum, lime, plant extracts, charcoal, clay, or plant materials have been employed since the 1600s. Modern methods of water disinfection were first used in Europe in the mid-to-late 1800s. One of the first known uses of chlorine as a germicide was Ignac Semmelweis' introduction of chlorine water for hand cleansing in the Vienna General Hospital maternity wards in 1846 (5).

Following research advances on the effect of microorganisms on human health in the 1870s, and improvements to physical water treatment technologies such as slow sand filtration in the 1880s, chlorine (as chloride of lime) and ozone were first used as drinking water disinfectants on a plant-scale basis at water treatment facilities in Hamburg, Germany and Oudshoorn, Holland, respectively, in 1893 (5,6). In 1897, Sims Woodhead used bleach to sterilize potable water at Maidstone, England after a typhoid outbreak. In 1903, a water treatment facility in Middlekerke, Belgium was the first to use chlorine gas as a disinfectant (4,7).

In North America, the first use of chemical disinfection at water treatment plants began in 1908 when chlorine was used as a disinfectant in Jersey City, New Jersey (as sodium hypochlorite) and Chicago, Illinois (as chloride of lime). Chloramination was first used in Ottawa, Canada and Denver, Colorado in 1917, whereas ozonation was first used in the United States in the 1940s (4). Today, chemical disinfection of drinking water is widely recognized as a necessity and is widely practiced at city, community, and point-of-use levels throughout the United States.

TYPES OF DISINFECTANTS

Chemical disinfection is considered the most effective treatment to inactivate pathogens in drinking water. A majority of the disinfectants that are in use in water treatment plants today are oxidants such as chloramine, chlorine dioxide, chlorine gas, electrochemically generated oxidant from sodium chloride (NaCl), hypochlorite, ozone, and ultraviolet (UV) light. Additional chemical disinfectants used to treat drinking water, especially in households, include acids and bases such as citric juices, lime, mineral acids and hydroxide salts, metals such as copper or silver, surfactants, and permanganate (8). Since each disinfectant has its own advantages and disadvantages (summarized in CHLORINATION BYPRODUCTS and the ALTERNATIVE DISINFECTANTS), a combination of multiple treatment processes including sedimentation, coagulation, flocculation, filtration, and disinfection is used in the majority of the water treatment plants in the world today. Table 1 provides a summary of the water treatment methods used, their availability, ease of use, cost, and efficacy in neutralizing the disease-causing pathogens.

DISINFECTION EFFICACY

Disinfection kinetics is usually expressed by Chick's law (also known as the CT law), which relates the activity [e.g., 3-log (99.9%) or 5-log (99.999%) reduction] to the product of disinfectant concentration (C) and contact time (T) (12). For example, to provide a given degree of disinfection, a low concentration and high contact time may be maintained or vice versa (13). The CT law may not provide adequate disinfection due to various factors that may affect the efficacy of the disinfectant, such as the type of pathogen; type of disinfectant; chemical factors such as pH, dissolved organic matter, salts, and ions; and particulate matter (14). Among the pathogens, vegetative bacteria are generally the easiest to disinfect followed by viruses, bacterial spores, fungal spores, and protozoan parasites (8). The formation of aggregates with other microorganisms or particulates in water may reduce the disinfectant's efficacy by preventing access to the pathogens. Among the most commonly used disinfectants, ozone's ability to disinfect is generally the highest followed by chlorine dioxide, electrochemically generated chlorine, and chloramine. However, ozone is the least stable disinfectant in water and is hence unable to provide a stable disinfectant residual in treated water that is necessary to prevent regrowth of the disease-causing pathogens (15). The chlorine-based disinfectants on the other hand are relatively stable in water in the absence of pathogens. At neutral pH, the half-life of chlorine dioxide is 30 min and 14 h for a 0.01 M and 0.0001 M solution, respectively (15). At ambient temperatures, the half-life of chloramines is approximately 100 h (16), whereas the half-life of sodium hypochlorite varies between 60 and 1700 d for water containing 18% and 3% available chlorine, respectively (17).

The characteristics of the source water also influence the efficacy of the disinfectants. Certain disinfectants such as hypochlorite are more effective at low pH, whereas chloramines are effective at a higher pH (5,15). The disinfectants may be consumed through reactions with other dissolved constituents in the water such as dissolved

Table 1. Advantages of Different Water Treatment Methods and Their Efficacy

Method	Availability	Difficulty	Cost	Pathogen Efficacy	Comments
Acids and bases	☺☺☺☺	×	$$	⊖⊖	Mostly used for pH control in water treatment plants; some microbial deactivation reported.
Adsorption	☺☺☺	×××	$$$$	Variable	Some bioreactors remove pathogens and organics.
Aeration	☺☺☺	×	$	⊖	Has to be used with other methods to be practical.
Boiling	☺☺☺☺	×	$$	⊖ ⊖ ⊖⊖	Used mostly at the point-of-use level.
Chloramines	☺☺☺☺	××	$$$	⊖ ⊖ ⊖	Less effective than free chlorine when used as a primary disinfectant; more practical as a secondary disinfectant.
Chlorine gas	☺☺☺☺	×××	$$$	⊖ ⊖ ⊖⊖	Widely used disinfectant.
Chlorine generated electrochemically from NaCl	☺☺☺☺	××	$$$	⊖ ⊖ ⊖⊖	Can be generated on site.
Chlorine dioxide	☺☺	×××	$$$$	⊖ ⊖ ⊖⊖	Highly effective as a primary disinfectant but is a poor secondary disinfectant.
Coagulation	☺☺☺	×××	$$$	⊖⊖	Useful in settling large flocculants of bacteria.
Combination of disinfection, coagulation, and filtration	☺	××××	$$$$	⊖ ⊖ ⊖ ⊖ ⊖	Best method, but is accompanied by high costs.
Filtration	☺☺☺	×××	$$$$	⊖ ⊖ ⊖	Ultrafiltration needed to remove viruses.
Hypochlorite	☺☺☺☺	××	$$$	⊖ ⊖ ⊖⊖	Most widely used disinfectant; highly unstable chemical.
Iodine	☺	××	$$$$	⊖ ⊖ ⊖⊖	Mostly used in tablet form at the point-of-use.
Ion exchange	☺	××××	$$$$	⊖	Can remove salts but not pathogens.
Ozone	☺☺	××××	$$$$	⊖ ⊖ ⊖⊖	Most effective as a primary disinfectant; cannot be used as a secondary disinfectant.
Sedimentation	☺☺☺☺	××	$$	⊖	Useful for removing adhering bacteria.
Silver or copper	☺☺☺☺	×	$$	⊖	Heated metal dipped into water at the point-of-use level in lieu of boiling.
Sunlight	☺☺☺☺	×	$	⊖⊖	Large open spaces and constant sunlight required; impractical for everyday use.
UV lamps	☺	×××	$$$	⊖ ⊖ ⊖	Effective as a primary disinfectant against pathogens but not as secondary disinfectant; space requirements per volume of water disinfected are impractical for larger systems.

Source: References 4, 5, 8–11.

organic matter and other salts to form DBPs, thereby limiting the amount of disinfectant available for pathogen inactivation.

CHEMISTRY OF DISINFECTANTS

The physical and chemical properties of disinfectants can affect their behavior in drinking water as well as their toxicity. Apart from reacting with natural organic matter or other solutes to form DBPs, disinfectants undergo a number of reactions to form products that may be toxic to humans and animals.

Free Chlorine

Chlorine gas (Cl_2) when exposed to water forms hypochlorous acid (HOCl) and hydrochloric acid ($HCl \rightleftharpoons H^+$ and Cl^-).

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{1}$$

At pH $>$ 7.5, HOCl will dissociate to form hypochlorite ion (OCl^-) (18). In addition, calcium hypochlorite [$Ca(OCl)_2$] and sodium hypochlorite (NaOCl) also immediately dissociate in water to form OCl^-. HOCl is a better disinfectant than OCl^- due to the relative ease with which it can penetrate cell walls (5). Hence, the pH of the water has to be lowered to improve the disinfection efficacy.

$$Ca(OCl)_2 \rightleftharpoons Ca^{2+} + 2OCl^- \tag{2}$$

$$NaOCl \rightleftharpoons Na^+ + OCl^- \tag{3}$$

$$H^+ + OCl^- \rightleftharpoons HOCl \tag{4}$$

At pH $>$ 12, hypochlorite ions can react to form chlorite ($ClO_2{}^-$) and chlorate ($ClO_3{}^-$), which are of major health concern (19,20).

$$OCl^- + OCl^- \rightarrow ClO_2{}^- + Cl^- \tag{5}$$

$$OCl^- + ClO_2{}^- \rightarrow ClO_3{}^- + Cl^- \tag{6}$$

In waters containing bromides, hypochlorite can react with bromide (Br^-) to form hypobromous acid (HOBr), thereby consuming the available free chlorine meant for disinfection (21).

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{7}$$

Chlorine Dioxide

Chlorine dioxide (ClO_2) dissolves in water under alkaline conditions to form chlorite ($ClO_2{}^-$) and chlorate

Table 2. Disinfectant Use in the United States

Disinfectant	Medium and Large Systems (>10,000 People)	Small Systems (<10,000 People) Using Groundwater	Small Systems (<10,000 People) Using Surface Water
Chloramines	29%	—	2%
Chlorine dioxide	8%	—	6%
Chlorine gas	84%	61%	82%
Hypochlorite	20%	34%	26%
Ozone	6%	—	—

Source: References 36 and 37.

(ClO_3^-)(22,23). However, unlike free chlorine, hypobromous acid and organohalogen DBPs are not produced.

$$2ClO_2 + 2OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O \qquad (8)$$

The half-life of aqueous ClO_2 decreases substantially with increasing ClO_2 molar concentration and with pH values above 9 (22,24). Even at neutral pH values and low ClO_2 concentrations, the half-life of ClO_2 is usually less than 24 h. Hence, the storage of stock solutions of ClO_2 for even a few hours is impractical.

Ozone

Dissolved ozone (O_3) either reacts with other dissolved solutes in water to form DBPs or decomposes in water to form highly reactive hydroxyl radicals ($OH^\bullet$) (25). Both ozone and hydroxyl radicals are effective disinfectants. Unlike ozone, hydroxyl radicals are highly nonselective in reactions with organic and inorganic solutes and are easily consumed, thereby limiting the amount available for disinfection.

$$O_3 + H_2O \rightarrow O_2 + OH^\bullet \qquad (9)$$

The kinetics of ozone reactions are favorable for disinfection and oxidation of many organic and inorganic contaminants in drinking water. However, for many difficult-to-oxidize organic compounds such as chloroform, some alcohols, and saturated alkyl moieties, the kinetics of ozone oxidation may be very slow (26–28).

Chloramines

When ammonia is added to drinking water containing free chlorine, hypochlorous acid will react with ammonia to form one of three types of chloramines depending on temperature, pH, and reaction time (29). Monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) are formed between pH 4.5 and 8.5 and are commonly found at pH typical of drinking water (pH 6–8.5). Monochloramine is most common when the pH is above 8. When the pH is below 4.5, the most common form of chloramine is trichloroamine (NCl_3), which produces a very foul odor and is sometimes found in swimming pools. Chloramines are effective disinfectants against bacteria but not viruses (30,31).

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \qquad (10)$$

$$NH_2Cl + 2HOCl \rightarrow NHCl_2 + 2H_2O \qquad (11)$$

$$NHCl_2 + 3HOCl \rightarrow NCl_3 + 3H_2O \qquad (12)$$

TOXICOLOGY OF DISINFECTANTS

At high concentrations, chlorine gas, chloramine, chlorine dioxide, dichloramine, monochloramine, and ozone have been shown to be strong respiratory irritants in humans (32). Hypochlorite is highly caustic and causes skin and esophagus irritation even at low concentrations (33). When household cleaning agents containing hypochlorite and ammonia are mixed, chloramine gas is formed, which can cause severe lung injury (34). The limited toxicological studies on the above-mentioned disinfectants suggest that their toxicity is likely not relevant at the low concentrations encountered in drinking water (35).

TYPICAL USE IN THE UNITED STATES

Chlorine-based disinfectants are used in more than 95% of the water treatment systems across the United States. Table 2 provides a breakdown of the percentages of water treatment systems that use the various disinfectants. Some water treatment systems use multiple disinfectants due to different primary and secondary disinfection practices. Additional information on the use of various disinfectants in other countries, their advantages and disadvantages, including DBP formation, are available in CHLORINATION BYPRODUCTS and ALTERNATIVE DISINFECTANTS.

BIBLIOGRAPHY

1. CDC (2000). *Safe Water Systems for the Developing World: A Handbook for Implementing Household-Based Water Treatment and Safe Storage Projects*. Department of Health and Human Services, Centers for Disease Control and Prevention, Atlanta.
2. American Water Works Association (1999). *Water Quality and Treatment*, 5th Edn. McGraw Hill, New York.
3. Najm, I. and Trussell, R.R. (1999). New and emerging drinking water treatment technologies. In: *Identifying Future Drinking Water Contaminants*. National Research Council, National Academy Press, Washington, DC.
4. Hall, E.L. and Dietrich, A.M. (2000). A brief history of drinking water. *Opflow* **26** (June).
5. White, G.C. (1972). *Handbook of Chlorination. For Potable Water, Wastewater, Cooling Water, Industrial Processes, and Swimming Pools*. Van Nostrand Reinhold, New York.
6. Langlais, B., Reckhow, D.A., and Brink, D.R. (1991). *Ozone in Water Treatment: Application and Engineering*. Lewis Publishers, Chelsea, MI.

7. Pontius, F. (1990). *Water Quality and Treatment*, 4th Edn. American Water Works Association/McGraw-Hill, New York.
8. Sobsey, M.D. (2002). *Managing Water in the Home: Accelerated Health Gains from Improved Water Supply*. World Health Organization, Geneva. Report WHO/SDE/WSH/02.07.
9. Trussell, R.R. (1991). Control strategy 1: alternative oxidants and disinfectants. Presentation at the 98th Annual American Water Works Association Conference.
10. Craun, G.F. et al. (1994). Balancing chemical and microbial risks of drinking water disinfection, Part I. Benefits and potential risks. *J. Water Res. Sci. Technol. Aqua.* **43**(4): 192–199.
11. Craun, G.F. et al. (1994). Balancing chemical and microbial risks of drinking water disinfection, Part II. Managing the risks. *J. Water Res. Sci. Technol. Aqua* **43**(5): 207–218.
12. Chick, H. (1908). An investigation of the laws of disinfection. *J. Hygiene* **8**: 92–157.
13. Haas, C.N. and Karra, S.B. (1984). Kinetics of microbial inactivation by chlorine-1. *Water Res.* **18**(11): 1443–1449.
14. Sobsey, M.D. (1989). Inactivation of health-related microorganisms in water by disinfection processes. *Water Sci. Technol.* **21**(3): 179–195.
15. Haas, C.N. (1990). Disinfection. In: *Water Quality and Treatment: A Handbook of Community Water Supplies*, F. Pontius (Ed.). American Water Works Association/McGraw-Hill, Washington, DC.
16. Kinman, R.N. and Layton, R.F. (1976). New method for water disinfection. *J. Am. Water Works Assoc.* **68**(6): 298–302.
17. Baker, R.J. (1969). Characteristics of chlorine compounds. *J. Water Pollut. Control Fed.* **41**: 482–485.
18. Morris, J.C. (1966). The acid ionization constant of HOCl from 5 °C to 35 °C. *J. Phys. Chem.* **70**: 3798–3805.
19. Gordon, G., Adam, L., and Bubnis, B. (1995). Minimizing chlorate ion formation. *J. Am. Water Works Assoc.* **87**(6): 97–106.
20. Gordon, G. (1997). Predicting liquid bleach decomposition. *J. Am. Water Works Assoc.* **89**(4): 142–149.
21. Farkas, L., Lewin, M., and Bloch, R. (1949). The reaction between hypochlorites and bromides. *J. Am. Chem. Soc.* **71**: 1988–1991.
22. Gordon, G., Kieffer, R.G., and Rosenblatt, D.H. (1972). The chemistry of chlorine dioxide. *Prog. Inorg. Chem.* **15**: 201–286.
23. Gordon, G. and Rosenblatt, A. (1996). Gaseous, chlorine-free chlorine dioxide for drinking water. In: *Proceedings of the Water Quality Technology Conference*. New Orleans, LA. American Water Works Association, Denver, CO.
24. Granstrom, M.L. and Lee, G.F. (1957). Rates and mechanisms of reactions involving oxychloro compounds. *Public Works* **88**(12): 90–92.
25. Reckhow, D.A. (1999). Control of disinfection by-product formation using ozone. In: P.C. Singer (ed.), *Formation and Control of Disinfection By-Products in Drinking Water*, AWWA, Denver, CO.
26. Hoigne, J. and Bader, H. (1979). Ozonation of water: selectivity and rate of oxidation of solutes. *Ozone Sci. Eng.* **1**(1): 73–85.
27. Staehelin, J. and Hoigne, J. (1983). Mechanism and kinetics of decomposition of ozone in water in the presence of organic solutes. *Vom Wasser* **61**: 337–348.
28. Hoigne, J., Bader, H., Haag, W.R., and Staehelin, J. (1985). Rate constants of reactions of ozone with organic and inorganic compounds in water: III. Inorganic compounds and radicals. *Water Res.* **19**(8): 993–1004.
29. Morris, J.C. (1965). Kinetics reactions between aqueous chlorine and nitrogen compounds. Fourth Rudolphs Research Conference, Rutgers University, June 15–18, 1965.
30. Chang, S.L. (1971). Modern concept of disinfection. *ASCE J. Sanitary Eng. Div.* **97**: 689–707.
31. Weber, G.R., Bender, R., and Levine, M. (1940). Effect of ammonia on the germicidal efficiency of chlorine in neutral solutions. *J. AWWA* **32**(11): 1904–1912.
32. MMWR (1991). Chlorine gas toxicity from mixture of bleach with other cleaning products—California. *MMWR* **40**(36): 619–621.
33. Cotter, J.L., Fader, R.C., Lilley, C., and Herndon, D.N. (1985). Chemical parameters, antimicrobial activities, and tissue toxicity of 0.1 and 0.5% sodium hypochlorite solutions. *Antimicrob. Agents Chemother.* **28**: 118–122.
34. Tanen, D.A., Graeme, K.A., and Raschke, R. (1999). Severe lung injury after exposure to chloramine gas from household cleaners. *N. Engl. J. Med.* **341**: 848–849.
35. WHO (2000). *Environmental Health Criteria 216: Disinfectants and Disinfectant By-products*, World Health Organization, Geneva.
36. American Water Works Association (2000). Committee report: disinfection at small systems. *J. Am. Water Works Assoc.* **92**(5): 24–31.
37. American Water Works Association (2000). Committee report: disinfection at large and medium-sized systems. *J. Am. Water Works Assoc.* **92**(5): 32–43.

DISINFECTION

National Drinking Water
Clearinghouse

Disinfection is an important step in ensuring that water is safe to drink. Water systems add disinfectants to destroy microorganisms that can cause disease in humans. The Surface Water Treatment Rule requires public water systems to disinfect water obtained from surface water supplies or groundwater sources under the influence of surface water.

Primary methods of disinfection are chlorination, chloramines, ozone, and ultraviolet light. Other disinfection methods include chlorine dioxide, potassium permanganate, and nanofiltration. Since certain forms of chlorine react with organic material naturally present in many water sources to form harmful chemical byproducts, the U.S. Environmental Protection Agency has proposed maximum levels for these contaminants.

DISINFECTION KEEPS WATER SAFE

Why Disinfect Drinking Water?

Disinfection kills or inactivates disease-causing organisms in a water supply and must provide a 99.9 percent inactivation of *Giardia lamblia* cysts and enteric viruses to protect health and to comply with the U.S. Environmental Protection Agency (EPA) regulations. There are two kinds of disinfection: primary disinfection achieves the desired level of microorganism kill or inactivation, while secondary disinfection maintains a disinfectant residual in the finished water that prevents the regrowth of microorganisms.

What Regulations Govern It?

The EPA Surface Water Treatment Rule (SWTR) requires systems using public water supplies from either surface water or groundwater under the direct influence of surface water to disinfect.

Also, since some disinfectants produce chemical by-products, the dual objective of disinfection is to provide the required level of organism destruction and remain within the maximum contaminant level (MCL) for the SWTR disinfection set by EPA. At this time, an MCL is set for only Total Trihalomethanes, and proposed for additional disinfection by-products.

How is Disinfection Achieved?

Our natural environment contains numerous microorganisms. Most of these present no concerns. However, some—such as *Giardia lamblia* and various viruses, which can be present in water supplies—are extremely harmful and can cause disease in humans. These disease-causing organisms are known as pathogens.

Because pathogens can be present in drinking water supplies, disinfection is very important—the EPA requires it for surface water and groundwater under the influence of surface water. Disinfection treatment methods include chlorination, chlorine dioxide, chloramines, ozone, and ultraviolet light.

When combined with conventional treatment, such as coagulation, flocculation, sedimentation, and filtration, good results have been obtained. Direct filtration, slow sand filtration, and diatomaceous earth filtration, along with disinfection, have been just as successful.

Groundwater systems that disinfect may have to add filtration if the water contains iron and manganese. In fact, insoluble oxides form when chlorine, chlorine dioxide, or ozone are added to these systems. Both ozonation and chlorination may cause flocculation of dissolved organics, thus increasing turbidity and necessitating filtration. The effectiveness of disinfection is judged by analyzing for an indicator organism (total coliform bacteria). This organism is considered harmless, but its presence indicates that pathogens may also have survived.

COMPARING DISINFECTANTS

Chlorination (Gas)

At normal pressures, elemental chlorine is a toxic, yellow-green gas, and is liquid at high pressures.

Advantages. Chlorine is very effective for removing almost all microbial pathogens and is appropriate as both a primary and secondary disinfectant.

Limitations. Chlorine is a dangerous gas that is lethal at concentrations as low as 0.1 percent air by volume.

Process. Chlorine gas is released from a liquid chlorine cylinder by a pressure reducing and flow control valve operating at a pressure less than atmospheric. The gas is led to an injector in the water supply pipe where highly pressurized water is passed through a venturi orifice creating a vacuum that draws the chlorine into the water stream. Adequate mixing and contact time must be provided after injection to ensure complete disinfection of pathogens. It may be necessary to control the pH of the water.

Equipment. A basic system consists of a chlorine cylinder, a cylinder-mounted chlorine gas vacuum regulator, a chlorine gas injector, and a contact tank or pipe (see Fig. 1). Prudence and/or state regulations would require that a second cylinder and gas regulator be provided with

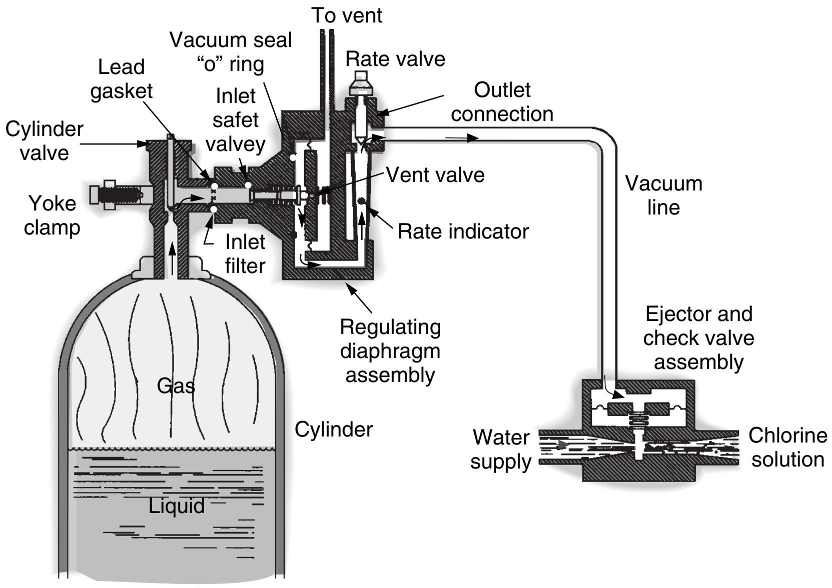

Figure 1. Cylinder-mounted chlorinator. Reprinted with permission from Capital Controls Company, Inc.

a change-over valve to ensure continuity of disinfection. Additional safety and control features may be required.

A gas chlorinator should be installed in a room or chamber with direct emergency access to outside air and fitted with an exhaust fan ventilation system.

Federal and state safety regulations must be observed. If not onsite, self-contained breathing apparatus and a chlorine cylinder repair kit should be available within a reasonable time frame and/or distance.

Chemicals. Chlorine gas is supplied as liquid in high pressure cylinders.

Chlorination (Sodium Hypochlorite Solution)

Sodium hypochlorite is available as a solution in concentrations of 5 to 15 percent chlorine, but is more expensive than chlorine gas (as available chlorine).

Advantages. Sodium hypochlorite is easier to handle than gaseous chlorine or calcium hypochlorite.

Limitations. Sodium hypochlorite is very corrosive and should be stored with care and kept away from equipment that can be damaged by corrosion. Hypochlorite solutions decompose and should not be stored for more than one month. It must be stored in a cool, dark, dry area.

Process. Sodium hypochlorite solution is diluted with water in a mixing/holding tank. The diluted solution is injected by a chemical pump into the water supply pipe at a controlled rate. Adequate mixing and contact time must be provided.

Equipment. A basic liquid chlorination system, or hypochlorinator, includes two metering pumps (one serving as a standby), a solution tank, a diffuser (to inject the solution into the water), and tubing.

Chemicals. Sodium hypochlorite solution is readily available.

Sodium hypochlorite can also be generated onsite by electrolysis of sodium chloride solution in specialized proprietary equipment. The only supplies required are common salt and electricity. Hydrogen is given off as a by-product and must be safely dispersed.

Chlorination (Solid Calcium Hypochlorite)

Calcium hypochlorite is a white solid that contains 65 percent available chlorine and dissolves easily in water.

Advantages. When packaged, calcium hypochlorite is very stable, allowing a year's supply to be bought at one time.

Limitations. Calcium hypochlorite is a corrosive material with a strong odor that requires proper handling. It must be kept away from organic materials such as wood, cloth, and petroleum products. Reactions between calcium hypochlorite and organic material can generate enough heat to cause a fire or explosion. Calcium hypochlorite readily absorbs moisture, forming chlorine gas. Therefore, shipping containers must be emptied completely or carefully resealed.

Process. Calcium hypochlorite may be dissolved in a mixing/holding tank and injected in the same manner as sodium hypochlorite. Alternatively, where the pressure can be lowered to atmospheric, such as at a storage tank, tablets of hypochlorite can be directly dissolved in the free flowing water by a proprietary device that provides flow-proportional chlorination with gravity feed of the tablets.

Equipment. The equipment used to mix the solution and inject it into the water is the same as that for sodium hypochlorite. Solutions of 1 or 2 percent available chlorine can be delivered by a diaphragm-type, chemical feed/metering pump or by tablet chlorinator.

Chemicals. Calcium hypochlorite can be purchased in granular, powdered, or tablet form.

Chloramine

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine (hypochlorite or hypochlorous acid).

Advantages. An effective bactericide that produces fewer disinfection by-products, chloramine is generated onsite. Usually, chloramine-forming reactions are 99 percent complete within a few minutes.

Limitations. Chloramine is a weak disinfectant. It is much less effective against viruses or protozoa than free chlorine. Chloramine is appropriate for use as a secondary disinfectant to prevent bacterial regrowth in a distribution system. Nitrogen trichloride appears to be the only detrimental reaction. It may be harmful to humans and imparts a disagreeable taste and odor to the water. The use of the proper amounts of each chemical reactant will avoid its production.

Process. Chlorine (gaseous solution or sodium hypochlorite) is injected into the supply main followed immediately by injection of ammonia (gaseous solution or as ammonium hydroxide). As before, adequate mixing and contact time must be provided. The mix of products produced when water, chlorine, and ammonia are combined depends on the ratio of chlorine to ammonia and the pH of the water. Chlorine-to-ammonia ratios of 5:1 should not be exceeded. If the pH drops below 5, some nitrogen trichloride may be formed.

Equipment. The generation of chloramines requires the same equipment as chlorination (gaseous or aqueous hypochlorination), plus equipment for adding ammonia (gaseous or aqueous).

All chlorine added to drinking water must meet American National Standards Institute (ANSI), and NSF *International*, formerly the National Sanitation Foundation (NSF) standards. *ANSI/NSF Standard 60: Drinking Water Chemicals—Health Effects* covers water treatment chemicals.

Chemicals. Chemicals used to generate chloramine from ammonia and chlorine gas depend on the ammonia-based chemical used. Anhydrous ammonia is the least expensive, while ammonium sulfate is the most expensive.

Ozonation

Ozone, an allotrope of oxygen having 3 atoms to each molecule, is a powerful oxidizing and disinfecting agent. It is formed by passing dry air through a system of high voltage electrodes.

Advantages. Requiring shorter contact time and dosage than chlorine, ozone is widely used as a primary disinfectant in many parts of the world—but is relatively new to the U.S. Ozone does not directly produce halogenated organic materials unless a bromide ion is present.

Limitations. Ozone gas is unstable and must be generated onsite. A secondary disinfectant, usually chlorine, is required because ozone does not maintain an adequate residual in water.

Process. The five major elements of an ozonation system are:

- air preparation or oxygen feed;
- electrical power supply;
- ozone generation—usually using a corona discharge cell consisting of two electrodes;
- ozone contact chamber; and
- ozone exhaust gas destruction.

Equipment. Ozonation equipment includes air preparation equipment; an ozone generator, contactor, destruction unit; and instrumentation and controls. The capital costs of ozonation systems are relatively high. Operation and maintenance are relatively complex. Electricity represents 26 to 43 percent of total operating and maintenance costs for small systems.

Chemicals. For many applications, pure oxygen is a more attractive ozone feed gas than air because:

- it has a higher production density,
- it requires lower energy consumption,
- it doubles the amount of ozone that can be generated per unit, and
- it requires smaller gas volumes for the same ozone output, thus lowering costs for ancillary equipment.

Ultraviolet Light (UV)

Ultraviolet (UV) radiation is generated by a special lamp. When it penetrates the cell wall of an organism, the cell's genetic material is disrupted and the cell is unable to reproduce.

Advantages. UV radiation effectively destroys bacteria and viruses. As with ozone, a secondary disinfectant must be used to prevent regrowth of micro-organisms. UV radiation can be attractive as a primary disinfectant for small systems because:

- it is readily available,
- it produces no known toxic residuals,
- it requires short contact times, and
- the equipment is easy to operate and maintain.

Limitations. UV radiation may not inactivate *Giardia lamblia* or *Cryptosporidium* cysts, and should be used only by groundwater systems not directly influenced by surface water—where there is virtually no risk of protozoan cyst contamination. UV radiation is unsuitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. These materials can react with or absorb the UV radiation, reducing the disinfection performance.

Process. The effectiveness of UV radiation disinfection depends on the energy dose absorbed by the organism, measured as the product of the lamp's intensity (the rate at which photons are delivered to the target) and the time of exposure. If the energy dosage is not high enough, the organism's genetic material might only be damaged instead of destroyed. To provide a safety factor, the dosage should be higher than needed to meet disinfection requirements.

Equipment. UV lamps and a reactor (see Fig. 2).

Chemicals. No chemical oxidant required; therefore, microorganisms can be killed without generating by-products of chemical oxidation or halogenation.

HOW DO YOU CONTROL DISINFECTION BYPRODUCTS?

A number of factors can affect the formation of disinfection byproducts. These include the types and concentrations of organic materials present when chlorine is added, the dosage of chlorine, the temperature and pH of the water, and the reaction time.

To control the formation of halogenated byproducts (compounds formed by the reaction of a disinfectant, such as chlorine with organic material in the water supply) during chlorination, EPA has identified these three strategies:

1. Remove the byproducts after they are formed, which can be difficult and costly.
2. Use alternative disinfectants that do not produce undesirable byproducts, which is often the most cost-effective strategy.
3. Reduce the concentration of organics in the water before oxidation or chlorination to minimize the formation of byproducts. This will provide the highest quality finished water.

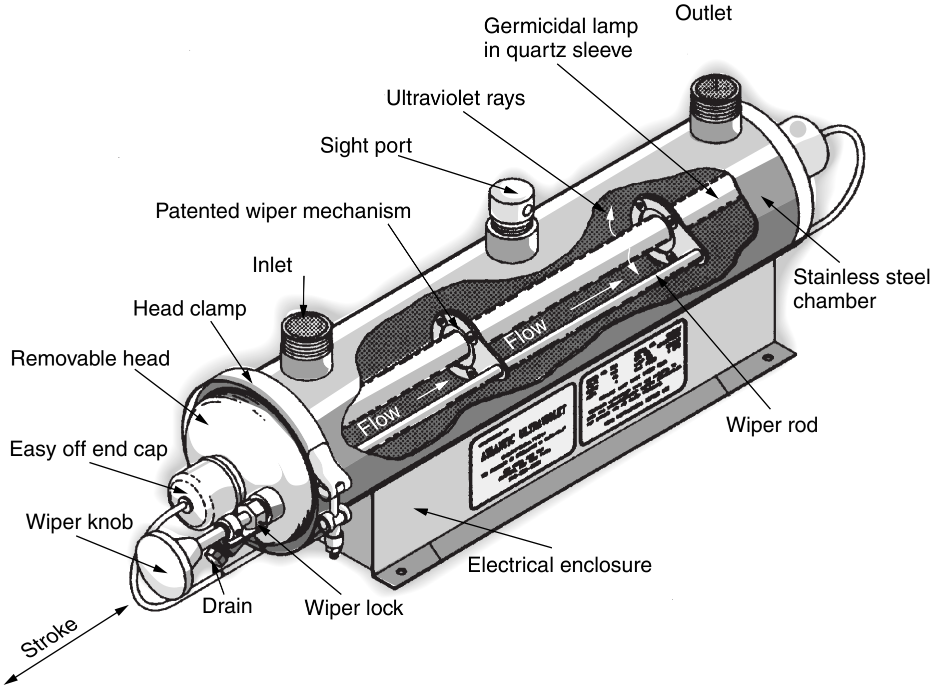

Figure 2. Ultraviolet water purifier. Reprinted with permission from Atlantic Ultraviolet Corporation.

WHERE CAN I FIND MORE INFORMATION

Information on disinfection was primarily obtained from two sources: Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities, *EPA/625/5-90/025*; *and* Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, *EPA/625/4-89/023. Both can be ordered free from the EPA Office of Research and Development at (513) 569-7562.*

These publications also can be ordered from the National Drinking Water Clearinghouse (NDWC); however, copying costs apply. The first book, item #DWBKGN09, an 82-page publication, costs $11.82; and the second, item #DWBKDM04, a 209-page book, costs $30.05. Shipping and handling charges apply.

For further information or to order additional copies of "Tech Brief: Disinfection," item #DWBRPE47, or the above publications call the NDWC at (800) 624-8301.

WATER DISTRIBUTION SYSTEM OPERATION

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OPERATION, MAINTENANCE, AND DESIGN OF WATER SERVICES

Contemporary cities and their inhabitants depend on a reliable and generous public water supply system for their functioning and to protect and promote health, productivity, and well-being. The possibility of having piped water and sewerage systems at home explains why cities can support such huge human concentrations. Some major technological and cultural changes to make cities less dependent on such public services are needed but still far in the future. These vast systems, almost invisible to many, as they are underground networks, are complex and delicate arteries that require daily operation and care by professional people devoted exclusively to such tasks.

Various and ample are the duties and responsibilities of any water utility, although there are some variants around the world. Some utilities deal exclusively with clean water distribution; others have broader functions such as extraction from a remote site, conduction, purification, distribution, sewerage, waste treatment, and even tasks such as operation of pipe networks for fire combat, or selling treated wastewater, pluvial drainage, solid waste collection, or energy supply.

The operational tasks for distributing clean water in a city involve monitoring flows, pressures, storage levels, and water quality at different network locations; controlling and moving valves; attending to reports and enquiries from the public; billing and charging for consumption; keeping updated infrastructure maps and consumer records and census; repairing leaks; and replacing or improving pipes, hydrants, pumps, and other water distribution networks components.

There is no clear or definite boundary between operational and maintenance tasks, and their distinction is merely the intensity or frequency of a given job. Sometimes, the same employee team performs operational, preventive, or corrective maintenance tasks. In contrast, other rather specialized tasks can require a contract with a private service provider (*as analyzing water samples to detect a specific and difficult pollutant or controlling and supervising a sophisticated automated pump*).

There is a strong bond between the system's "hydraulic design" and its "operation," and often they can be synonymous. For instance, pressure may be controlled automatically by properly locating storage tanks or automatic valves. Although in some not-so-well-designed systems, frequent manual movements (*operation*) of valves may be needed. The same can be said for filling and emptying water volumes in regulating tanks to meet differences in demand and supply flows. When storage tanks are properly sized to accommodate daily variations of demand, with timing of supply pumps, they will function correctly, but if not, a lot of work is required from "operations personnel" (*usually accompanied by uneasiness and complaints from consumers*).

One practical definition of our topic, although not accepted everywhere (*and not even here*), is this: *Operation* is the organized procedure for causing a piece of equipment, a treatment plant, or other facility or system to perform its intended function, but not including the initial building or installation of the unit. Usually operation and maintenance are referred simultaneously, as *O & M*, meaning the management of a facility involving operating, repair, and replacement.

Another more general definition (*World Bank*) states that *operation* includes the planning and control of the extraction/collection, treatment, conveyance, and delivery of water, and/or the collection, treatment, and disposal of effluent. It also covers the management of client and public relations, legal, personnel, commercial, and accounting functions.

DESIRABLE OPERATING CONDITIONS

Not all cities offer the same service standards of water quality, pressure, and reliability, although most of them guide their performance and duties by a certain set of local goals or regulations. Sometimes, an external autonomous supervisory board exists, sponsored by consumers or by an international agency, to guarantee the provider's accountability in protecting people's health and economy.

Some of these operational goals may be

— Continuity of supply (*24 hours, 365 days per year*).
— Keep low water tariffs (*in balance with expenditures and investments*), and in an increasing block fashion (*the more you consume, the more you pay per water unit to keep the water demand as small as possible and preserve the resource*).
— Promote and advise customers to keep their water consumption low (*demand management*).
— Keep pressure not too weak, nor too strong at each house connection (*around 10 m to 30 m of water column, that is, between 1 to 3 bars*).
— Curb water leaks (*pipes burst*), and when they occur, repair them within a few hours.
— Satisfy daily and seasonal variations in water demand without spillage or damage to infrastructure or inconvenience to consumers.
— Use the least possible energy for pumping and other processes (*low operating costs*).
— Courteous, fair, and undiscriminatory treatment to all consumers.
— Water quality in all points of the network must meet established standards.
— Optimize the use of the system's installed capacity for water storage, pumping, and conduction (*profit from and use the existing infrastructure, keep it in good shape, and avoid the need for building more of it*).

ELEMENTS OF WATER DISTRIBUTION SYSTEM

It is convenient that any water supply system operator be simultaneously involved in, or at least aware of, the sewerage system and the treatment and disposal of wastewater. However, focusing only on the supply side, a water network may depend on the water coming from remote sources, purification plants, aqueducts and pumping stations. All these installations rely on various minor components and devices such as gates, valves, cisterns, and filters. All such items require careful operation and maintenance by the same institution attending to the distribution network in the city. Sometimes, the water sources are within the urban area, as in the case of pumping wells intermingled with the network. In that case, the water quality and pressure can be assured merely by local additions of chlorine or equivalent, and through booster pumps or pressure-breaking valves or tanks.

Some of the elements in a water distribution network are elevated tanks, underground reservoirs or cisterns, booster stations, valves of different types, meters (*for water mains and for customer consumption*), pipes, house connections, various types of fittings and protection cages, fire and public hydrants, local chlorination equipment, monitoring and sampling devices, and telemetry and SCADA systems (*supervisory control and data acquisition*) and all their electronic and electric apparatuses and connections. Besides those previously mentioned "fixed" (*on-site*) elements, there is a wide range of necessary mobile equipment such as vehicles, cranes, winches, mobile laboratories, and maintenance and repair equipment.

Water distribution pipes are normally arranged in grid or loop designs to provide easy flow of water by different routes (*particularly during hours of high demand*) and to avoid lines that dead-end and may cause water quality problems. All distribution systems should contain sufficient valving so that any area can be isolated for repair or for scrutiny in case of contamination risk, and only a minimum number of customers should be affected during the disruption.

PRINCIPAL OPERATIONS

Public water systems are designed to provide and maintain a reliable, high-quality water source (*e.g., groundwater or surface water*). Although one important operation to meet drinking water standards is water treatment, it will not be covered here to concentrate on what happens and is required in the water distribution network. Operations there deal with different cares and purposes, among which is preserving the water quality in the network.

The operation of a water distribution system (*inevitably linked to its maintenance and design*) includes attending to all kinds of requests or complaints from customers; meeting local standards and federal regulations; and the upkeep of pipes, storage tanks, and pumps that convey the water. Some of the activities are

- Hydraulic performance to meet water demands
- Map control and updating
- Modeling and corroboration of system's hydraulic behavior
- Records (*telemetry, samplings*), control, and analysis
- Leak detection and repair
- Cross connection control and backflow prevention
- Gauging flow (*district metering areas, DMA*) and consumption (*meters*)
- Billing consumers and collecting money from them
- Exercising of valves
- Water pipe flushing and internal cleaning
- Water quality monitoring
- Chlorination or dechlorination at local points
- Water main repair/replacement
- Electric and electronic equipment conservation and upgrading
- Inspecting quality of materials (*pipes, joints, chlorine*) and performance of equipment (*water meters, valves, etc.*)
- Storage tank maintenance
- Pump maintenance
- Prevention and training against vandalism, terrorism, and emergencies (*drought, flooding, earthquake, etc.*)

It would take too long to give details of all these operations, so only brief comments for some of them will be given in the following sections:

WATER DELIVERY AND MONITORING

The most important operation of any water distributing system is ensuring that enough and timely water arrives at each house. Therefore, one basic operation is the regulation of flows to adapt them to the hours of peak demand (*e.g., from 6 AM to 8 AM*), and to those of low demand (*e.g., during the night*). Usually, in well-designed and developed countries' systems, these maneuvers are performed "automatically" through "*operational storage*" from regulating tanks around the city. These tanks have float or diaphragm actuated valves that close the inflow when full, preventing spillage, and besides can send a signal to halt a remote pump. This exemplifies how operation depends on design, which in poor or simple systems, or in emergencies, has to be done manually.

Pumps and valves can be preprogrammed to start or stop on given schedules and can be monitored and acted-on through automatic or semiautomatic computerized *supervisory control* systems (*SCADA*) that can check pressure and flow at selected network points. On the other hand, they could simply be controlled manually, according to certain seasonal rules (*e.g., rationing of water in drought times*).

Telemetry and the ability to *communicate* efficiently are important in the successful operation and maintenance of a complex and expanded water supply system. One option is the use of mobile radiotelephones. Telemetry can provide a complete updated picture of the status of all components in the network, such as reservoir contents, water movements and trends, and pump stations. Condition monitoring is part of preventive maintenance and will help to minimize unscheduled shutdowns and improve reliability of service. Sites operating as unmanned installations require that intrusion and hazard *alarms* be reported as soon as possible, so that steps can be taken to limit possible damage. Remote operation of pumps, gates, etc. is required to ensure coordinated operation of tandem plants and to alleviate staff shortages.

One important and routine monitoring task is *reading the house meters* of all consumers. This will not only give data for billing according to consumption, but also gives clues about possible leaks in the system or about clandestine connections, when combined with information of *DMA* (*district metering areas*), which is another important monitoring operation. The purpose of these is to have knowledge about volumes supplied and consumed to detect possible money losses, leaks, bursts and waste, and to correct them as soon as possible.

Water balances (*audits*) and statistics will give information to decide if, instead of a local repair, full pipe replacement is more convenient. Water *leaks* can be visible, but often they are hidden, requiring specialized equipment and personnel to locate them.

Continuous *surveying and sampling* of water quality and hydraulic parameters (*pressure, flow direction, volume supplied*) at different locations is an important task. Those records must be compared to written standards and particular utility goals and performance rules. The purpose of that would be to detect failures and correct them, as well as to find opportunities to improve service quality and efficiency, besides the utility's revenues, through the design of better operating strategies. In this regard, an important tool is *hydraulic modeling* of the distribution system.

Hydraulic transients, or *surges*, occur during rapid flow changes in pressurized water conveying pipelines. Normally, such transients (*water hammer*) are considered a problem as they might damage the pipeline due to strong pressure peaks, subatmospheric pressures, or fatigue. By using simulating models incorporated into hydroinformatic tools, it is possible to assess existing water distribution systems, to suggest more efficient hydraulic performance and propose rehabilitative strategies.

PREVENTION AND SAFETY

Many operational tasks could be classed as related to "prevention and safety." Some of them, such as leak detection and control and water quality sampling, have already been mentioned. Some others are cross connection control, backflow prevention, and protection and vigilance against vandalism or emergencies.

Continuous positive pressure is necessary in all distribution systems to prevent a vacuum in the water-supply main. These vacuums can lead to back-siphonage and possible contamination or even collapse of pipe sections.

Cross connection control and backflow prevention are operational programs that both the utility and its customers must implement to prevent contaminants and nonpotable water (*e.g., wastewater, storm water, process water*) from being drawn into the drinking water system.

Backflow typically occurs when the distribution system's pressure drops, due to a water main break or due to firefighting demands. It has two interpretations: (1) a flow condition, induced by a differential in pressure, which causes the flow of water or other liquid into the distribution pipes of a potable water supply from any source or sources other than its intended source; (2) back up of water through a conduit or channel in the direction opposite to normal flow.

Cross connections are physical piped connections between potable water and an unsafe or polluted water source. They threaten water quality and public health through the backflow of such hazardous substances as antifreeze, boiler water, and sewage. Cross connection control operation, besides building codes and regulations to avoid them, consists of inspection routines and checking backflow prevention devices on particularly high-risk service connections (*e.g., a wastewater treatment plant*).

Numerous recommendations, concerns, and routines can be implemented for *general protection and vigilance* against vandalism or emergencies. Their selection and adoption depend on the risks, the characteristics of the utility and its infrastructure, and even the present or expected climate and political and socioeconomic atmosphere. These are some examples: *Lock all doors and set alarms at offices and main installations. Limit access to facilities, especially to water supply reservoirs. Secure hatches, meter boxes, hydrants, manholes, and other access points to the water distribution system. Control access to computer networks and control systems. Write and periodically review security and emergency plans, and train employees frequently. Assess the vulnerability of water sources, drinking water treatment plants, distribution networks, and other key infrastructure elements. Improve the computer system and remote operational security.*

MAINTENANCE AND REPAIR

It is important to operate all network valves periodically, merely to ensure their proper performance when really needed. A dead-end line must be flushed frequently or the customer on that line will receive poor quality water.

Water pipe flushing is a preventive maintenance task intended to preserve the hydraulic characteristics of the pipe, besides the quality of the water flowing through it. It removes any accumulated sediments or other impurities deposited in the pipe. Flushing is performed by isolating sections of the distribution system and opening flushing valves or, more commonly, fire hydrants to cause a large volume of flow to pass through the isolated pipeline and suspend the settled sediment.

Water *mains* may also be *mechanically cleaned* by using swabs or pigs which are devices that are pulled through a section of line to scrape the accumulated debris off the inside of the pipe. The major environmental concern of water pipe flushing is the discharge of flushed water, which may be high in suspended solids and other contaminants that can harm water bodies. The negative impacts of the discharge may be minimized by discharging the flush water into a sanitary sewer of adequate capacity or by discharging the flush water into a separate storm sewer system, preferably using management measures such as a detention pond, where solids can settle before the water is discharged.

Water *mains* must be *repaired* or *replaced* frequently to correct or substitute broken, corroded, or leaking sections of pipe. Either the broken pipe section is replaced or, as is often the case, a repair sleeve is placed around the outside of the broken pipe section and clamped into place. Following the pipe repair, the line is typically flushed and then disinfected with a chlorine solution. The chlorine solution is usually mixed on site using powdered calcium hypochlorite or sodium hypochlorite. Pipe repair and replacement could affect the environment (*erosion of soil, sediments, high concentrations of chlorine, etc.*), and such impacts should be minimized by control measures.

Storage tanks require frequent inspection and maybe occasional repairs. The most frequent repairs are repainting of walls and replacing screens over vents and other points of access to insects, birds, and rodents. Steel tanks are subject to corrosion, which is prevented by painting them regularly.

Pumps must be maintained to ensure that booster and other distribution pumps stay in working order. Their maintenance involves frequent inspection and tests for excessive vibration or noise, providing grease and lubrication regularly, and checking the pump bearings and packing glands.

PUBLIC RELATIONS AND MANAGEMENT

Operation of a water distribution system has much to do with the management of client and public relations, legal, personnel, commercial, and accounting functions.

To be sustainable, an operation must be *financially viable*. Because of the pressure to expand the area served, viability generally implies recovering the costs of operation and maintenance, as well as capital. Public utilities often have difficulty getting approval for increasing their charges to levels that are financially and economically adequate. Sometimes, this is for political reasons, but often it is also because the requests are poorly prepared and their urgency is not well perceived. Higher charges must be justified not only to the parent entity but also to consumers. Public relations campaigns can be helpful here, but quality service is often crucial to securing consumers' acceptance of increases.

Demand management to keep water needs low and congruent with natural local resources is a vital task. For this purpose, education campaigns directed to the public, installation and reading of water meters, appropriate and fair setting up of water tariffs, proper operation and location of consumer information and attention modules (*telephone, internet, direct presence*) are basic. Employees must be trained and aware of their role in transmitting correct information and messages to the public.

READING LIST

ABPA. *Recent Backflow Incidents and Articles*. American Backflow Prevention Association, http://www.abpa.org/, http://www.abpa.org/incidents.htm.

AWWA. (1976). *Water Distribution Operator Training Handbook*. American Water Works Association, Denver, USA: AWWA, http://www.awwa.org/wdoth.htm.

Chase, D., Savic, D., and Walski, T. *Water Distribution Modeling*. Haestad Methods, Inc. http://www.haestad.com/library/books/wdm/authors.asp.

CIWEM. (1984). *Water Distribution Systems. Water practice manual 4*. The Chartered Institution of Water and Environmental Management, CIWEM (formerly Institution of Water Engineers and Scientists, IWES), http://www.ciwem.org.uk/publications/manuals/index.asp.

Environment Canada. (1998). *The management of water*. National Water Issues Branch, Environment Canada, http://www.ec.gc.ca/water/en/manage/e_manag.htm.

EPA, Environmental Protection Agency, USA. (2001). *Recommendations to Improve Security at Drinking Water Facilities*, http://www.lgean.org/html/whatsnew.cfm?id=259.

Greater Vancouver Regional District Drinking Water Treatment Program. (1997). *Best Management Practice for Pigging and Flushing Water Mains*. http://www.gvrd.bc.ca/services/water/chlorlin/flushing.pdf.

Hawken, P., Lovins, A., and Lovins, L.H. *Aqueous Solutions*. Chapter 11 of book *"Natural Capitalism: Creating the next industrial revolution"*, Rocky Mountain Institute. http://www.natcap.org, http://www.natcap.org/images/other/NCchapter11.pdf http://www.rmi.org/sitepages/pid172.php, http://www.rmi.org/images/other/W-AqueousSol.pdf.

Havlik, V. *Solution of water supply and distribution networks*. Danish Hydraulic Institute (DHI). http://www.dhisoftware.com/mikenet/Download/Papers/hague97.pdf.

James, W. (1999). *Urban Water Systems*. Guelph University, Canada. http://www.eos.uoguelph.ca/webfiles/james/homepage/Teaching/661/wj661Modules.html.

James, W. (1996). *Hydraulics and hydrology vocabulary*. Web Manual. U. of Guelph, Sch of Eng'rg. http://www.eos.uoguelph.ca/webfiles/james/homepage/stillunclassified/wjvocab.html.

Jönsson, L. *Hydraulic transients as a monitoring device*. Department of Water Resources Engineering, University of Lund, Sweden, IAHR, International Association of Hydraulic Engineering and Research. http://www.iahr.org/membersonly/grazproceedings99/doc/000/000/110.htm.

Kenneth, K. (1994). *Water Distribution System Operation and Maintenance*.—3a. Ed.—Sacramento: California Department of Health Services, EPA. http://www.owp.csus.edu/WDS.html.

LGEAN, Local Government Environmental Assistance Network. *Water Distribution System Operation and Maintenance*. http://www.lgean.org/html/lgo/WTRSPPLY-01.html.

Mays, M.W. (1999). *Water Distribution System Handbook*. AWWA American Water Works Association, McGraw-Hill Professional Publishing. http://www.amazon.com/exec/obidos/ASIN/0071342133/002-3075060-0220023.

OIEAU, Office International de l' Eau (International Office for Water). (1998). *Overview of Training Services*. France. http://www.oieau.fr/espagnol/stages/smt97.htm#1997_4 or http://www.oieau.fr/english/stages/smt97.htm#1997_4.

University of Florida. *Backflow / Cross-Connection Control Program*. http://www.dep.state.fl.us/water/drinkingwater/bfp.htm, http://www.TREEO.ufl.edu/backflow/.

World Bank. *Managing Urban Water Supply and Sanitation: Operation and Maintenance*. GDRC, Global Development Research Center. http://www.gdrc.org/uem/water/wb-urbanwater.html.

WATER QUALITY IN DISTRIBUTION SYSTEMS

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A drinking water system's water quality may be acceptable when the water leaves a treatment plant. However, a variety of physical, chemical, and biological transformations can happen once the water enters and travels through a distribution system. Water producers need to understand the sources of water quality degradation during the distribution process because, in addition to taste and odor problems that can occur, research also suggests that degraded water quality increases the risk of gastrointestinal illnesses

WATER QUALITY DETERIORATION FACTORS

A distribution system's pipes and storage facilities constitute a complex network of uncontrolled physical, chemical, and biological reactors that can produce significant variations in water quality. The principal factors that affect water degradation during distribution are the system's structure, its operation, and a number of water quality factors.

STRUCTURAL FACTORS

Drinking water distribution systems are typically thought of as the underground network of interconnecting mains or pipes. They also can include storage facilities, valves, fire hydrants, service connections, and pumping stations.

Historically, water system designers tended to create oversized pipelines and storage facilities. While system designers may be considering an area's future drinking water needs, oversized facilities result in long detention times, loss of chlorine residual, taste and odor concerns, and other water quality problems.

Furthermore, some of the materials designers choose to install in distribution systems create suitable environments for microorganism growth. Materials, such as cast or ductile iron, asbestos-cement, or pressurized concrete, can pit and make way for microorganisms to colonize.

In addition, oxidant-resistant microorganisms settle on pipe surfaces and produce a complex microenvironment known as biofilm. Biofilms form when organisms enter the distribution system and become entrapped in slow-flow areas, line obstructions, or dead-end sections. They usually appear as a patchy mass in pipe sections or as a uniform layer along the inner walls of a storage tank.

While not all biofilm is bad, researchers are currently unsure of its exact effect. Coliform bacteria may colonize in it, and biofilm may interfere with coliform detection. It may also cause taste and odor problems.

Designers now theorize that the material manufacturers use in pipes, as well as the condition of pipes, valves, and storage facilities, may exert a high-chlorine demand.

Pipe materials can cause water quality to deteriorate in other ways. Iron pipes can corrode, and lead and copper from pipe walls can dissolve. For example, unlined or exposed ferrous materials in pipelines can corrode and cause red or rusty-colored water. To avoid corrosion problems, systems are turning to plastic materials, such as polyethylene and polyvinyl chloride (PVC).

Finally, contamination via cross-connection, leaky pipe joints, or pipe breaks may influence water quality. Pathogens, such as *Cryptosporidium* and *Giardia lamblia*, may enter the system through contaminated raw water, in-line reservoirs, or breaks in pipelines. System personnel need to carefully and thoroughly perform flushing and disinfection procedures following repairs.

OPERATIONAL FACTORS

From an operations standpoint, network operating conditions—such as slow water velocities, supply sources going on and off-line, and the amount of time that systems store water—greatly affect water quality. Any of these factors can cause chlorine residual to fade, and, thus, allow microbial growth in the network. Further, hydraulic conditions can cause sediment to deposit, accumulate, and serve as both habitat and protection from disinfectants for microbial growth.

What's more, many storage facilities are kept full so that the system can be better prepared for emergency conditions. However, the long detention times result in degraded water quality.

WATER QUALITY FACTORS

Some of the factors that provide optimal conditions for microorganisms to multiply include long water-detention times in tanks and pipes, adequate nutrient levels, and warm temperatures.

In addition, research has shown that the level of biodegradable organic matter in the distribution system strongly affects bacterial re-growth and harbors opportunistic pathogens. An opportunistic pathogen can be any disease-causing organism, bacterium, virus, helminth, or protozoan that slips through the treatment processes or enters the distribution system during pressure loss and finds the opportunity or favorable circumstances to lodge or reproduce in organic material, bacterial slime, or other material that it finds attractive.

A number of other conditions also can affect water quality. For example, disinfectants may react with organic and inorganic compounds and cause taste and odor problems or form disinfection by-products. Also, particulate re-suspension may cause increased turbidity.

CONTAMINATION PREVENTION AND CONTROL

Drinking water systems can improve water quality or prevent its deterioration in the distribution system. They can modify system operations and maintenance alternatives, make changes in treatment practices, and improve water quality monitoring and modeling. Generally, systems need to find an optimal combination of these actions, which can involve trade-offs between cost, water supply needs, and water quality considerations.

MODIFICATIONS TO SYSTEM OPERATION

Systems can use five primary operation procedures to maintain water quality:

1. minimize bulk water detention time,
2. maintain positive pressure,
3. control the direction and velocity of the bulk water (see Fig. 1),
4. maintain a disinfectant residual in the distribution system (Disinfectant residual, usually chlorine, provides a relatively effective barrier to the growth of microorganisms in bulk water and biofilm.), and
5. prevent cross-connections and backflow.

Utilities should minimize bulk water detention time because the interactions between the pipe walls and the bulk water result in water quality deterioration. Furthermore, stored finished water should be turned over frequently because the stored water's age contributes to the overall water age in the distribution system.

To reduce possible pathogen intrusions, drinking water utilities should maintain minimal water pressure in the distribution network, particularly if cross-connections are present. Further, the utilities should maintain a positive pressure throughout the distribution system to minimize the potential for back siphonage or backflow of contaminants to occur. However, excessive water pressure may cause pipe leaks or even breaks.

Utilities should minimize rapid or extreme fluctuations in flow velocities and should minimize the frequency of reversals. Activities that may affect flow velocities include rapidly opening or closing a valve, a power loss, and hydrant flushing. Changes in flow velocity can scour

Distribution Material	Corrosion Resistance	Potential Contaminants
Copper	Resists corrosion well, but is subject to corrosive attack from high velocities, soft water, chlorine, dissolved oxygen, and low pH.	Copper
Lead	Corrodes in soft water with low pH	Lead, arsenic, and cadmium
Mild steel	Subject to uniform corrosion, particularly sensitive to high dissolved oxygen levels	Iron, resulting in turbidity and red-water complaints
Cast or ductile iron	Aggressive waters can cause surface erosion	Iron, resulting in turbidity and red-water complaints
Galvanized iron	Aggressive waters can cause galvanic corrosion of zinc	Zinc and iron
Asbestos-cement	Good corrosion resistance; aggressive waters can leach calcium from cement	Asbestos fibers
Plastic	Resistant to corrosion	

Figure 1. Corrosion properties of different materials used in distribution systems. *Source*: Larry Mays, 1999.

sediments, tubercles, and deposits from interior pipe surfaces and degrade water quality.

MAINTENANCE ALTERNATIVES

Distribution system flushing is an important tool to keep the water system clean and free of sediment, remove stagnant water, and remove unwanted contaminants that may have inadvertently entered the system. (See summer 2002 *On Tap* "How to Flush a Distribution System.")

Drinking water systems can use a variety of pipeline cleaning techniques. These techniques include mechanical scraping, pigging, swabbing, chemical cleaning, and flow jetting. Utility maintenance also includes emergency pipe repairs with sanitary precautions in place. Utilities should:

- try to keep contaminated water out of the trench and pipe;
- flush the line in the vicinity of the break;
- apply disinfectant to potentially contaminated components;
- disinfect new mains;
- disinfect storage tanks after construction, inspection, or maintenance; and
- conduct bacteriological testing to confirm the absence of contaminates.

Other maintenance activities that utilities can use to minimize water quality degradation:

- prevent and eliminate cross-connections;
- cover and vent storage tanks;
- maintain an adequate separation from sewers; and
- enforce applicable building plumbing codes.

CHANGES IN TREATMENT PRACTICES

Disinfection means using chemicals to inactivate harmful microorganisms that might be present in water. This practice protects distributed water from pathogen regrowth or recontamination. Water systems treating surface water supplies maintain a level of residual chemical disinfectant throughout the distribution system. They also usually use some kind of booster disinfection or a more stable secondary disinfecting chemical, such as chloramines.

On the other hand, excessive chlorine levels will produce taste and odor problems, may accelerate pipe corrosion, may enhance formation of harmful disinfection by-products, or produce health concerns for the system's customers.

Pipes can and do corrode internally, reacting with the water and deteriorating. Internal corrosion can cause toxic metals, such as lead and copper, to leach into water, impart a metallic taste to water, stain plumbing fixtures, harbor nuisance and pathogenic microorganisms, reduce a pipe's hydraulic carrying capacity, and ultimately result in leaks and clogs.

Numerous physical, chemical, and biological factors can increase corrosion's rate and occurrence. Some individual factors can either promote or inhibit corrosion, depending upon other conditions. The most significant factors include temperature, pH, alkalinity, dissolved oxygen, total dissolved solids, hardness, and bacteria.

THREE APPROACHES TO CONTROL CORROSION

1. Modify the water quality to make the water less corrosive, such as adjusting the pH.
2. Lay down a protective lining between the water and the pipe, such as using chemical inhibitors.
3. Switch to plastic pipe, which is less prone to corrosion.

Attempts to control biofilm in the distribution system have taken several directions. To avoid releases of biofilm, utilities can manipulate their water chemistry, such as adjusting pH, alkalinity, or the Langlier Index (an indicator of corrosiveness). They also can apply corrosion inhibitors not only to protect pipe materials but also to firm up the coating of the sediments that harbor microbial communities.

WATER QUALITY MONITORING AND MODELING

Utilities should develop a sampling plan to address monitoring and modeling issues, such as selecting sampling sites, establishing test parameters and monitoring frequencies, establishing field-monitoring protocols, and addressing laboratory considerations. The most commonly monitored test parameters to determine general distribution system water quality include coliform bacteria, heterotrophic plate count (HPC) bacteria, disinfectant residual, temperature, turbidity, pH, and color.

Utilities may find that it is difficult to use monitoring data alone to understand all the possible interactions among the multiple parameters that affect water quality between the treatment plant and the user's tap. The flow pathways and travel times of water through these systems are highly variable because of the looped layout of the pipe network and the continuous changes in water usage over space and time. In addition, utilities commonly use storage facilities that are not part of the distribution system, making matters even more variable.

For these reasons, water utility managers are turning to hydraulic and water quality models as attractive monitoring supplements. They can use these models to perform a variety of water quality-related studies. Systems can:

- use chemical tracers to calibrate and test hydraulic models of the system,
- locate and size storage facilities,
- modify system operations to reduce the age of the water,
- modify the design and operation of the system to provide a desired blend of waters from different sources,
- find the best combination of pipe replacement, pipe relining, pipe cleaning, reduction in storage holding time, and location and injection rate at booster stations to maintain desired disinfectant levels throughout the system,
- assess and minimize the risk of consumer exposure to disinfectant by-products, and
- assess the system's vulnerability to incidents of external contamination.

Furthermore, as water utilities make more use of such tools as geographic information systems (GIS) and supervisory control and acquisition (SCADA) technologies, they can achieve a degree of data integration that enables more reliable network analysis and management.

WHERE CAN I FIND MORE INFORMATION?

American Water Works Research Foundation. 2000. *Guidance Manual for Maintaining Distribution System Water Quality*. Denver, CO.

American Water Works Association. 1999. *Water Distribution Operator Training Handbook*. Denver, CO.

American Water Works Association. 2001. *Rehabilitation of Water Mains (M28)*. Denver, CO.

Besner et al. 2001. "Understanding Distribution System Water Quality." *Journal of the American Water Works Association*. July, pp: 101–114.

Kirmeyer et al. 2001. "Practical Guidelines for Maintaining Distribution System Water Quality." *Journal of the American Water Works Association*. July, pp: 62–73.

Lei, J. and S. Saegrov. 1998. "Statistical Approach for Describing Failures and Lifetimes of Water Mains." *Water Science and Technology*. 38:6:209.

Mays, L. W. 2000. *Water Distribution Systems Handbook*. American Water Works Association. McGraw-Hill: New York.

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DESIGN OF WATER DISTRIBUTION SYSTEMS

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INTRODUCTION

Providing quality service at minimum possible cost is the ultimate goal of drinking water utilities. Quality of service includes delivering adequate and reliable quantities of water at sufficient pressures, meeting drinking water quality standards throughout the distribution system, and providing for adequate fire protection within the service area. Water distribution systems that help achieve this goal are generally designed in three stages: planning, preliminary design, and detailed design. The planning stage should properly identify the service-related constraints (e.g., limits on pressures, flows, and water quality parameters) along with the right set of decision variables (i.e., distribution system components).

The preliminary design should identify the alignment of pipelines, locations for storage and pumping facilities, availability of easement or right-of-way, and so on. Precise quantification of the decision variables takes place in the detailed design phase. The following sections describe various components of water distribution systems, the constraints associated with quality of service, and the steps involved in detailed design.

COMPONENTS OF A WATER DISTRIBUTION SYSTEM

Depending on the size of the population served, a water distribution system (WDS) could be a small network of branching pipes gravity fed by an elevated source to a highly complex web of pipe loops, isolation and control valves, multiple supply sources and associated pumping facilities, elevated/ground/pumped storage tanks, hydrants and blow-off valves, and so on. The following section describes various groups of components and their importance in the design of a WDS.

Pipes and Joints

Pipes and joints constitute the most abundant group of components in a WDS. Pipes owned and maintained by a water utility may generally range from 2 inches (50 mm) to several feet (or meters) in diameter, although for those systems that provide fire protection, a minimum diameter of 6 inches is usually specified (1,2). Pipes for water distribution are available in a variety of material—cast iron, ductile iron, steel, concrete, asbestos cement, polyvinylchloride, polyethylene, and so on. Selection of an appropriate pipe material is an important step in the design of a WDS as it influences initial and maintenance costs, type and number of joints, and hence leakage potential, load bearing capacity, capacity to withstand static and transient (water hammer) pressures, corrosion/tuberculation and consequent loss of capacity, pipe roughness characteristics, and so on. The relative advantages of one material over the other, along with many other relevant data needed for the design, may be obtained from the handbooks prepared by the respective manufacturers associations (3–5). Pipes should be buried to protect them against various natural and other forces, and care must be taken to provide minimum cover based on maximum frost-depth in cold climate regions.

Pumps

Although some water distribution systems rely completely on gravity for supplying water to the consumers, most systems employ pumps in some shape or form. Pumps in a distribution system may appear near clear wells or other sources, at pressure boosting stations, and at pumped storage tanks. Power requirements or the head-flow characteristic curve may define the pump capacity. It is common practice to use system head curves in sizing the pumps. The net positive suction head (NPSH) requirements play a crucial role in locating and sizing the pumps. Variable-speed pumps are becoming more common as they offer a wide range of operating conditions. For detailed description on different types of pumps, their operating characteristics, along with their relative advantages and disadvantages, the readers should refer to ANSI/HI (6) and Sanks et al. (7). Irrespective of the size of the pumps employed, the use of pumps in a WDS adds additional operating costs that should not be overlooked at the design stage. The use of pumps, however, allows for smaller transmission mains, thereby reducing the capital costs. From a design perspective, there will be an optimal tradeoff between the capital cost associated with the pipes and the operating costs associated with the pumps.

Tanks

Tanks in a WDS are used for a variety of reasons. Treated water may be stored in ground storage tanks or clear wells. Elevated storage tanks are generally used as balancing tanks that are filled during slack demand periods so they can feed the distribution system during peak demand periods. Such an operation minimizes frequent cycling (on/off status or pump speed changes) of pumps, thereby permitting efficient operation. Small distribution systems employ hydropneumatic tanks to maintain specified pressure ranges in an effort to minimize or eliminate continuous pump operation. Tank capacities are dictated by the need for emergency storage requirements (e.g., to temporarily offset treatment plant failures), for fire fighting requirements over extended periods, and to cater for peak-hour demands where the treatment plant capacities are limited to maximum-day demands. However, larger tank capacities—beyond the need to cater for peak-hour demands—could lead to water quality problems as water in storage for extended periods tends to lose disinfection potential. As water quality requirements on tank capacities are in direct conflict with other requirements for storage (e.g., fire fighting needs), a careful tradeoff must be arrived at when sizing the tanks. It is not uncommon for most systems to be designed to provide excess storage in the system equivalent to meet an average-day demand.

Valves

Valves in a WDS may be classified into isolation valves and control valves. Isolation valves are needed to isolate portions of WDS during emergency situations such as pipe breaks, or for routine maintenance purposes such as pipe rehabilitation, and flushing operations. Control valves, such as pressure-reducing valves and pressure-sustaining valves, throttle or maintain specified pressures in certain portions of the distribution system. They are also employed to isolate multiple pressure zones within a WDS. Flow control valves may regulate flowrates to certain processes that draw water directly from the WDS. Other types of control valves that are frequently used in a WDS include check valves, pump operational control valves, throttle control valves, and so on. Control of transient pressures might warrant the use of special types of valves such as pressure relief valves and air relief/vacuum valves.

Hydrants

Most water utilities are mandated to provide water for adequate fire protection within the service area. Hydrants connected to the pipes provide easy access for water for fighting fires. Insurance companies in the United States make use of hydrant ratings (hydrant flowrates without dropping the pressures below 20 psi during peak demand conditions) in setting the property insurance premiums. Hydrants are also used for flushing the pipelines as part of routine maintenance.

DESIGN CONSTRAINTS

Efficient design of a WDS must satisfy several constraints. These constraints include water quantity requirements, limits on pressures and velocities, limits on water quality parameters, and fire protection requirements, besides the usual constraints on overall system costs.

Constraints on Water Quantity

A well-designed WDS should supply adequate quantities of water to all consumers, including fire demands. Therefore, estimating the desired quantities of water by various consumers becomes an important task. Normal water consumption originates from three distinct groups of consumers: residential, commercial, and industrial. State and local guidelines on per-capita consumptions would be helpful in estimating the commercial and residential demands (8). Industrial demands should be estimated in consultation with the industries being served. Demands may also be estimated based on land-use and associated consumption data from neighboring systems of similar characteristics (population and commercial activities). Demand calculations for the existing WDS should come from monthly meter records. Peaking factors must be applied to the average daily demands to account for maximum-day demand as well as maximum-hour (peak–hour) demand (9). Most water utilities ensure that the supplies (treatment plant and pumping capacities) are adequate to meet maximum-day demand and rely on the floating storage tank capacities to meet the maximum-hour demand.

Constraints on Pressures and Velocities

It is not only important to deliver adequate quantities of water to the consumers but also to ensure that the water is delivered at adequate pressures. Pressures less than 30 psi under maximum-hour demand conditions are not acceptable for most water systems. Although the upper bound on pressure would depend on the pressure rating of the pipe material or the pipe joints, many water utilities are mandated to maintain pressures well below the rated capacities of pipes (e.g., 70–80 psi) to safeguard the appliances that derive water directly from the distribution network. Limiting the upper bound on pressures would also reduce the leakage losses as well as the pump operating costs (10). Lower and upper bounds on velocities may also be imposed when designing a WDS. Lower bounds on velocity ensure adequate scouring, thereby reducing sedimentation problems. Upper bounds on velocities minimize the transient pressure-related problems.

Constraints on Water Quality

With the new safe drinking water regulations, the utilities are required to ensure delivery of water that meets or exceeds all drinking water standards (limits on physical, chemical, and microbial parameters) right at the consumer connection. In addition, the water supplied should also carry specified minimum levels of residual disinfectant (e.g., chlorine or chloramines). As most disinfectants are nonconservative chemicals (i.e., concentrations drop with time), concentration levels higher than the required minimum values are necessary near the supply sources (11). Very high disinfectant concentration levels may not be acceptable either because of their perceived or real carcinogenicity or simply because of the resulting taste and odor problems. As a last resort, supplemental or chlorine booster stations must sometimes be installed at more remote or isolated sections of the system to ensure residual protection.

Constraints on Fire Demands

Except for certain small systems serving scattered rural communities, most WDS in the United States are expected to provide water for adequate fire protection. Hydrants are expected to provide water at a minimum of 500 gpm without dropping the pressures in the system below 20 psi under maximum-hour conditions. Many hydrants in a WDS are rated and are color coded based on the flowrates they can deliver while maintaining a minimum of 20-psi pressure (12). Hydrants that are capable of supplying 1500 gpm or more are painted light blue-green for 1000–1499-gpm capacity, orange for 500–999-gpm capacity, and red for those that cannot supply 500 gpm. Many utilities are not only mandated to ensure minimum specified instantaneous (or static) hydrant flowrates (e.g., 500 gpm) while maintaining the specified minimum pressures (e.g., 20 psi), but they are also required to ensure adequate hydrant flowrates over extended periods (e.g., 2 hours). The latter requirement would influence the capacity requirements of storage facilities.

DESIGN OF WATER DISTRIBUTION SYSTEMS

The need for designing an entirely new drinking water distribution system develops less frequently in modern times. Most current-day designs involve enhancements to existing systems, such as adding pipelines to serve areas of new development, strengthening the existing pipelines to improve the reliability of service, and/or replacing old and deteriorated pipelines. Current-day designs also include sizing new transmission mains, pumping stations, storage facilities, and so on. Whether a WDS is being designed from the ground-up or a few of its components are being strengthened, the use of mathematical models representing the WDS would greatly simplify the design process. The debate on the use of mathematical models in designing WDS dates back to the days of wood-stove pipes (13). Recent advances in computing power, both in terms of hardware and software, resulted in routine use of mathematical models in designing WDS. In addition, scores of optimization techniques have been proposed in the literature to help with the design process. An optimization technique involves formulating an objective function and the associated constraints as functions of decision variables and solving for the decision variables that optimize the objective function while satisfying all the constraints. Most optimization techniques for WDS design use minimization of annualized total costs as the objective function. Lansey (14) summarizes various methods proposed in literature for optimal design of WDS.

A robust and efficient optimization technique is supposed to provide an optimal set of decision variables that result in a minimal cost design while satisfying all constraints. However, design of water distribution systems involves an extensive and diverse set of decision variables and a complex set of constraints in addition to an elaborate cost function. Although a particular design may not involve all decision variables and constraints outlined in the previous sections, a robust optimization platform should allow the designer to choose any combination of constraints and decision variables besides allowing specification of a desired cost function. In addition, such optimization platforms could also work with existing mathematical models of the water distribution systems. Lack of such robust optimization platforms within the popular WDS modeling software packages prevented the widespread use of seemingly powerful optimization techniques in designing water distribution systems. Most designers continue to work with trial-and-error methods for sizing various components of a WDS with the help of a hydraulic network model representing the WDS being designed. A comprehensive iterative method for the design of a WDS is presented in the following. Although the method presented is meant for the design of new water distribution systems, the method can be easily adapted for designing enhancements to existing systems.

Iterative Method for Designing Water Distribution Systems

- Identify the supply sources: clear wells, natural springs, groundwater wells, and so on. Choose a layout for the distribution network. Start with trunk mains; other mains and laterals may be added later. The points to be connected by trunk mains include supply sources, large consumers, and storage tanks. Use a skeleton layout for preliminary designs and a complete layout for detailed designs. Most systems serving 100,000 populations or more do not model pipes less than 4 inches (100 mm) in diameter to simplify the design process. Most systems exclude all branching pipelines from the design process as well, unless the design is specifically aimed at sizing the branch lines. In addition, the hydraulic modeling software package might limit the number of pipes in the model, which in turn limits the ability to model all pipes in the network.
- Estimate nodal demands, taking future growth into account. Refer to the subsection *Constraints on Water Quantities* for details. If the WDS being designed is for serving a rural community with no mandatory provision for fire flows, special care must be taken in estimating the nodal demands. Refer to the section on *Rural Water Systems* in Appendix A for more details.
- Develop a hydraulic network model for the chosen layout, and provide all known data—supply sources, pump nodes, nodal elevations, demands and pipe lengths, and so on.
- Assign pipe diameters and roughness values for all pipes. Use larger diameters for pipes closer to the supply points and smaller diameters for pipes at the extremities of the system. Estimates of pipe roughness values may be obtained from manufacturer handbooks (3–5).
- If the WDS design involves pump stations, provide an estimated useful power (horsepower or kilowatt units) data for the pumps. Choose an arbitrary pump power that can be adjusted later to satisfy the pressure and flow constraints. If the supply source is a pressure main, collect head-flow data for the location where the distribution system will be connected to the pressure main. Refer to the section on *Pressure Supplies* in Appendix A for more details.
- Identify all constraints on the proposed design. Refer to the section on *Design Constraints* for details.
- Perform hydraulic analysis of the network model, and review the pressures and flowrates throughout the distribution system.
- Adjust pipe and/or pump sizes until pressures and velocities in the distribution system are well within the required range. Make sure the minimum pressures are at least 20% greater than the lower limit and the maximum pressures are at least 20% lesser than the upper limit to allow for eventual variation in pressures with diurnal demand changes.
- Replace the constant power data with suitable head-flow characteristic data obtained from the pump manufacturers. If required, use multiple pumps in parallel and/or series. Satisfactory design should include a standby pump in case of mechanical failure of a duty pump.
- Analyze the network model with maximum-day peak-hour and average-day slack-hour demand conditions, and review the pressures and velocities. Adjust the pipe and/or pump sizes if needed.
- Note the lowest and highest hydraulic gradeline (HGL) values at locations near the elevated storage tanks.
- Update the model to include the elevated storage tanks. Use an overflow elevation slightly below the highest HGL and a tank bowl elevation slightly above the minimum HGL. Choose a tank diameter large enough to hold a predetermined quantity of water (1/4 to 1/2 of the daily average demand or the specified minimum required storage, whichever is greater).
- Run an extended period simulation (EPS) with an appropriate diurnal demand curve. Use an AWWA-recommended diurnal demand curve (9), if no other information on the demand variation is available.
- Adjust the pump/pipe/tank characteristics, and rerun the analysis, if needed.
- Simulate hydrant flows, and verify if the flows to maintain the required residual pressure (e.g., 20 psi) are satisfactory. Revise network data, and rerun the hydrant flow simulation, if needed.
- Perform system reliability studies. Remove (or close) one pipeline at a time from the network model,

and quantify the reduction in service—pressures less than required values (15,16). Provide necessary improvements to the model to enhance the system performance under crippled conditions.

- Run water quality simulations with appropriate bulk and wall reaction rates and supply concentrations. Adjust network characteristics if the residual disinfectant concentrations are not within the specified bounds. Consider booster chlorination stations. Security and easement issues are of biggest concern when designing booster chlorination stations.
- Perform transient analysis on the model with several different operating scenarios to ensure no unwanted low/high pressures are generated. Modify the model characteristics or provide adequate surge protection, if needed. Refer to the section on *Transient Analysis* in Appendix A for more details on the significance of transient modeling studies.

The procedure outlined in this section ensures satisfactory design but not necessarily an optimal design. One could repeat this process by adjusting design variables, each time quantifying the total cost of the system. The readers should refer to the section on *Cost Calculations* in Appendix A for a discussion on various costs associated with WDS design and the use of annualized costs to compare various design alternatives. Figure 1 shows the design procedure in a flowchart format.

SUMMARY

The design of water distribution systems is a complex and tedious process. Several optimization techniques have been reported in literature to automate and reduce the complexity of the design process. However, lack of robust optimization platforms that allow specification of preferred objective functions and desired combinations of constraints and decision variables have seriously limited the use of available optimization technology for water distribution systems design. This article presents a comprehensive iterative method that makes use of a hydraulic network model for design of water distribution systems. Although the procedure presented is for design of new water distribution systems, the method can be easily adapted for sizing enhancements to existing systems.

BIBLIOGRAPHY

1. TSS (2003). *Recommended Standards for Water Works (Ten State Standards), Great Lakes-Upper Mississippi River Board of State Sanitary Engineers*. Health Education Services, Albany, NY.
2. AWWA (2002). *ANSI/AWWA C151/A21.51—Specification for Ductile Iron Pipe and Fittings for Water and Other Liquids*. American Water Works Association.
3. ACPA (2000). *Concrete Pipe Design Manual*. American Concrete Pipe Association, Texas.
4. CISPI (1994). *Cast Iron Soil Pipe and Fittings Handbook*. Cast Iron Soil Pipe Institute, Tennessee.
5. UBPPA (1991). *Handbook of PVC Pipe—Design and Construction*. Uni-Bell Pipe Association, Texas.
6. ANSI/HI (2002). ANSI/HI Pump Standards Set. Hydraulic Institute, Parsippany, NJ.
7. Sanks, R.L., Tchobanoglous, G., Bosserman, B.E., II, and Jones, G.M. (1998). Pumping *Station Design*. Butterworth-Heinemann, Massachusetts.
8. VAC (2002). *Chapter 590—Water Works Regulations*. Virginia Administrative Code.
9. AWWA. M32 (1989). *Manual 32—Distribution Network Analysis for Water Utilities*. American Water Works Association.
10. Lingireddy, S. and Wood, D.J. (1998). Improved operation of water distribution systems using variable speed pumps. *J. Energy Eng. Am. Soc. Civil Eng.* **124**(3).
11. Lingireddy, S., Ormsbee, L.E., and Wood, D.J. (1995). Time averaging water quality assessment for water distribution systems. *J. Am. Water Works Assoc.*
12. NFPA (2002). NFPA 291—Recommended practice for fire flow testing and marking of hydrants. National Fire Protection Association, Massachusetts.
13. Ramalingam, D., Lingireddy, S., and Ormsbee, L.E. (2002). History of water distribution network analysis: Over 100 years of progress. *Proceedings of the ASCE 150th Anniversary Conference on Environmental and Water Resources History*, EWRI of ASCE, Washington, DC.
14. Lansey, K.E. (2000). Optimal design of water distribution systems. In: *Water Distribution Systems Handbook*, Mays, L.W. (Ed.). McGraw-Hill, New York.
15. Lingireddy, S., Ormsbee, L.E., and Neelakantan, T.R. (2000). Application of genetic optimization in maximizing hydraulic network redundancy. *Proceedings of the 2000 Joint Conference on Water Resource Engineering and Water Resources Planning and Management*, ASCE, Section 51, Chapter 4.
16. Ormsbee, L. and Kessler, A. (1990). Optimal upgrading of hydraulic-network reliability. *J. Water Resour. Planning Manage., ASCE* **116**(6): 784–802.
17. Means, R.S. (2004). *Site Work & Landscape Cost Data*. R.S. Means Company, Inc. Kingston, MA.
18. LeChevallier, M.W., Gullick, R.W., and Karim, M. (2002). The potential for health risks from intrusion of contaminants into the distribution system from pressure transients. American Water Works Service Company, Inc., Voorhees, NJ. Distribution System White Paper prepared for the U.S. Environmental Protection Agency.
19. Wood, D.J. and Lingireddy, S. (2004). *Surge2000 Short Course Training Manual*. University of Kentucky, Lexington, KY.
20. Lingireddy, S., Wood, D.J., and Nelson, A. (1998). Modified network model for rural water systems. *J. Water Resour. Planning Manage., ASCE*, **124**(5): 296–299.

APPENDIX A

Cost Calculations

Cost is a major factor in designing a water distribution system. Two types of costs influence the decision-making process: capital costs and operating costs. One way of comparing competing designs is to annualize the capital costs and add the annual operating costs to arrive at annualized total costs. If C_P is the total capital cost, i is the annual interest rate for a period of N years and then the annualized capital cost C_A is given by

$$C_A = C_P \left[\frac{i}{(i+1)^N - 1} + i \right]$$

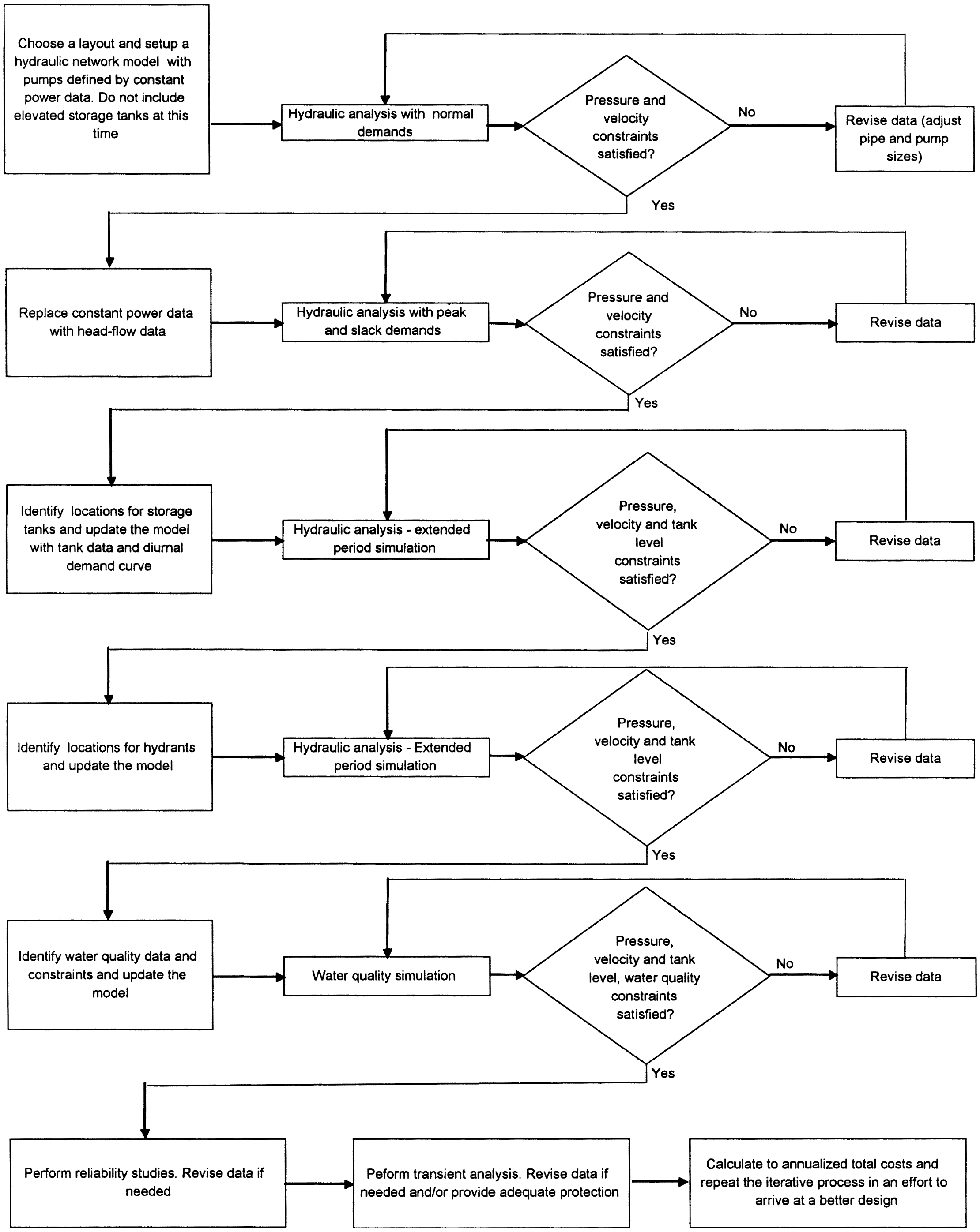

Figure 1. Iterative method for designing water distribution systems.

The total capital costs comprise primarily cost of easement or right-of-way, cost of piping including joints, excavation and backfill costs, cost of pumps and pumping station, cost of storage facilities, and cost of valves. Means' Construction Data Handbooks, in particular, the *Site Work and Landscape Cost Data Handbook* are excellent sources of information on capital costs (17). Operating costs are primarily the energy costs resulting from pumping operation. The energy costs vary inversely and nonlinearly with the piping costs. That is, the pressure constraints in the system could be met by using small-diameter pipes that require large-pump energy requirements or by using large-diameter pipes that require small-pump energy requirements. Figure A1 shows a typical capital and energy costs tradeoff curve.

Pressure Supplies

When designing pipelines serving a new subdivision, there are two ways to approach the problem (1). Append calibrated model of the existing distribution system with

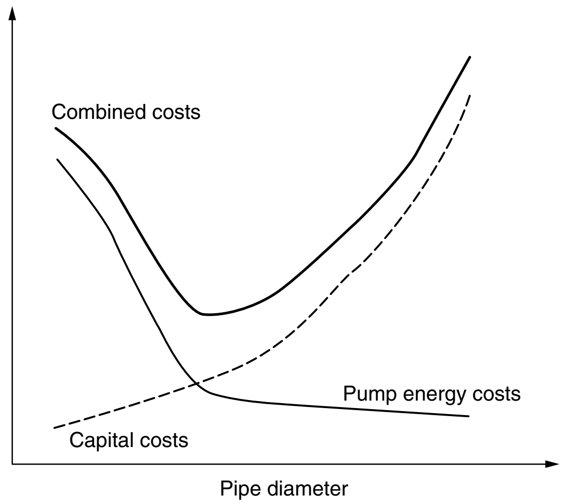

Figure A1. Typical capital and energy costs tradeoff curve.

new pipes and other network elements, and use the complete model in the iterative design process of sizing the new network elements (3). Create and use a network model pertaining to the proposed distribution system only, and use that model in the iterative design process. Although the first approach is more accurate, it requires a well-calibrated model of the existing distribution system along with a right set of demands and other boundary conditions. On the other hand, the use of the second approach requires head-flow characteristics at the location where the new piping will be tapped into the existing system. The head-flow characteristic curve at this location may be obtained by performing a hydrant flow test at or near the location where the new system will be tapped into the main distribution system. The hydrant flow test should record the static pressure as well as two other head-flow values to generate a head-flow characteristic curve. Figure A2 shows a typical head-flow characteristic curve generated from a hydrant flow test. This approach of using a head-flow characteristic curve in lieu of using the entire network model may not work well if a significant diurnal variation in static head is expected at the test location.

Transient Analysis. Rapid flow changes in a WDS can result in unexpectedly high or low pressures that can damage pipes or other components of the distribution system. Rapid flow changes are not uncommon in WDS. Routine pump startup and shutdown and pump trip resulting from power failure situations can result in rapid flow variations. High transient pressures might result in pipe breakages or loosening of pipe joints. Pressures below the vapor pressure of water lead to formation of vapor cavities. Subsequent high pressures can collapse the vapor cavities producing high-pressure spikes. Recent studies have shown that pressures below atmospheric levels can lead to pathogen intrusion problems at certain vulnerable points such as leaky pipe joints (18). Therefore, it would be prudent to perform a transient analysis of potential rapid flow variation scenarios and provide adequate protection to the WDS. The protection methods include use of pressure vessels (surge tanks), relief valves, rupture disks, and air release/vacuum valves (19).

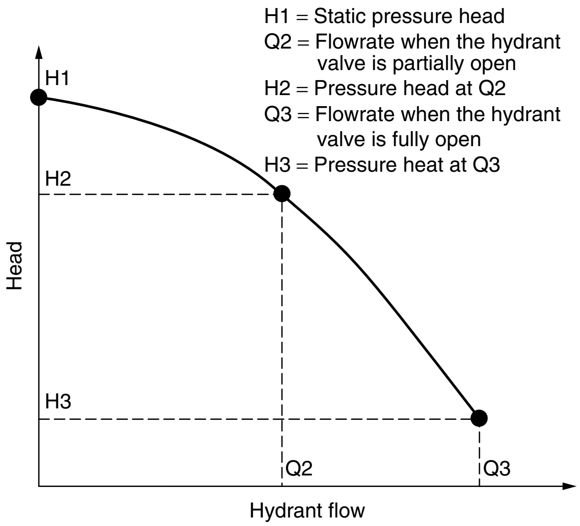

Figure A2. Example head-flow characteristic curve for a pressure supply.

Rural Water Systems

If rural water systems are not designed to provide fire flows, then special handling of long branch-lines serving few customers may be necessary. Requirements for residential water delivered through branched lines depend on the number of residential (domestic) connections served by each branch. These requirements should be based on probability considerations, and the requirement per connection served decreases as the number of connections increase. Relationships called Instantaneous peak demand curves (IPD) are available to calculate these requirements as a function of the number of connections served by each branch line. Additional conventional demands can be added at junctions. Branch line pipes should be sized to accommodate residential requirements calculated in this manner (20).

WHAT IS IN OUR DRINKING WATER?

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WHAT IS A DBP?

A drinking water disinfection by-product (DBP) is formed when the chemical used for disinfecting the drinking water reacts with natural organic matter in the source water. Popular disinfectants include chlorine, ozone, chlorine dioxide, and chloramine. Source waters include rivers, lakes, streams, groundwater, and sometimes seawater. DBPs have only been known since 1974, when chloroform was identified as a DBP resulting from the chlorination

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Figure 1. Chloroform and trichloroacetic acid, two common DBPs, in chlorinated tap water.

of tap water. Since then, hundreds of DBPs have been identified in drinking water.

WHY IT'S IMPORTANT

Millions of people in the U.S. are exposed to these drinking water DBPs every day. While it is vitally important to disinfect drinking water, as thousands of people died from waterborne illnesses before we started disinfection practices in the early 1900s, it is also important to minimize the chemical DBPs formed. Several DBPs have been linked to cancer in laboratory animals, and as a result, the U.S. EPA has some of these DBPs regulated (Fig. 1). However, there are many more DBPs that have still not been identified and tested for toxicity or cancer effects. Currently, less than 50% of the total organic halide that is formed in chlorinated drinking water has been identified. Total organic halide is a measure of all of the organic compounds that contain a halogen atom (chlorine, bromine, iodine), and includes DBPs such as chloroform, bromoform, and trichloroacetic acid. There is much less known about DBPs from the newer alternative disinfectants, such as ozone, chlorine dioxide, and chloramine, which are gaining in popularity in the U.S. Are these alternative disinfectants safer than chlorine? Or do they produce more harmful by-products? And, what about the unidentified chlorine DBPs that people are exposed to through their drinking water—both from drinking and showering/bathing? The objective of our research is to find out what these DBPs are—to thoroughly characterize the chemicals formed in drinking water treatment—and to ultimately minimize any harmful ones that are formed.

OUR RESEARCH APPROACH

- Gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), and gas chromatography/infrared spectroscopy (GC/IR) techniques are used to identify the unknown by-products
- NIST and Wiley mass spectral databases are used first to identify any DBPs that happen to be present in these databases
- Because many DBPs are not in these databases, most of our work involves unconventional MS and IR techniques, as well as a great deal of scientific interpretation of the spectra
  - High resolution MS provides empirical formula information for the unknown chemical (e.g., how many carbons, hydrogens, oxygens, nitrogens, etc. are in the chemical's structure)
  - Chemical ionization MS provides molecular weight information when this is not provided in conventional electron ionization mass spectra
  - IR spectroscopy provides functional group information (e.g., whether the oxygens are due to a carboxylic acid group, a ketone, an alcohol, or an aldehyde)
  - LC/MS is used to identify compounds that cannot be extracted from water (the highly polar, hydrophilic ones). This is a major missing gap in our knowledge about DBPs—so far, most DBPs identified have been those that are easily extracted from water
  - Novel derivatization techniques are also applied to aid in the identification of highly polar DBPs
- Once DBPs are identified, ones that are predicted to have adverse health effects are studied in order to determine how they are formed (so that the treatment can be modified to ultimately minimize their presence in drinking water)

CURRENTLY

We have a major nationwide DBP occurrence study underway, where we are sampling drinking water across the U.S. (disinfected with the different disinfectants and with different water quality, including elevated levels of bromide in the source water).

SOME RESULTS

More than 180 previously unidentified DBPs have been identified for the first time.

Ozone is tending to produce oxygen-containing DBPs, with carboxylic acids, aldehydes, ketones, and di-carbonyl compounds the most prominent.

The presence of natural bromide in the source water is resulting in a tremendous shift from chlorine-containing DBPs to bromine-containing DBPs when chlorine or chloramine is used as a disinfectant (even in combination with ozone).

Chlorine dioxide is producing very few halogenated DBPs by itself, but when chlorine impurities are present, and natural levels of bromide or iodide are present in the source water, many bromo- and iodo-DBPs are formed.

New analytical methods have been developed (and are continuing to be developed) for the analysis of highly polar DBPs.

Collaborations have been forged with health effects researchers to study selected DBPs for potential adverse health effects.

BIBLIOGRAPHY

1. Richardson, S.D., Thruston, Jr., A.D., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, Jr., B.W., Sun, G.-R., Majetich, G. Identification of New Ozone Disinfection By-products in Drinking Water. *Environmental Science & Technology*, 1999, **33**, 3368–3377.
2. Richardson, S.D., Thruston, Jr., A.D., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, Jr., B.W., Sun, G.-R., Majetich, G. Identification of New Drinking Water Disinfection By-products Formed in the Presence of Bromide. *Environmental Science & Technology*, 1999, **33**, 3378–3383.
3. Richardson, S.D., Thruston, Jr., A.D., Caughran, T.V., Chen, P.H., Collette, Schenck, K.M., Lykins, Jr., B.W., Rav-Acha, C., Glezer, V. Identification of New Drinking Water Disinfection By-products from Ozone, Chlorine Dioxide, Chloramine, and Chlorine. *Water, Air, and Soil Pollution*, 2000, **123**, 95–102.
4. Richardson, S.D., Caughran, T.V., Poiger, T., Guo, Y., Crumley, F.G. Application of DNPH Derivatization with LC/MS to the Identification of Polar Carbonyl Disinfection By-products in Drinking Water. *Ozone: Science & Engineering*, 2000, **22**, 653–675.

THE ECONOMICS OF WATER RESOURCES ALLOCATION

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No one would doubt “the principle that water is a scarce good with dimensions of economic efficiency, social equity, and environmental sustainability.” Yet as articulated in the World Bank’s (1) *African Water Resources* document, the principle disguises two polar-opposite positions about pricing water.

On the one hand, *The Economist* magazine’s (2; pp. 1–5) survey on water declared the central dilemma: “Throughout history, and especially over the past century, it has been ill-governed and, above all, collossally underpriced.” Identifying this problem, naturally begets this solution: “The best way to deal with water is to price it more sensibly,” for “although water is special, both its provision and its use will respond to market signals.” In rural areas where there is competition among farmers for irrigation water, “The best solution is water trading.” As for the problem of allocating and delivering water to the poor, “The best way of solving it is to treat water pretty much as a business like any other.” We can call this the “neoliberal” position.

Six months later, on the other hand, an international movement with “progressive” politics, the People’s World Water Forum (PWWF), emerged in Delhi, India, to promote the “decommodification” of water, based on feeder social movements from around the world in both cities and rural sites of struggle over water access. The PWWF (3; p. 1) founding statement declared that “Water is a human right; that corporations have no business profiting from peoples’ need for water; and that governments are failing in their responsibilities to their citizens and nature.”

Because there are many different ways that the pricing of water can be considered in bulk and retail settings, it makes sense first to outline the positions using a simple graph that distinguishes between neoliberal and progressive values. At the extreme where maximizing the production of economic goods is the prime objective, a leaked 1991 World Bank memo by then chief economist Lawrence Summers proposed an environmentally and socially insensitive allocation of resources: “I think the economic logic behind dumping a load of toxic waste in the lowest-wage country is impeccable and we should face up to that” (http://www.whirledbank.org). Rather than “internalize the externalities” of social impact or ecological damage, Summers’ solution was simply to displace these to someplace where political power was negligible and the immediate environmental implications were less visible, in the name of overall economic growth.

And yet there are well-established critiques of gross domestic product (GDP), the most common measure of the aggregation of economic goods. Contrary to a more nuanced “economic logic,” GDP treats the depletion of natural capital (including water resources) as income instead of depreciation of an asset; ignores the nonmarket economy of household and community, in turn devaluing child care, elder care, other home-based tasks and volunteer work (all of which rely on access to clean water); and considers natural disasters and pollution as economic gain because of associated service sector employment and repair/clean-up/replacement opportunities, not as a debit from social welfare or, with respect to drought and flooding, from ecosystem integrity.

Even as a caricature of neoclassical economics in the memo cited, the promotion of commodifed nature and society struck a chord during the neoliberal epoch of the late twentieth century. Throughout, those lobbying to treat water “much as any other business” grew in strength, and privatization and commercialization of water supplies expanded in many parts of the world. The intense conflict over the economics of water resources allocation was prefigured by the 1992 International Conference on Water and the Environment in Dublin, where water was formally declared an “economic good.” Four years later, the formation of the Global Water Partnership and World Water Council advanced the position that commodification of water would lead to both private sector investments and more efficient use. In the same spirit, 1997 witnessed the first World Water Forum in Marrakesh, the founding of the World Commission for Water in the 21st Century, and an emblematic statement by the Swedish International Development Agency (4; pp. 11–13): “As the realisation increases that fresh water of satisfactory quality is a scarce and limited resource, matters related to management of the water resources have become more into focus .... At least four conditions need to be fulfilled to carry through efficient water allocation: (1) well defined user rights; (2) pricing at its marginal cost; (3) information related to availability, value, quality, delivery times; and (4) flexibility in allocation responding to technologic, economic and institutional changes." The United Nations Panel on Water declared in 1998 that "water should be paid for as a commodity rather than be treated as an essential staple to be provided free of cost" (5).

At the same time, the International Monetary Fund (IMF) and World Bank became much more explicit in promoting water commodification through what were once mainly macro-oriented structural adjustment programs, whether the Enhanced Structural Adjustment Facility, Poverty Reduction and Growth Facility, or Poverty Reduction Strategy Programme (6). According to one NGO critique by the Globalization Challenge Initiative (http://www.challengeglobalization.org), "A review of IMF loan policies in 40 random countries reveals that, during 2000, IMF loan agreements in 12 countries included conditions imposing water privatization or full cost recovery. In general, it is African countries, and the smallest, poorest and most debt-ridden countries that are being subjected to IMF conditions on water privatization and full cost recovery." When the World Bank (7, Annex 2) instructed its field staff on how to handle water pricing in even impoverished rural Africa, the mandate was explicit: "Work is still needed with political leaders in some national governments to move away from the concept of free water for all. . . . Promote increased capital cost recovery from users. An upfront cash contribution based on their willingness-to-pay is required from users to demonstrate demand and develop community capacity to administer funds and tariffs. Ensure 100% recovery of operation and maintenance costs." It was not long before a bureaucratic class emerged within Africa to work on cost recovery, for according to the 2001 Kampala Statement coauthored by the World Bank and the African Utility Partnership (8; p. 4), "The poor performance of a number of public utilities is rooted in a policy of repressed tariffs."

But a debate quickly followed over the merits of full cost recovery of operating and maintenance costs. In most urban systems, the cost of supplying an additional drop of water—the "short-run marginal cost curve" (Line A in Fig. 1)—tends to fall as users increase their consumption, because it is cheaper to provide the next unit to a large consumer than to a small consumer. Reasons for this include the large-volume consumers' economies of scale (i.e., bulk sales), their smaller per unit costs of maintenance, the lower administrative costs of billing one large-volume consumer instead of many small ones, and the ability of larger consumers to buy water at a time when it is not in demand—for example, during the middle of the night—and store it for use during peak demand periods. The premise here is that the pricing of water should correspond directly to the cost of the service all the way along the supply curve. Such a system might then include a profit markup across the board (Line B) that ensures the proper functioning of the market and an incentive for contracting or even full privatization by private suppliers.

The progressive principle of cross subsidization, in contrast, violates the logic of the market. By imposing a block tariff that rises for larger consumers (Line C), the state would consciously distort the relationship of cost to price and hence send economically "inefficient" pricing signals to consumers. In turn, argue neoliberal critics of progressive block tariffs, such distortions of market logic introduce a disincentive to supply low-volume users. For example, in advocating against South Africa's subsequent move toward a free lifeline and rising block tariff, the World Bank advised that water privatization contracts "would be much harder to establish" if poor consumers had the expectation of getting something for nothing. If consumers did not pay, the Bank suggested, South African authorities required a "credible threat of cutting service" (9; pp. 49–53).

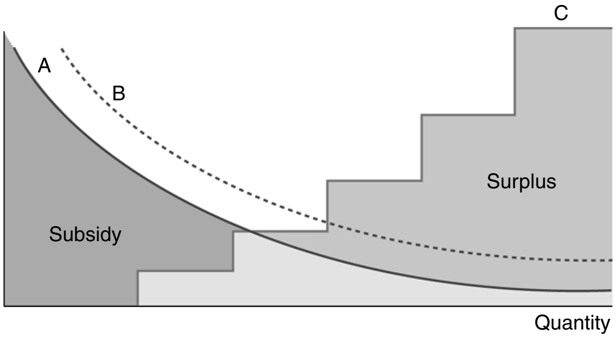

Figure 1. Three ways to price water: marginal cost (A), for-profit (B), and cross-subsidized lifeline plus rising block tariff (C).

The progressive rebuttal is that the difference between Lines A and C allows free universal lifeline services and a cross-subsidy from hedonistic users to low-volume users. There are also two additional benefits of providing free water services to some and extremely expensive services to those who have hedonistic consumption habits:

- Higher prices for high-volume consumption should encourage conservation, which would keep the longer run costs of supply down (i.e., by delaying the construction of new dams or supply-side enhancements).
- Benefits accrue to society from the "merit goods" and "public goods" associated with free provision of services, such as improved public health, gender equity, environmental protection, economic spinoffs, and the possibility of desegregating residential areas by class.

By way of definition, public goods can be observed and measured, for underlying their existence are two characteristics: "nonrival consumption" and "nonexclusion" from consumption. Nonrival consumption means that the consumption of a public good/service by one person need not diminish the quantity consumed by anyone else. A classic example is a national defense system, which is "consumed" by all citizens in a quantity that is not affected by the consumption of defense benefits by fellow citizens. Likewise, the benefits of a clean environment and hygienic public water system—reflecting a strong municipal water system and lifeline access to all—are enjoyed by all municipal consumers, regardless of how much water is consumed by a particular individual, although a minimum consumption level is required for all citizens to prevent the spread of infectious diseases. The principle of nonexclusion simply means that it is impossible to prevent other citizens from enjoying the benefits of public goods, regardless of whether they are paid for. This is important, as a state determines the detailed character of water pricing policy and distinguishes between necessities guaranteed by the state versus luxuries that people must pay for. A simpler way of putting it is that where the net benefits to society outweigh the costs of consumption of a good/service, the result is a "merit good." When the merit good benefits apply universally so that no one can be excluded from their positive effects, the result is a "public good." Markets usually underprovide for public goods, so the "Post-Washington Consensus" style of economics attempts to correct this market imperfection, even if it might mean introducing other market distortions, such as a free lifeline supply of water.

Another progressive critique of private suppliers who require tariffs reflecting marginal cost plus profit is that water infrastructure is a classic natural monopoly. The large investments in pipes, treatment centers, and sewage plants are "lumpy" insofar as they often require extensive financing and a long-term commitment, of which the state is more capable. To the argument that a progressive tariff could still coincide with a private sector supplier through a strong state regulator, progressives mistrust "captive regulatory" relations, given the long history of corruption in the water sector. Rebutting those who argue that Third World states are intrinsically incapable of providing water services, progressives cite more proximate reasons for the recent degeneration of state water sectors: 1980s–1990s structural adjustment programs that decapacitated most states, corrupt state bureaucrats, weak trade unions, and disempowered consumers/communities.

Finally, the progressive argument for making a water subsidy universal—not means-tested for only "indigent" people—is both practical and deeply political. If the service is means-tested, it invariably leads to state coercion and stigmatization of low-income people by bureaucrats. Furthermore, it is an administrative nightmare to sort out who qualifies because so many people depend on informal and erratic sources of income. More philosophically, though, it is a premise of most human rights discourse that socioeconomic rights such as water access are *universally* granted, not judged on the basis of a subjective income cutoff line, especially given the differences in household size for which different low-income people are responsible. This is partly because international experience shows that defense of a social welfare policy requires universality, so that the alliance of poor, working-class and middle-class people that usually win such concessions from the state can be kept intact (10).

As *The Economist* observed in mid-2003, one of the most important sites for considering the economics of water resources allocation is South Africa. One reason is that because of the international drive to commercialize water, even postapartheid South African citizens were subject to neoliberal cost recovery and disconnection regimes. This affected many who simply could not pay their bills. From the late 1990s through 2002, as a result, approximately 10 million people suffered water disconnections. Africa's worst-ever recorded cholera outbreak—affecting more than 150,000 people—can be traced to an August 2000 decision to cut water to people who were not paying a South African regional water board.

After the ruling, the African National Congress promised free basic water supplies in December 2000 during a municipal election campaign; the same bureaucrats responsible for water disconnections began redesigning the water tariffs. In July 2001, revised price schedules provided a very small free lifeline: 6000 liters per household per month, followed by a very steep, convex curve (see Fig. 2). But the next consumption block was unaffordable, leading to even higher rates of water disconnections in poor areas. The 6000 liters represent just two toilet flushes a day per person for a household of eight, for those lucky enough to have flush toilets. It left no additional water to drink, wash with, clean clothes, or for any other household purposes. In contrast, from the progressive point of view, an optimal strategy would provide a larger free lifeline tariff, ideally on a per-person, not a per-household basis, and then rise in a *concave* manner to penalize luxury consumption.

Johannesburg's tariff was set by the council with help from Suez Lyonnaise des Eaux, a Paris-based conglomerate, and began in July 2001 with a high price increase for the second block of consumption. Two years later, the price of that second block was raised 32%, with a 10% overall increase, putting an enormous burden on poor households that used more than 6000 liters each month. The rich got off with relatively small increases and a flat tariff after 40 kiloliters/household/month, which did nothing to encourage water conservation and hence did not mitigate the need for further construction of large dams, which in turn would drive up the long-run marginal cost curve and further penalize low-income Johannesburg townships residents.

This discussion of the economics of water resources allocation shows, simply, that pricing is political, and indeed the pursuit of "impeccable economic logic" in the water sector has generated some of the most intense struggles in the world today, calling into question the

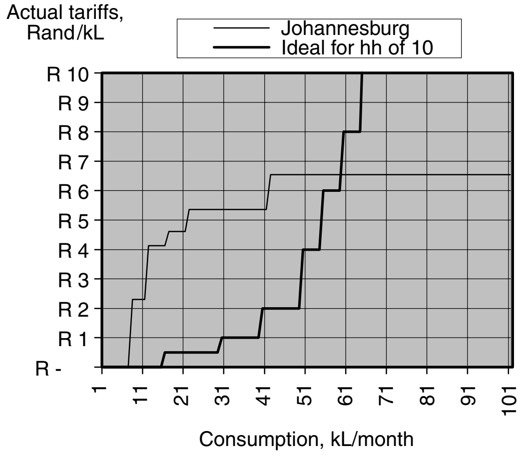

Figure 2. Divergent water pricing strategies—Johannesburg (2001) vs. ideal tariff for large household. *Source*: Johannesburg Water (thin) and own projection (thick).

very tenets of neoliberalism. The economics of privatized or commercialized urban water services have been challenged from Cochabamba, Bolivia—where the U.S. firm Bechtel tried to take ownership of rainwater collected by poor residents in the context of huge price increases—to Accra, Ghana, to most Argentine cities, to Manila and Jakarta, to Atlanta and Johannesburg, and to many other sites in between. Working out the contrasting discourses in political-economic analysis is crucial to any resolution of the problem in public policy.

BIBLIOGRAPHY

1. World Bank. (1996). *African Water Resources*, Technical Paper 331. Washington, DC.
2. *The Economist*. Survey of water. July 19, 2003.
3. People's World Water Forum. (2004). Statement. http://www.pwwf.org, January.
4. Swedish International Development Agency. (1997). *Environmental security and water management in Southern Africa*. Stockholm.
5. *New York Times*, Mar 22, 1998.
6. Hennig. 2001.
7. World Bank. (2000). *Sourcebook on Community Driven Development in the Africa Region*. Washington, DC, Annex 2.
8. World Bank and African Utilities Partnership. (2001). *The Kampala Statement*. Washington, DC, March 14.
9. Roome, J. (1995). *Water pricing and management*. World Bank Presentation to the *SA Water Conserv. Conf.*, unpublished paper, South Africa, October 2.
10. Esping-Andersen, G. (1990). *The Three Worlds of Welfare Capitalism*. Princeton University Press, Princeton.

ANSWERING THE CHALLENGE

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The City of San Diego, California shares a problem in common with many other western cities. The problem is how to meet the water supply demands of a rapidly growing region when new sources are not readily available, at least not without spending huge sums of money.

In the late 1990s, San Diego (Fig. 1) took a major step to help solve this problem by equipping the brand new North City Reclamation Plant with an EDR (electrodialysis reversal) system, from Ionics, Incorporated. The system would desalinate tertiary treated wastewater and provide a new source of high-quality irrigation water, which would then reduce demands on the freshwater supply. Wastewater to be treated had salinity levels up to 1300-ppm TDS during the summer and early fall months.

With desalinated and blended reclaimed water having lower sodium levels (and less than 1000-ppm total TDS), San Diego used an existing 47-mile-long pipeline system to deliver high-quality irrigation water to golf courses, plant nurseries, parks, highway green belts, and homeowner associations. The strategy of selling this water as an attractive alternative to the use of hard-to-replace drinking water supplies caught on quickly.

In 1998, the EDR plant produced 2.2 mgd—with blending, 3.3 mgd was available. After two expansions, the latest of which will be completed in early 2005, EDR will produce 5.5 mgd of approximately 300-ppm TDS water. With blending, up to 12 million gallons per day of irrigation water can be supplied through a recently lengthened 67-mile-long pipeline. Future EDR expansion will increase this blended flow up to 15 mgd.

Originally, the city looked into desalination through the conventional use of microfiltration and reverse osmosis (MF-RO). This approach had already been installed at several locations in the Los Angeles area. Before making a final commitment, the city investigated to see if another alternative was possible (Fig. 2).

They found that electrodialysis reversal (EDR) had been successfully used at a number of wastewater locations to desalinate reclaimed irrigation water.

EDR offered the opportunity to use a less expensive single treatment membrane process, with a higher water recovery to make better use of available wastewater supplies. Overall, MF-RO water recovery would be about

Figure 1. San Diego uses EDR technology to produce low salinity irrigation water from reclaimed municipal wastewater.

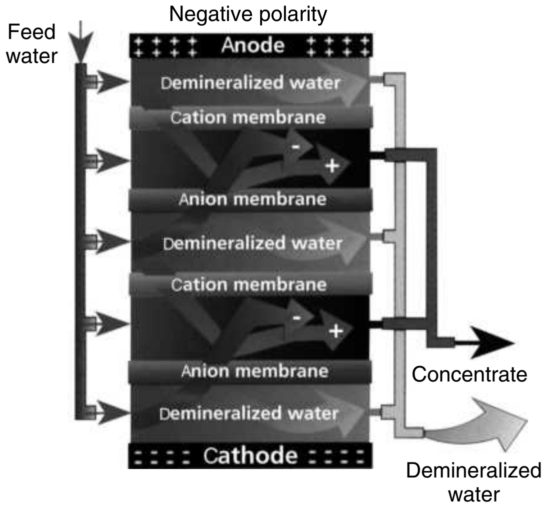

Figure 2. Electrodialysis reversal system.

80%. EDR would operate at 85% recovery. MF-RO required chemical pretreatment to control salt scale buildup on the RO membranes. EDR would operate with no chemical addition to the feedwater. One more major advantage to using EDR was that future capacity could be added by installing fully preassembled EDR systems within 53-foot-long enclosed trailers for up to 1.2 mgd flow per trailer (Fig. 3).

In 1997, city officials elected to use an EDR 2020 system for the North City irrigation water project after receiving bids from several general contractors. When all bids were opened, the least expensive MF-RO option was priced at US $4,775,975. The EDR cost was $3,569,000, or 25% less than MF-RO. This price was for the initial 2.2-mgd capacity EDR system.

With sequential use of MF and RO, water is forced through a membrane under pressure. MF membranes are used to pretreat RO feedwater, removing suspended solids materials, some organics, and other fouling-type materials that will affect the salt-removing RO membranes. With RO, water is pressure-driven through the membrane leaving unwanted salts behind. Chemicals (acid and antiscalants) are added to control scale buildup on the brine side of the membrane from concentrated wastewater constituents such as calcium phosphate, calcium carbonate, calcium sulphate, and others. One problem with today's high-performance RO membranes is that they cannot treat water containing chlorine, an essential ingredient in helping maintain bacterial control with wastewater. Chlorine will destroy RO membranes. It must be removed prior to the RO membranes.

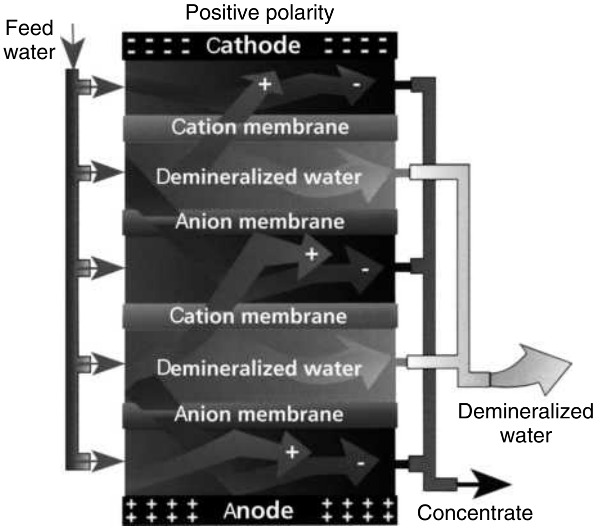

Figure 3. Electrodialysis reversal system.

ED (electrodialysis) was first commercially applied in 1954 for desalting brackish groundwater in a remote area of Saudi Arabia. ED is an electrically driven process in which a DC field generated between electrode plates pulls charged ions making up the water salinity through flat sheet cation and anion membranes. Water is not transported through the membranes—it continues on through the process. The ions (depending on their charge) are attracted to the anode or cathode electrode. Alternating cation and anion membranes generate a segregated product stream and a recirculating concentrated wastewater loop from which waste is eventually bled off. A single "ED stage" will remove up to 50–60% TDS. For still greater salt reduction, membrane and electrode plate stacks are staged in series one after another. Typically, up to 200,000 gpd can be treated in a single line of stacks. For higher flow applications, multiple lines of ED stacks are installed in parallel (Fig. 4).

By automatically switching the membrane stack DC field orientation every 15 to 30 minutes, the EDR system keeps ED membranes free of salt scale buildup without having to add chemicals in the feedwater. Even at 85% water recovery, with highly concentrated levels of salts in the EDR brine, the EDR systems in San Diego operate without chemical feed to control salt scale buildup. By choice, one chemical that is added is a 0.5 ppm of free residual chlorine to keep EDR membrane stacks free from unwanted bacterial growth. Compared with MF-RO, the only pretreatment used with EDR are 10-micron disposable cartridge filters to remove solid particulate matter prior to the membrane stacks.

PAST RESULTS AND TODAY'S LATEST DEVELOPMENTS

When the initial system started operation in 1998, it was supplied as two parallel, land-based 1.1-million gallon per day units located under a sunshade. The systems had a single-stage membrane stack design. Approximately 55% of the salt was removed in this process, and then ED product water was blended up to 3.3 mgd at less than 1000-ppm TDS.

The demand for EDR product flow increased as the city continued to sell more reclaimed irrigation water. In 1999, the EDR system was expanded with the addition of a third land-based unit (a two-stage, 1.1-mgd EDR unit), and with the retrofitting of second-stage membrane stacks to the original EDR equipment. With EDR product flow of 3.3 mgd now having still better quality (less than

Figure 4. San Diego took a major step in the late 1990s by equipping a new high-technology wastewater reclamation plant with EDR (electrodialysis reversal) system from Ionics, Incorporated, to desalinate tertiary treated wastewater.

300 ppm), more non-desalted water is blended with EDR product. The plant is now rated to deliver over 7 mgd of <1000-ppm irrigation water.

To continue development of this alternative irrigation water supply, city officials purchased still more EDR capacity in the fall of 2003. Two options were available. The first used the conventional approach of adding more "land-based" EDR systems. This option required a major rework of the site, with more conventional building of sunshades, concrete pads, and extensive site installation work. The second approach called for the installation of fully preassembled EDR systems within 53-ft-long over-the-road enclosed trailers. On arrival at site, a simpler retrofit using preassembled trailers allows for the quick installation of two additional 1.1-mgd EDR systems (Fig. 5).

Total EDR production will be 5.5 mgd when the latest EDR units go online in January 2005. With blending, up to 12 mgd of irrigation water will be supplied to a now further expanded irrigation water pipeline infrastructure system. This water will go to additional golf courses and new home developments. The latest expansion also includes adding enough concrete pad area and water treatment site pipeline capacity to bring in a third EDR trailer in the future. EDR's ultimate plant will then have 6.6 mgd of EDR capacity and up to 15 mgd + total blended flow. Results at North City have proven very positive for San Diego and for the EDR process

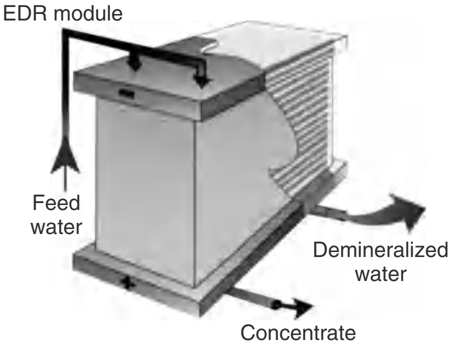

Figure 5. Preassembled EDR module.

FUTURE OUTLOOK

Based on San Diego's success, other municipal agencies in California are looking at EDR to treat their municipal wastewaters for irrigation reuse. In a recent tertiary-treated wastewater pilot test performed in California, EDR and MF-RO were run side-by-side for 9 months. Based on a present worth analysis of capital cost, installation cost, and 20 years O&M, EDR was rated as 40% less expensive than MF-RO.

In another case, where EDR or MF-RO could be used, highly concentrated brines have to be trucked 15 miles to a sewer line disposal site. Transportation costs are very high. The ability of EDR to operate at over 90% water recovery makes treatment practical. The greater volume of MF-RO treatment does not pencil out for this project.

AUTHOR'S NOTE

Eugene R. Reahl is the Western Regional Sales Manager for municipal systems sales at Ionics, Incorporated, based in Watertown, Massachusetts. Reahl sold the second and third EDR system expansions at North City and has been involved with many municipal EDR and RO systems since 1981. Contact the author at ereahl@ionics.com.

KEY CAUSES OF DRINKING WATER QUALITY FAILURE IN A RURAL SMALL WATER SUPPLY OF SOUTH AFRICA

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INTRODUCTION

Of the advances made possible through science and technology, the treatment and distribution of safe water use is truly one of the greatest. Abundant, clean water is essential for good public health. It has been increasingly recognized by world leaders that safe drinking water is a critical building block of sustainable development. Disinfection, a chemical process whose objective is to control disease-causing micro-organisms by killing or inactivating them, is critically important in drinking water treatment. However, research has shown that about 1.2 billion people lack access to safe drinking water worldwide (1). As a result, the World Health Organization estimates that 3.4 million people, mostly children, die every year from water-related diseases (2).

The provision of adequate water services was one of the more difficult and pressing challenges inherited by the new South Africa. Prior to the change of government in 1994, an estimated 30–40% of South Africa's population (14–18 million people) were without adequate water supply services and some 21 million people were without adequate sanitation (3). As of 2004, some 10 million additional people have been supplied with drinking water, thereby reducing the backlog in 2003 to some 4 million (4). Provision of access to a basic level of water can be regarded as the first step up the water ladder, and progress achieved to date is indeed impressive. Although great strides have been made in the effort to provide safe and clean water to all South Africans, studies have shown that in small rural towns and small remote villages with adequate water supply services, the drinking water quality is generally poor and often not fit for human consumption at the point of use (5–7). A study aimed at determining the upgrading needs of small and rural surface water treatment plants in South Africa and the subsequent process of drawing up guidelines on how to address these needs also revealed that most small water treatment plants in the country do not produce safe, clean potable water (8).

The study presented here was undertaken in the town of Alice, a small rural town in the Eastern Cape, one of South Africa's poorest provinces. The Alice Water Treatment Plant (AWTP) is one of many small water treatment plants in the Eastern Cape Province that has difficulty providing safe drinking water. Previous studies (6,7,9) on the microbiological quality of Alice drinking water indicated a high number of fecal and total coliforms and heterotrophic bacteria far exceeding the limit allowed for potable water (10). *Aeromonas hydrophila, Escherichia coli, Serratia odorifera, Salmonella arizonae, Pseudomonas aeroginosa, Pseudomonas fluorescens, Serratia liquefaciens*, and *Serratia marcescens* were present in all water samples collected from various sites of the distribution system. The possibility of *Vibrio* species existed in one of these sites (7). This situation, therefore, places the Alice community at risk of disease outbreaks. A crucial need exists for scientifically sound answers to the problems of the inadequate treatment of drinking water in small water treatment plants in the country in general and the Alice Water Treatment Plant (AWTP) in particular.

The present study aimed at assessing the causes of the drinking water quality failure within the Alice Water Treatment Plant from the raw water intake to the finished water in the in-plant reservoir and at identifying the key causes affecting the performance of the plant including the effectiveness of the disinfection process for the removal of indicator bacteria.

METHODOLOGY

Plant Description

The Alice plant is a conventional water treatment plant, which includes coagulation, flocculation, sedimentation, rapid sand filtration, and chlorination. Water drawn from the Binfield Dam on the Tyume River (approximately 12 km from Alice) is fed under gravity to the head of the works. The design capacity of the plant is 7 mL/d; however, it is currently operating between 3 and 4 mL/d. A number of surrounding villages currently without water services are to be connected to the Alice system in the near future.

At the beginning of the investigation (June 2002) until November 2002, lime and alum were used for the pretreatment of the raw water. The coagulants are dosed at the same point, just ahead of a 90° V-notch weir and hydraulic jump. Powdered hydrated lime and granular alum were mixed with domestic water in separate dissolving/slurry tanks and then fed under gravity to the dosing point. Flash mixing of the chemicals with the raw water results from the turbulence generated over the hydraulic jump. Granular alum and hydrated lime were replaced by ultrafloc (a polyaluminium chloride and polyamide mix supplied by Sudchemie) at the beginning of December 2002. At the foot of the jump, the water enters a relatively short hydraulic flocculator before flowing under gravity to a three-way flow splitter via an underground pipe. From the splitter, the water flows through short intermediate channels into each of the three-clarifier inlet channels. From the influent channels, the water flows into the clarifier inlet chambers via pipes passing through the clarifier walls (nine per clarifier). The discharge into the inlet chambers induces gentle hydraulic mixing, which promotes the formation of large settleable floc. The water passes over a vertical baffle wall into the main body of each of the three rectangular horizontal clarifiers. Settled water overflows into a common channel, which feeds into the filter influent pipe. The filter influent is split among three 4.3-m-diameter self-backwashing valveless sand filters. Chlorine gas is added to the combined filtrate just before the onsite reservoir from where it is fed into the bulk distribution system.

Identification of the Problems Affecting the Performance of the AWTP

The following activities were undertaken from June 2002 to January 2003, with the exception of the experimental study on the dissolved organic carbon, biodegradable dissolved organic carbon, the bacterial regrowth, and the growth factor, which was performed from August to October 2003. The chlorine residual was determined during both periods of the study.

- A tour of the plant and a visual inspection of the various unit processes.
- Interviewing of the operators and plant superintendent about operating practices and the monitoring program.
- Measurement of the raw water flow rate using the V-notch weir.
- Determination of the optimum doses of alum and lime using Jar tests.
- Measurement and interpretation of the turbidity at each step in the treatment process.
- Opening and inspecting one of the valveless filters.
- Measurement of the initial chlorine dose and free chlorine residual concentration in the onsite reservoirs.
- Monitoring of the bacterial quality of the finished water.
- Investigation of the removal of dissolved organic carbon and assessment of the impact of the biodegradable dissolved organic carbon on the bacterial regrowth in the finished water. Details of these activities are given below.

Flow Rate Measurement and Control. The plant was equipped with a flow meter; however, this was located in a sump, which was flooded and the meter had not been read for several years. The flow could also be measured at the V-notch weir at the hydraulic jump; however, the plant operating personnel were unaware of this prior to the project team's visit. During the investigation, the flow of the raw water was calculated using the existing 90° V-notch weir according to Kawamura (11).

For a 90° V-notch weir, the total flow rate, Q, is related to the height of the crest over the weir, H, as follows:

$$Q(\mathrm{m}^3/\mathrm{s}) = 1.40\ \mathrm{H}^{2.5}$$

where H (m) is the height of water above the weir crest.

Table 1 shows H values with corresponding flows as calculated using the hydraulic equation given above.

Alum and Lime Consumption and Cost Estimation. The consumption of alum and lime onsite was estimated by collecting and weighing the amount of dry chemical fed to the mixing tanks during a given time interval. Using the flow rate measured on each day, the corresponding dosages in mg/L and the cost were estimated, which were compared with the optimum doses determined from standard jar tests (11). The costs of chemicals corresponding to the various dose estimates were then calculated taking into account the cost of a 50-kg bag of alum, which is R 96 (US$ 14.9), and a 25-kg bag of lime, which is R 30 (US$ 467).

Clarifier and Filter Performance. The turbidity of the clarified and filtered waters was measured for each settling tank and filter using a Microprocessor Turbidity Meter (HACH Co., Model 2100P). The filtrate was allowed to run out of a sampling tap on the filter under the drain until the measured turbidity stabilized. One filter was opened directly after it had backwashed to assess the state of the filter media. The impact of backwashing on filtrate turbidity was investigated by measuring turbidity before, immediately after, and 4 h and 6 h after backwashing.

Disinfection. The chlorine residual and the turbidity of the treated water were measured in the in-plant reservoir using a multiparameter ion-specific meter (Hanna-BDH laboratory supplies) and Microprocessor Turbidity Meter (HACH company, Model 2100P), respectively.

Monitoring of Bacterial Quality of the Finished Water. To assess the performance of the AWTP for the removal of bacterial indicators, the intake raw water and the chlorinated water samples from the in-plant reservoir were collected twice a week. Treated waters for microbiological analysis were collected in sterile 1-L glass bottles, which contained sodium thiosulphate (ca 17.5 mg/L), and placed in an ice bag. Microbiological analyses were conducted within 1 h after the collection of the water samples. Total coliforms (TC), fecal coliforms (FC), presumptive Salmonella (PS) spp., and heterotrophic plate count bacteria (HPC) were used as bacterial indicators. The membrane filtration technique and chromocult coliform agar (Merck) were used for the enumeration of coliforms and PS. Standard spread plate procedure and R2A agar (Oxoid) were used for the

Table 1. Examples of Flow Rate Measurement Considering Height (*H*) of Water

H (cm)	20	21	22	23	24	25	26	27	28	29	30
Q (m3/s) ⇒ $1.4H^{2.5}$	0.025	0.028	0.032	0.034	0.040	0.044	0.048	0.053	0.058	0.063	0.069
Q (Ml/d) ⇒ $121H^{2.5}$	2.16	2.45	2.75	3.07	3.41	3.78	4.17	4.58	5.02	5.48	5.96

enumeration of HPC bacteria. Water samples were analyzed for the above micro-organisms using internationally accepted techniques and principles (12). Bacterial colonies differing in size, shape, and color were randomly selected from the different plates and further isolated on MacConkey agar (Biolab) by the streak plate technique and incubated at 37 °C for 24 h. These were further purified by the same method at least three times using nutrient agar (Biolab) before Gram staining was done. Oxidase tests were then done on those colonies that were gram negative. The API 20E kit was used for the oxidase-negative colonies, and the strips were incubated at $35 \pm 2\,^{\circ}\mathrm{C}$ for 24 h. The strips were then read, and the final identification was done using API LAB PLUS computer software (BioMérieux).

Dissolved Organic Carbon (DOC), BDOC, and Bacterial Regrowth Analyses. Water samples (raw water, water after filtration, and water after chlorination) for the dissolved organic carbon (DOC), biodegradable dissolved organic carbon, bacterial regrowth, and growth factor were collected weekly using sterile glass bottles (brown sterile bottles for raw water and water after filtration). Prior to use, all glassware (except the filter frit) was pretreated according to Servais et al.'s (13) methods, which were modified by Grundlingh et al. (14) to make sure that there were no traces of organic matter left in the glassware, as this might lead to false results. Water samples for DOC analysis were prepared according to Mathieu et al. (15). The DOC concentrations were determined using an AQUADOC™ TOC Analyzer.

The preparation of the inoculums was performed according to Grundlingh et al. (14). A 50-mL raw water sample was filtered through a 2.0-μm nucleopore polycarbonate membrane, 47-mm diameter (Merck, Cat. No. 111111), and was stored in a sealed glass bottle. This water sample was used for the analysis of BDOC and for the growth factor. The BDOC was determined according to the method previously used by Servais et al. (13) modified by Grundlingh et al. (14). Briefly, a water sample was vacuum-filtered through a 0.2-μm nucleopore polycarbonate membrane, 47-mm diameter (Merck, Cat. No. 111106), and 200 mL of this water sample was measured using a glass measuring cylinder into a brown bottle. Two milliliters of the innoculum was added. The water sample was then incubated for 28 days in a dark cupboard to prevent the breakdown of DOC by sunlight. After every 7 days, 20 mL was removed and prepared for the DOC analysis. The concentration of BDOC was calculated as the difference in the DOC concentration before incubation and on the last day of incubation. Bacterial regrowth was then determined using total coliforms (TC), fecal coliforms (FC), and heterotrophic plate count (HPC) as main parameters, which were enumerated as described for the monitoring of the bacterial quality of the finished water using standard methods (12).

Growth Factor. The growth factor was analyzed according to Page et al. (16) to evaluate the potential of the water to support the regrowth of bacteria. Each water sample was allowed to warm to room temperature after collection and was then vacuum-filtered through a 2.0-μm nucleopore polycarbonate membrane, 47-mm diameter (Merck, Cat. No. 111111), and 200 mL of this water sample were measured into a brown bottle, 20 mL of sterile nutrient broth were added to the sample. This water sample was then vacuum-filtered using a 0.2-μm nucleopore polycarbonate membrane, 47-mm diameter (Merck, Cat. No. 111106), and then poured into three sterile turbidity cuvettes. A Microprocessor Turbidity Meter (HACH Co., model 2100P) was zeroed using this sample. The inoculum (bacteria from raw water) was added until the turbidity readings were between 0.2 and 0.4 NTU. The turbidity meter was zeroed again to ensure that only the growth of new bacteria was enumerated. Turbidity readings were taken after every 30 minutes until a plateau was reached. The growth factor was calculated as follows:

$$\frac{\text{Turbidity at the plateau}}{\text{Turbidity at the lag phase}}$$

Results and Discussion

To ensure effective water treatment processes, which will result in the production of safe and clean potable water, trained and skilled personnel remain a prerequisite. However, this is not the case in most small water supplies in rural developing communities. Lack of trained operators at the AWTP resulted in the malfunctioning of the plant.

Coagulant Dosing and Control. Two major operating problems identified during this investigation were the lack of flow rate measurement and chemical dosing control. Raw water flow rates were adjusted based on the level of the in-plant reservoir, but coagulant chemical feed rates were not automatically adjusted in proportion to the raw water flow rate, resulting in large fluctuations in coagulant doses. The operating staff apparently sometimes adjusted the alum and lime doses based on the taste and appearance of the final water and the formation of floc in the clarifiers; however, the coagulant demand was not determined. Table 2 summarizes the raw water flow rates, coagulant feed rates and doses for 4 different days, and an estimate of the annual cost of alum and lime used. Jar tests on the raw water indicated that the optimum alum dose was approximately 15 mg/L, three to five times smaller than the doses used by the plant operators during the study period. With an average flow of 3.27 mL/d obtained during the investigation, the cost of alum per year at a dosage rate of 15 mg/L was calculated at R 33,323 (US$ 5182.43), which represents one quarter of the cost of the dose currently used by the plant. The jar tests conducted also indicated that lime addition was not necessary for coagulation at the time the tests were undertaken and was probably detrimental to the process. Theoretically, lime addition should only be necessary if insufficient alkalinity exists in the raw water to prevent the pH dropping below 6 or the colloidal particles becoming restabilized. If the coagulated water pH is above 6, then the addition of lime increases the solubility of aluminium and the amount of alum required. Lime may have been necessary at other times of the year. Overdosing lime free chlorine residual for each month. It can also be seen that chlorine residual increased as the filtrate turbidity decreased. Alice drinking water at the point of treatment contained less chlorine than the target chlorine residual concentration, i.e., 1 mg/L. The present results confirm those of previous investigators who also observed a low level of chlorine residual in the AWTP's reservoirs (9).

Microbiological quality of drinking water at the point of treatment. The bacterial quality of the finished water as suggested by the indicator organisms used (Figs. 3 and 4) did not meet the standards for potable water. Among 14 species of potential pathogenic bacteria identified from the raw water (*Aeromonas hydrophila, Aeromonas caviae, Aeromonas sobria, Escherichia coli, Serratia odorifera, Serratia liquefaciens, Serratia marcescens, Salmonella arizonae, Pseudomonas aeruginosa, Pseudomonas fluorescens, Vibrio fluvialis, Chryseomonas luteola, Enterobacter aerogenus, Enterobacter sakazakii),* 8 species were still prevalent in the chlorinated water from the reservoirs (*Aeromonas hydrophila, Escherichia coli, Serratia odorifera, Serratia liquefaciens, Serratia marcescens, Salmonella arizonae, Pseudomonas aeruginosa, Pseudomonas fluorescens*). In general, the result suggested that the performance of the AWTP for the removal of indicator bacteria (HPC, TC, FC, and PS) was not adequate. The finished water produced by this plant places the consumers at a serious health risk. These results confirm our recent study, which also showed the failure of the AWTP to provide potable water to its consumers at the point of use (7).

The removal of DOC and the impact of BDOC on bacterial regrowth. Sand filtration processes are performed to decrease the DOC concentration from the raw water to the filtered water. Overall, DOC removal at the AWTP appeared to have been very poor for the entire monitoring period, as indicated in Table 3. The AWTP's filtration system did not decrease the DOC concentration to the level recommended by the water industries, which ranges between 0 and 5 mg/L (10). The DOC concentrations in the filtered water samples were above these limits (Table 3). The highest DOC concentration in raw water was found in October and the removal was at 59.57%, whereas the lowest concentration of the DOC in raw water was recorded in August. No removal of the DOC was noted in August and in September; in contrast, an increase in DOC concentration occurred at rates of 13.64% and 35.34%, respectively. The inefficiency of the filtration process could be attributed to the lack of backwashing of the sand filters in the AWTP. It was noted that the filters went for days without backwashing, which impacted the quality of the filtrate in terms of the DOC removal.

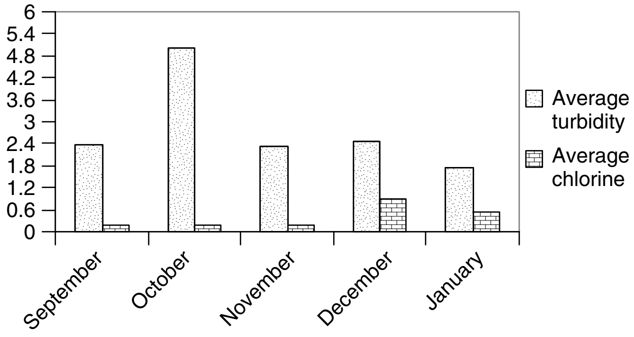

Figure 2. Average turbidity values (NTU) vs. average free chlorine residual concentration (mg/L) in the in-plant reservoir.

The concentration of the DOC in the filtered water accounted for the presence of that in the finished water

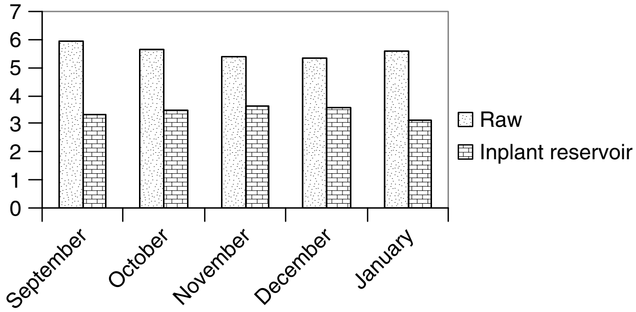

Figure 3. Average log HPC bacterial counts (cfu/mL) in raw water and the in-plant reservoir.

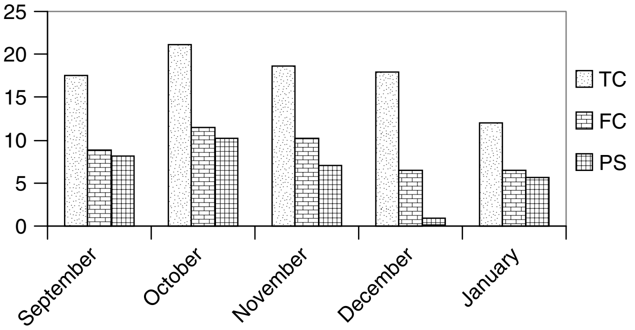

Figure 4. Average counts (cfu/100 mL) for total coliforms (TC), fecal coliforms (FC), and presumptive *Salmonella* (PS) in the in-plant reservoir.

Table 3. The Performance of AWTP in Terms of the DOC (mg/L) and BDOC (mg/L) Concentrations, the Growth Factor, and the Chlorine Residual Concentration

		DOC		BDOC	GF	CR
MONTH		FW	CW	CW	CW	CW
	MIN	13.00	15.00	1.00	2.90	0.00
	MAX	12.00	16.00	6.70	3.04	0.00
AUGUST	$\bar{x}$	12.50	15.50	3.85	2.97	0.00
	Sx	0.71	0.71	4.03	2.05	0.00
	MIN	13.00	13.00	4.20	3.29	0.00
	MAX	18.00	33.00	14.80	6.54	2.77
SEPTEMBER	$\bar{x}$	15.70	23.00	14.00	5.76	1.19
	Sx	2.52	10.00	9.43	0.74	1.42
	MIN	9.00	27.00	4.00	4.41	2.52
	MAX	133.00	50.00	40.00	7.12	3.58
OCTOBER	$\bar{x}$	37.20	31.00	18.80	6.86	2.82
	Sx	57.30	15.79	16.45	1.34	0.44

DOC = dissolved organic carbon, BDOC = biodegradable dissolved organic carbon, GF = growth factor, MIN = minimum value, MAX = maximum value, Sx = standard deviation, $\bar{x}$ = average value, CR = chlorine residual.

samples at the point of chlorination. Although no free chlorine residual was noted in August and during the first week of September (Table 3), the DOC concentrations increased by 24% and by 46.5%, respectively, during the monitoring period. In October, the free chlorine residual concentrations exceeded the limits recommended for potable water, which are in ranges of 0.3–0.6 mg/L as ideal free chlorine residual concentration and 0.6–0.8 mg/L as good free chlorine residual concentration for insignificant risk of health effects (19). During this month, the DOC concentration decreased by 16.67%. As indicated in Table 3, high concentrations of the DOC in the Alice finished water contributed to the biodegradability of the organic matter in the drinking water, which followed the trend of chlorine residual as it increased each month.

Biologically stable water is free of biologically available substances. In addition, it is well known that the degree of bacterial regrowth is determined by the overall content of biodegradable organic carbon present in the water and is largely determined by the origin of the drinking water produced (20). The results of the present experimental study showed close relationship between the DOC concentrations and both BDOC concentrations and the growth factors (Table 3). The concentration of BDOC and the growth factor revealed that water distributed by the AWTP was biologically unstable. Water with growth factors below 5 is considered biologically stable (16). In the AWTP, the average values of growth factors were found to be high in September (7.72), and October (5.97), exceeding the above limit. The lowest values of the growth factor were found in August (4.37).

Removal of BDOC to the level that limits microbial regrowth provides not only a direct control of bacterial population but also an indirect control of protozoan population through a trophic food web (21). A high BDOC concentration in finished water indicates poor quality and a potential for micro-organisms to multiply in the water (22). It has been reported that treated water containing a BDOC concentration of less than 1 mg/L is not prone to regrowth (23). However, treated water supplied by the AWTP had very high concentrations of BDOC, up to 40 mg/L (Table 3), which resulted in high bacterial regrowth during the study period (Fig. 5). The increase of the bacterial counts was parallel to the increase in the BDOC concentration from August to September, but bacterial regrowth decreased in October contrary to the increase in the BDOC concentration. This decrease in bacterial regrowth could be related to a high concentration of free chlorine residual, which was up to 3.58 mg/L (Table 3). The variation of the free chlorine residual concentration was associated with the fact that the operators in the AWTP have little understanding of the chlorination process in the purification system. Chlorination in the AWTP was done without considering the chlorine demand of the water.

CONCLUSION AND RECOMMENDATIONS

The Alice Water Treatment Plant should be operated to consistently produce a combined filtrate turbidity (measured at the first clear well) of less than 0.5 NTU and a free chlorine residual of at least 0.5 mg/L in the main storage reservoirs for the town and 0.2 mg/L at the end of the distribution system. If the water is to be stored for considerable periods of time at the point of use, then higher residuals may be required.

Coagulation should ideally also be optimized for maximum DOC removal prior to disinfection. The operating staff should aim to meet turbidity removal goals with the minimum amount of coagulants necessary. Jar tests should be used to determine what these optimum doses are, which will result in a reduction of sludge production and disposal problems, lower solids loading, and less risk of post-precipitation in the filters, as well as cost savings for the plant. Filters should backwash at least once a day. If necessary, manual backwash should be initiated to prevent filter run times of greater than 24 to 36 h.

The success of any attempt to optimize the plant operation requires the full cooperation of the operating staff, especially because they will be required to undertake additional duties. All decisions and strategies should be discussed with the operators, and they should be encouraged to take a personal interest and pride in any improvements achieved.

Acknowledgments

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BIBLIOGRAPHY

1. Chlorine Chemistry Council. (2003). Drinking water chlorination, a review of disinfection practices and issues. Available: http://c3.org/chlorine_issues/disinfection/c3white2003.html.
2. World Health Organization. (2002). *Water and Sanitation: Facts and Figures*. Available: http://www.who.int/water_sanitation_health/General/facts&fig.htm.
3. Van der Merwe, L.H. (2003). *Water Sewage Effluent*. **23**(5): 50–51.
4. Kasrils, R. (2003). *Media Release. Statement by Minister Ronnie Kasrils on the Celebration of the 9 Millionth Person to Receive Safe Water Since 1994*. July 5.
5. Pearson, I. and Idema, G. (1998). An assessment of common problems associated with drinking water disinfection in developing areas. *WRC Report No.* 649/1/98: 1–17.
6. Momba, M.N.B. and Kaleni, P. (2002). Regrowth and survival of indicator microorganisms on the surfaces of household containers used for the storage of drinking water in rural communities of South Africa. *Water Res.* **36**: 3023–3028.
7. Momba, M.N.B., Makala, N., Tyafa, Z., Brouckaert, B.M., Buckly, C.A., and Thompson, P.A. (2004). *Improving the Efficiency and Sustainability of Disinfection at a Small Rural Water Treatment Plant. Presented at the WISA Biennial Conference held at the Cape Town International Conference Centre*. May 2–6.
8. Swartz, C.D. (2000). Guidelines for the upgrading of existing small water treatment plants. *WRC Report No.* 730/1/00.
9. Muyima, N.Y.O. and Ngcakani, F. (1998). Indicator bacteria and regrowth potential of the drinking water in Alice, Eastern Cape. *Water SA*. **24**: 29–34.
10. Department of Water Affairs and Forestry. (1996). *South African Water Quality Guideline for Domestic Use*. 2nd ed. Pretoria.

11. Kawamura, S. (1991). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York.
12. American Public Health Association. (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th Edn. AWWA. Water Environmental Federation, Washington, DC.
13. Servais, P., Billen, G., and Harscoet, M.C. (1987). Determination of the biodegradable fraction of dissolved organic matter in water. *Wat. Res. (G.B.)* **21**(4): 445–450.
14. Grundlingh, J.A., Nel, C., Kotze, E., and De Wet, C.M.E. (1999). Biodegradable compounds and microbial regrowth in water. *WRC Report No.* 541/1/99.
15. Matthieu, L., Block, J.C., Dutang, M., Mailard, J., and Reasoner, D.J. (1993). Control of biofilm accumulation in drinking water distribution systems. *Wat. Suppl.* **11**(3–4): 365–376.
16. Page, D.W. et al. (2002). Effect of alum treatment on the trihalomethane formation and bacterial regrowth potential of natural and synthetic waters. *WRC.* **36**(12): 4884–4892.
17. World Health Organization. (1993). *Guidelines for Drinking Water Quality*, Vol. 1, 2nd Edn. Recommendations, Geneva.
18. Brouckaert, B.M., Pryor, M.J., Pillay, P., Zondi, T.A., and Amirtharajah. (2002). Assessing the use of autonomous valveless filters for turbidity removalin rural applications. *Proceedings of IWA Biennal Conference and Exhibition*. Durban, May 19–23.
19. Department of Water Affairs and Forestry, Department of Health, Water Research Commission. (1998). *Quality of Domestic Water Supplies*, Vol. 1: Assessment Guide, 2nd Edn. Water Research Commision No: TT 101/98.
20. Momba, M.N.B., Cloete, T.E., Venter, S.N., and Kfir, R. (2000). Influence of disinfection processes on the microbial quality of potable groundwater in a laboratory-scale system model. *J. Water SRT—Aqua.* **49**: 23–33.
21. Servais, P., Anzil, A., and Ventersque, C. (1989). Simple method for determination of biodegradable dissolved organic carbon in water. *Appl. Environ. Microbiol.* **55**: 2732.
22. Lechevallier, M.W., Cawthon, C.D., and Lee, R.G. (1988). Mechanisms of bacterial survival in chlorinated drinking water. *Water Sci. Technol.* **20**(11/12): 145–151.
23. Bernhardt, H. and Wilhelms, A. (1985). Erfahrungen mit der desinfektion von trinkwasser durch chlordioxid. *38 Int. CFBEDEAU Konf.—CEBEDOC*, Liège, pp. 193–231.

FILTRATION

National Drinking Water
Clearinghouse

Filtration is the process of removing suspended solids from water by passing the water through a permeable fabric or porous bed of materials. Groundwater is naturally filtered as it flows through porous layers of soil. However, surface water and groundwater under the influence of surface water is subject to contamination from many sources. Some contaminants pose a threat to human health, and filtration is one of the oldest and simplest methods of removing them. Federal and state laws require many water systems to filter their water. Filtration methods include slow and rapid sand filtration, diatomaceous earth filtration, direct filtration, packaged filtration, membrane filtration, and cartridge filtration.

FILTRATION KEEPS WATER SAFE

Why Filter Drinking Water?

Natural filtration removes most suspended matter from groundwater as the water passes through porous layers of soil into aquifers. Surface water, however, may be subject to direct animal, human, and industrial contamination that can cause disease or illness in humans, so they must be filtered by a constructed treatment system.

What Regulations Govern Filtration?

The Surface Water Treatment Rule under the 1986 Safe Drinking Water Act (SDWA) Amendments requires that many surface water supply systems and groundwater under the influence of surface water filter their water supplies.

What Processes Precede Filtration?

Conventional filtration processes are normally preceded by coagulation, flocculation, and sedimentation. Direct filtration processes are preceded by coagulation and flocculation only; the floc is removed directly by the filters.

Filtration processes may include one or all of the following pretreatment procedures:

Chemical Feed and Rapid Mix: Chemicals may be added to the water to improve the treatment processes that occur later. These may include pH adjusters and coagulants. A variety of devices, such as baffles, and static mixers can be used to mix the water and distribute the chemicals evenly.

Flocculation: The chemically treated water is sent into a basin where the suspended particles can collide and form heavier particles called floc. Gentle agitation and appropriate detention times facilitate this process.

Sedimentation: The velocity of water is decreased so that suspended material (including flocculated particles) can settle out of the water stream by gravity. Once settled, the particles combine to form a sludge that is later removed from the clarified supernatant (the liquid removed from settled sludge) water.

How is Filtration Achieved?

Filtration is usually a combination of physical and chemical processes. Mechanical straining removes some particles by trapping them between the grains of the filter medium (such as sand). Adhesion is an equally important process by which suspended particles stick to the surface of filter grains or previously deposited material. Biological processes are also important in slow sand filters. These filters form a filter skin containing microorganisms that trap and break down algae, bacteria, and other organic matter before the water reaches the filter medium itself.

COMPARING FILTRATION SYSTEMS

Slow Sand Filtration

The filter consists of a bed of fine sand approximately 3 to 4 feet deep supported by a 1-foot layer of gravel and an underdrain system (Fig. 1).

Advantages. Low cost, simplex2 operation, reliable, and able to achieve greater than 99.9 percent *Giardia* cyst removal. It also does not require extensive active control by an operator.

Limitations. It is not suitable for water with high turbidity. Filter surface requires maintenance. Extensive land is required due to low-flow operation (0.03 to 0.10 gallons per minute per square foot [gal/min/ft^2] of filter bed area).

Process. Filters are operated under continuous, submerged conditions maintained by adjusting a control valve located on the discharge line from the underdrain system. Biological processes and chemical/physical processes common to various types of filters occur at the surface of the filter bed. A biological slime or mat referred to as "schmutzdecke" forms on the surface of the bed, which traps small particles and degrades organic material present in the raw water. Slow sand filters do not require coagulation/flocculation and may not require sedimentation.

Equipment. Small plants are typically designed with cast-in-place concrete structures with wood or concrete structures with wood or concrete slab covers. Piping is either cast iron or polyvinyl chloride (PVC). Flow meters are used to monitor the output for each filter. In climates subject to freezing temperatures, filters usually must be housed, and may require heating, lighting, and ventilation. Unhoused filters in cold climates develop an ice layer that prevents cleaning during winter months.

Chemicals. Water applied to slow sand filters is not prechlorinated because the chlorine can destroy organisms in the schmutzdecke.

Diatomaceous Earth Filtration

Diatomaceous earth filtration, also known as precoat or diatomite filtration, relies on a layer of diatomaceous earth approximately 1/8-inch thick placed on a septum or filter element. Septums may be placed in pressure vessels or operated under a vacuum in open vessels.

Advantages. The filters are simple to operate and effective in removing cysts, algae, and asbestos. They have been chosen for projects with limited initial capital, and for emergency or standby capacity to service large seasonal increases in demand.

Limitations. This filter is most suitable for water with low bacterial counts and low turbidity (less than 10 nephelometric turbidity units [NTU]). Coagulant and filter aids are required for effective virus removal. There is potential difficulty in maintaining complete and uniform thickness of diatomaceous earth on the filter septum.

Process. Operation and maintenance of diatomaceous earth filters require: preparing slurries of filter body feed (diatomaceous earth) and precoat diatomaceous earth; adjusting body feed dosages for effective turbidity removal; periodic backwashing—every 1 to 4 days; disposing of spent filter cake; periodically inspecting the filter septum for cleanliness and damage; and verifying effluent quality.

Equipment. The minimum amount of filter precoat should be 0.2 pounds per square foot (lb/ft^2); and minimum thickness of the precoat should be increased from 1/8 to 1/5 inch to enhance *Giardia* cyst removal. In addition, minimum design criteria outlined in the *Recommended Standards for Water Works* (better known as 10 State Standards) should be met.

Chemicals. Use coagulant to coat the body feed to improve removal rates for viruses, bacteria, and turbidity.

Direct Filtration

Direct filtration systems are similar to conventional systems, but omit sedimentation.

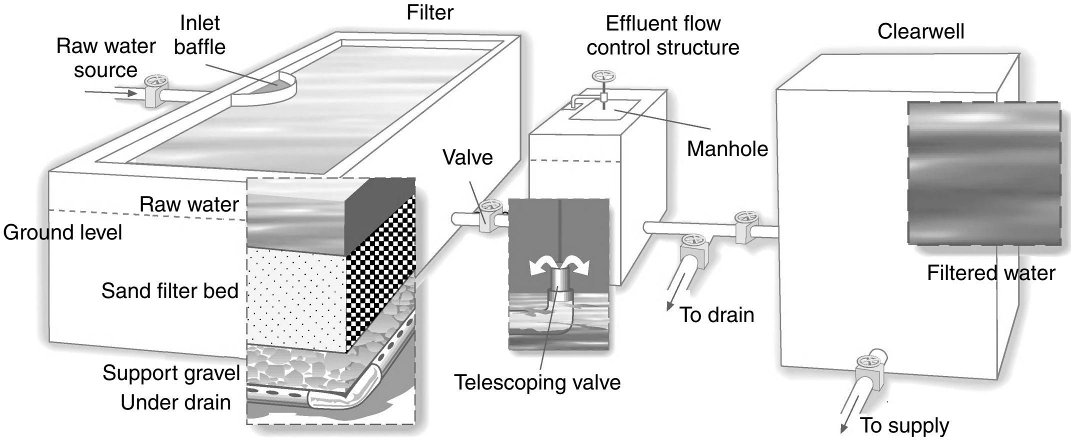

Figure 1. Slow sand filter.

Advantages. Effective direct filtration performance ranges from 90 to 99 percent for virus removal and from 10 to 99.99 percent for *Giardia* removal. The most effective direct filtration configurations for *Giardia* removal must include coagulation. Often used with steel pressure vessels to maintain the pressure in a water line to avoid repumping after filtration.

Limitations. Direct filtration is only applicable for systems with high quality and seasonally consistent influent supplies. The influent generally should have turbidity of less than 5 to 10 NTU and color of less than 20 to 30 units. (Water with 15 or more units of color causes aesthetic problems, such as staining.)

Process. Direct filtration consists of several combinations of treatment processes. It always includes coagulation and filtration, and may require a flocculation tank or a pressure vessel after the coagulation addition.

Equipment. Dual- and mixed-media filters are used to effectively process higher influent turbidities without the use of sedimentation.

Chemicals. Typical coagulant dosages range from less than 1 to 30 milligrams per liter. Cationic polymers often successfully coagulate water supplies and assist direct filtration. Nonionic polymers are sometimes added to the filtration step to increase filter efficiency.

Packaged Filtration

Packaged filtration is simply all of the features of filtration—chemical addition, flocculation, sedimentation, filtration—mounted as a unit on a frame for simple hookup of pipes and services. It is most widely used to treat surface water supplies for removal of turbidity, color, and coliform organisms with filtration processes. Packaged filtration is often used to treat small community water supplies, as well as supplies in recreational areas, state parks, construction sites, ski areas, and military installations, among others.

Advantages. The four major advantages of package plants are their compact size, cost effectiveness, relative ease of operation, and design for unattended operation. (Some states require that an operator be in attendance at all times. Check your state regulations.)

Limitations. When the turbidity of the raw water varies a great deal, these package plants require a high level of operator attention and skill.

Process. Package plants are most appropriate for plant sizes ranging from 0.025 to 6 million gallons per day. The most important factor to consider in selecting a package plant is the influent characteristics, such as temperature, turbidity, and color levels. Pilot tests might be necessary before a final system can be selected.

Equipment. Package plants are assembled in a factory, skid mounted, and transported to the treatment site, or they are transported as component units to the site and then assembled.

Chemicals. Chemical feed controls are especially important for plants without full-time operators or with variable influent characteristics. Even with these automated devices, however, the operator needs to be properly trained and well acquainted with the process and control system.

Membrane Filtration

A membrane is a thin layer of material capable of separating substances when a driving force is applied across the membrane.

Advantages. Membrane filtration can be an attractive option for small systems because of its small size and automated operation. Membrane processes are increasingly employed for removal of bacteria and other microorganisms, particulate material, and natural organic material, which can impart color, tastes, and odors to water.

Limitations. Fouling of the membranes is the major problem preventing widespread application of this technology.

Process. Membrane filtration works by passing water at high pressure through a thin membrane in the form of hollow fiber or spiral-wound composite sheets. Organic and other contaminants are retained on the high-pressure side and frequently must be removed by reversing the flow and flushing the waste. Periodic chemical cleaning may be required to remove persistent contaminants. Membrane assemblies are contained in pressure vessels or cartridges.

Equipment. The membrane technologies are relatively simple to install and for groundwater sources that do not need pretreatment, the systems require little more than a feed pump, a cleaning pump, the membrane modules, and some holding tanks.

Chemicals. Periodic backflushing and occasional chemical cleaning is necessary to maintain the membrane or fibers.

Cartridge Filtration

Cartridge filters are considered an emerging technology suitable for removing microbes and turbidity in small systems (Fig. 2).

Advantages. Cartridge filters are easy to operate and maintain, making them suitable for small systems with low-turbidity influent.

Limitations. Cartridge filtration systems require raw water with low turbidity. Polypropylene cartridges become fouled relatively quickly and must be replaced with new units. Although these filter systems are operationally simple, they are not automated and can require relatively large operating budgets.

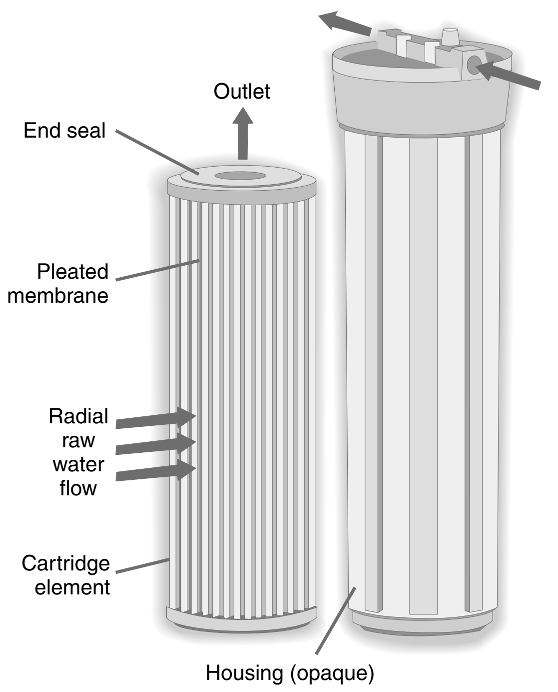

Figure 2. Cartridge filter with replaceable inner package.

Process. Cartridge filtration uses a physical process—straining water through porous media. It can exclude particles 0.2 micrometers (μm) or smaller. The pore sizes that are suitable for producing potable water range from 0.2 to 1.0 μm. Roughing filters, for pretreatment prior to cartridge filtration, are sometimes necessary to remove larger suspended solids and prevent the rapid fouling of the cartridges. Roughing filters can be rapid sand filters, multimedia filters, fine mesh screens, or bag filters.

Equipment. A cartridge consists of ceramic or polypropylene filter elements fitted into pressurized housings.

Chemicals. A disinfectant is recommended to prevent surface-fouling microbial growth on the cartridge filters and to reduce microbial pass-through. Except for a disinfectant, no chemical additions are necessary. However, corrosive chemicals may be required for the periodic membrane cleaning process.

How Does One Select the Appropriate Filtration System?

First, review all raw water quality data to establish the requirements for the alternatives. Once the potential alternatives are selected, determine the necessity of pilot or bench-scale tests. If the desired performance of one or more of the alternatives is in doubt, testing is appropriate. (Testing is always useful if time and budget allow).

Otherwise, literature surveys, bench-scale studies, or pilot-test results can be used to derive each alternative's performance characteristics and design considerations. Following this initial selection, the basic process concerns for the various alternatives should be identified and evaluated, including:

- turbidity removal performance,
- *Giardia* removal performance,
- color removal performance,
- cleaning cycle frequency,
- necessary chemicals/chemical dosages,
- applicable regulatory standards,
- required operational skills, and
- necessary sludge management.

Where Can I Find More Information?

Information in this fact sheet was primarily obtained from two sources: Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities, *EPA/625/5-90/025; and* Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, *EPA/625/4-89/023. Both can be ordered free from the U.S. Environmental Protection Agency Office of Research and Development at (513) 569-7562.*

If these publications are no longer available from the EPA, call the National Drinking Water Clearinghouse (NDWC). Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities, *item #DWBKGN09, an 82-page publication, costs $11.82.* Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, *item #DWBKDM04, a 209-page book, costs $30.05. Shipping and handling charges apply.*

Also, the NDWC's Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS) is a public reference database that contains information about technologies in use at small water systems around the country. For further information on accessing or ordering RESULTS, call the NDWC at (800) 624-8301.

For additional copies of "Tech Brief: Filtration," item #DWBRPE5O, or a copy of "Tech Brief: Disinfection," item #DWBRPE47, call NDWC at the number above.

WATER FILTRATION

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Particulates that are removed by a water filtration process include microorganisms (bacteria, viruses, and protozoan cysts), clay and silt particles, colloidal and precipitated humic substances and other organic particulates from natural decay of vegetation, precipitates of an aluminum or iron coagulation process, calcium carbonate and magnesium hydroxide precipitates from lime softening, and iron and manganese precipitates.

Granular medium filtration is a water treatment process that uses a porous medium through which water passes to remove particulates or suspended solids (Fig. 1). There are different types of filters classified by various schemes. Filters can be classified based on the type of medium (single medium, dual medium), hydraulic arrangement (gravity or pressure), rate of filtration (rapid

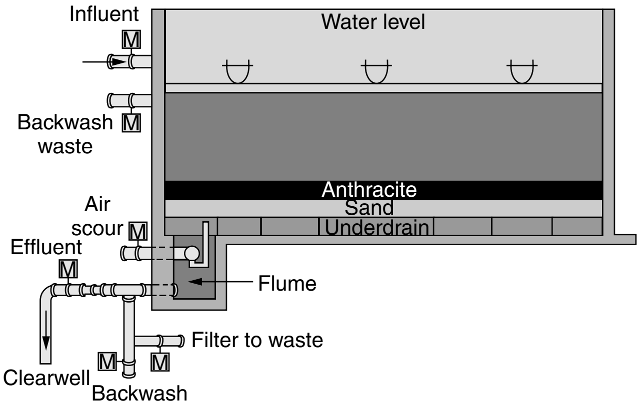

Figure 1. Rapid gravity filter (*Source*: F.B. Leopold Company).

or slow), and depth of solids removal (deep or cake). The most common types of filter media used in granular bed filters are silica sand, anthracite coal, and garnet. These may be used alone or in dual- or triple-media combinations. Granular-activated carbon (GAC), another type of medium, has been used to reduce taste and odor in granular beds that serve for both filtration and adsorption.

Rapid granular bed filtration consists of passing pretreated water through a granular bed at rates ranging from 2 to 10 gpm/sq ft (5 to 25 m/h). Flow is typically downward through the bed. During the filtration cycle, solids are removed from the water and accumulate within the voids and on the top surface of the filter medium. This accumulation results in clogging and a gradual increase in head loss. When the head loss becomes excessive (generally 8–9 ft), the filtrate quality begins to deteriorate, and/or the filter cycle reaches a predetermined time limit (usually 3 or 4 days), then rapid filters need cleaning.

Dirty/clogged filters may be cleaned by scouring the clogged portion or by reversing the flow through the bed. This application of expanding and washing out trapped particles is called backwashing. Backwashing by water fluidization is frequently assisted by a surface wash or an air scour. The most effective backwash is achieved by simultaneous air scour and subfluidization water backwash. Typical backwash rates range from 15 to 23 gpm/sq ft depending on media sizes. The bed expansion varies from 20% to 50%. The backwash usually lasts from 5 to 15 minutes. The air-scour rate varies from 2 to 4 cu ft/min/sq ft (0.6 to 1.2 cu meter/min/sq meter). For effective rapid granular bed filtration, source water must be pretreated.

Chemical destabilization is an essential prerequisite for effective filtration. Chemicals used for particle destabilization are limited primarily to metal salts or cationic polymers as primary coagulants. Pretreatment may also include aeration or introducing an oxidant if water treatment aims to remove iron or manganese. Sometimes, a filter aid polymer is added in the influent to the filter to improve particle capture efficiency.

Granular bed filtration consists of three principal mechanisms: (1) transport, (2) attachment, and (3) detachment. *Transport* mechanisms move a particle into and through a filter pore so that it comes very close to the surface of the filter medium or existing deposits where *attachment* mechanisms retain the suspended particle in contact with the medium's surface or with previously deposited solids. *Detachment* mechanisms result from the hydrodynamic forces of the flow acting so that a certain portion of the previously attached particles, less strongly adhered to others, is detached from the filter medium or previous deposits and carried further, deep into or through the filter. Important transport mechanisms include screening, interception, inertial forces, sedimentation, diffusion, and hydrodynamic forces. Attachment of particles to media surfaces is generally governed by physicochemical and molecular forces. Detachment is caused by the impact of arriving particles on unstable deposits and by hydraulic shear stresses without the influence of arriving particles. A number of properties of a filter medium are important for filtration performance and for characterizing the medium. Important media properties include size, shape, density, and hardness. The efficiency of a filter is more sensitive to changes in the filtration rate rather than in the actual rate. Therefore, filtration process control is critical to successful operation.

In recent years, direct filtration has received considerable attention and application in treating of drinking water. Direct filtration is not preceded by sedimentation. It offers several advantages over conventional treatment of "good-quality" surface water. Because there is no sedimentation process and a lower coagulant dose, the capital and operating costs are lower compared with conventional treatment. Sludge volumes are lower, which results in lower chemical costs for sludge treatment and disposal. Because of the increased interest in ozone application in potable water, biological filtration has received noticeable attention and application in recent years. Granular filters become biologically active when ozone is used as a preoxidant. Ozone reacts with organic compounds in water and forms several ozonation byproducts such as aldehydes, carboxylic acids, and keto acids, which are relatively easy to biodegrade. By operating filters in a biological mode, these ozonation byproducts can be effectively removed and in turn reduce the potential for bacterial regrowth in a distribution system and formation of chlorination byproducts.

A slow sand filter generally consists of a watertight basin containing a layer of sand over a layer of gravel (Fig. 2). It is operated at very low filtration rates without coagulation in pretreatment. A smaller grain size and lower filtration rate result in removing the solids almost entirely in a thin layer on the top of the sand bed. This layer, composed of dirt and living and dead micro- and macro-organisms from the water, is called *schmutzdecke* or dirty skin. Most of the solid removals in a slow sand filter take place in the *schmutzdecke* layer. The dominant removal mechanisms are both physical and biological. A typical filter cycle may vary from 1 to 6 months (or longer) depending on the source water quality and the filtration rate. Filtration rates range from 0.016 to 0.16 gpm/sq ft (0.04 to 0.40 m/h). Effective sand sizes ranged from 0.15 to 0.40 mm, sand uniformity coefficients from 1.5 to 3.6, and initial bed depths from 1.5 to 5.0 ft. The sand is supported on graded gravel 6 to 36 inches deep. Slow sand filters

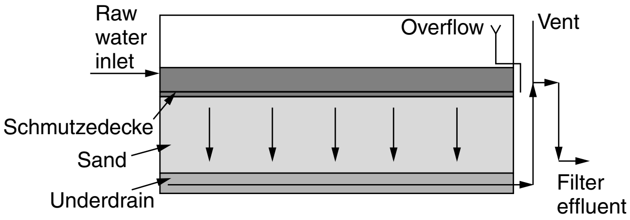

Figure 2. Conventional slow sand filter.

are cleaned by scraping *schmutzdecke* and a small amount of sand depth. Usually scraping is done manually but, in some cases, mechanically. The scraped sand is cleaned hydraulically and stockpiled for later reuse.

Diatomaceous earth filtration, also called precoat or diatomite filtration, uses a layer of diatomaceous earth approximately one-eighth inch thick placed on a septum or filter element as a filter medium. The septum may be placed in a pressure vessel or operated under a vacuum in an open vessel. As the water passes through the filter medium and septum, the suspended particles are captured and deposited. The majority of particles removed by the filters are strained at the surface layer of the filter medium, and some are trapped within the layer. As the filter cycle proceeds, additional filter medium called *body feed* is regularly metered into the influent water in proportion to the solids removed. Ultimately, a gradually increasing pressure drop through the filter system reaches a point where continued filtration is impractical. The forward filtration process is stopped, the filter medium and collected dirt are washed off the septum, a new precoat of filter medium is applied, and the filtration process continues. Diatomaceous earth filters are widely used in industrial filtration applications and in swimming pool filtration. They have also been used in municipal potable water treatment, primarily in direct, in-line filtration of high-quality surface water (turbidity 10 NTU or less and acceptable color), and in filtering iron and manganese from groundwater after appropriate pretreatment to precipitate these contaminants. Precoat filters are simple to operate and are effective in removing cysts, algae, and asbestos.

Membrane filtration represents an important set of processes for drinking water treatment. A membrane is a thin layer of natural or synthetic material that can separate substances when a driving force is applied across the membrane. Membranes used for water treatment are commonly made of a synthetic organic polymer. Membrane processes applicable to potable water treatment are reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED), ultrafiltration (UF), and microfiltration (MF). Reverse osmosis is primarily used to remove salts from brackish water or seawater. Nanofiltration is used to soften freshwaters and remove disinfection byproduct (DBP) precursors. Electrodialysis is used to demineralize brackish water and seawater and to soften freshwater. Ultrafiltration and microfiltration are used to remove turbidity, pathogens, and other particulates from freshwater (Fig. 3).

Figure 3. Microfiltration (MF) system (*Source*: U.S. Filter).

Membranes are normally classified by solute exclusion size, which is sometimes referred to as *pore size*. Membrane filtration works by passing water at high pressure through a thin membrane in the form of hollow fiber or spiral-wound composite sheets. The contaminants are retained on the high-pressure side and frequently must be cleaned by reversing the flow and flushing the waste. Periodic chemical cleaning may be required to remove persistent contaminants. Membrane assemblies are contained in pressure vessels or cartridges. Low-pressure membranes, in the form of either ultrafiltration (UF) or microfiltration (MF), have become more economical in both capital and operating costs and have received increased attention in drinking water applications. Fouling of the membrane is the major problem preventing widespread use of this technology.

Cartridge filters traditionally have been applied to point-of-use systems and for pretreatment prior to membrane treatment systems. Composed of membrane, fabric, or string filter media, the filter material is supported by a filter element and housed in a pressure vessel. The application of cartridge filters using either a cleanable ceramic or disposable polypropylene cartridge seems to be a feasible method for removing modest levels of turbidity, algae, and microbiological contaminants. As water is filtered through a cartridge filter, the pressure drop increases, which necessitates terminating the filter run. When this process is done, the filter is not backwashed, but rather the cartridge is thrown away and replaced by a clean filter.

The desire to reduce costs or to treat some waters more effectively is driving the development of new technologies involving filtration. Several examples of such proprietary filters include low-head continuous backwash filters, two-stage filtration systems, bag filters, moving media filters, and flotation and filtration systems.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, Inc., New York, NY.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, Inc., New York, NY.

HDR, Inc. (2001). *Handbook of Public Water System*, 2nd Edn. John Wiley & Sons, New York, NY.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold Company, New York, NY.

Kawamura, S. (2000) *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York, NY.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000). *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

FILTRATION WITH GRANULAR MEDIA

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REGULATORY REQUIREMENTS FOR DRINKING WATER FILTRATION

The U.S. Environmental Protection Agency's (USEPA) Surface Water Treatment Rule (SWTR), promulgated on June 29, 1989 (Federal Register 40 CFR Parts 140 and 141), requires community water systems to disinfect all surface waters and requires filtration for most surface water sources. The 1998 Interim Enhanced Surface Water Treatment Rule (IESWTR) requires that surface water or groundwater systems under the influence of surface waters must produce a turbidity of less than or equal to 0.3 NTU in 95% of measurements taken each month. This rule was later extended to smaller systems as part of the Long Term Enhanced Surface Water Treatment Rule (LTESWTR).

FILTRATION HYDRAULICS

Pressure drop (i.e., head loss) occurs when water flows through a bed of a clean medium. The head loss caused by water flowing through a filter medium can be calculated from well-known equations such as the Kozeny equation. At the velocities commonly employed in granular water filters, flow is normally laminar. Initial head losses in clean filters commonly range from less than 1 to 2.5 ft, depending on the particle size distribution of the medium and the overflow rate (flow/filter surface area). The error in the head loss equation increases at flow rates used for filter backwashing where calculations show that the Reynolds number of particles lies in the transitional range. The most commonly used expression to calculate these head losses is the two-term Ergun equation, which applies to all regimes of flow. The flow through the underdrain system and effluent pipes is frequently turbulent. Negative head (less than atmospheric pressure) can occur in a gravity filter when the summation of head loss from the filter medium surface downward exceeds the pressure available.

PARTICLE REMOVAL MECHANISMS DURING FILTRATION

Filtration consists of three principal mechanisms: (1) transport, (2) attachment, and (3) detachment. *Transport* mechanisms move a particle into and through a filter pore so that it comes very close to the surface of the filter medium or existing deposits where *attachment* mechanisms retain the suspended particle in contact with the medium's surface or with previously deposited solids. *Detachment* mechanisms result from the hydrodynamic forces of the flow acting so that a certain portion of the previously attached particles, less strongly adhered to others, is detached from the filter medium or previous deposits and is carried further, deep into or through the filter. Important transport mechanisms include screening, interception, inertial forces, sedimentation, diffusion, and hydrodynamic forces. Physicochemical and molecular forces generally govern attachment of particles to media surfaces. Detachment is caused by the impact of arriving particles on unstable deposits and by hydraulic shear stresses without the influence of arriving particles.

TYPES OF FILTER MEDIA AND PROPERTIES

The most common types of filter media used in granular bed filters are silica sand, anthracite coal, and garnet. These media may be used alone or in dual- or triple-media combinations. Granular-activated carbon (GAC), another type of medium, has been used in granular beds for both filtration and adsorption to reduce taste and odor. A number of properties of a filter medium are important in filtration performance and in characterizing the medium. Important media properties include size, shape, density, and hardness. The porosity of the granular bed formed by the grains is also an important governing factor in filtration performance. Selection of filter media type and characteristics is based on a number of design decisions concerning source water quality, pretreatment, and desired filtered water quality. Filter media cleaning requirements and underdrain system options depend on the filter configuration and filter medium selected. Pilot plant studies using alternative filter media and filtration rates can determine the most effective and efficient medium for a particular water.

FILTER CLASSIFICATION

Several different types of filters are based on various classification schemes. Filters can be classified by type of media (single media, dual media), hydraulic arrangement (gravity or pressure), rate of filtration (rapid or slow), or depth of solids removal (deep or cake).

Slow Sand Filters

A slow sand filter generally consists of a watertight basin containing a layer of sand over a layer of gravel. It is operated at very low filtration rates without coagulation in pretreatment. Smaller grain size and lower filtration rate remove the solids almost entirely in a thin layer on top of the sand bed. This layer, composed of dirt and living and alum appeared to have a negative impact on plant performance. There was a large amount of floc deposited throughout the plant, including in the in-plant reservoir. Post-precipitation of floc after the filters because of alum overdosing was evident on at least one occasion.

Clarification. The general performance goal of a settling tank preceded by chemical coagulation is that its effluent (settled water) must have turbidity of less than 5 NTU (17). This protects subsequent sand filtration processes against high loads of suspended solids, preventing turbidity breakthrough and/or short filter runs. However, the clarified water turbidities measured in the AWTP during the study period were found to range between 8.5 and 17.9 NTU. During the plant inspections, it was noted that the flow splitter was not being operated correctly: Gate valves downstream of the overflow weirs had been set so that one of the three weirs was submerged. An uneven flow split may have contributed to poor clarifier performance; however, the major problem appeared to be overdosing with lime and alum. Clarifiers were usually manually desludged twice a week. No written procedures or records for desludging existed.

Filtration. For efficient disinfection, WHO guidelines (17) for potable water production state that the filtrate must have turbidity of <1 NTU because high turbidities exert high disinfectant demands, and particles may shield micro-organisms from disinfectants. However, the average filtered water turbidity recorded from October 2002 to January 2003 was greater than 1 NTU (Fig. 1). When alum and lime were used, poor filter performance was sometimes linked to post-precipitation of alum floc. However, switching to Ultra-floc did not have a positive effect on filtrate quality. The small improvement in filtrate turbidity in December and January is not necessarily attributable to the change in coagulant because the raw water turbidity decreased at the same time. Filtration rates of ~ 2–4 m/h were recorded during the evaluation of the AWTP, which are conservative rates for rapid sand filtration and should not have unduly challenged the filter performance if pretreatment had been adequate. Apart from inadequate pretreatment, the most common source of problems in rapid filtration is inadequate backwashing. Valveless filters are designed to backwash automatically when a specific headloss across the filter media is developed. Their chief advantage and the reason they are a popular choice for small treatment plants is that they backwash without any operator intervention. Important disadvantages include the following (18): (a) no auxiliary backwash is used, so cleaning is relatively inefficient; and (b) slow headloss development may result in excessively long run times, which could, in turn, lead to mudballing problems. The recommended maximum run length is 24 hours. No records of filter backwash were kept at the AWTP, but the filters appeared to go for days without backwashing. This may have been attributable to low filtration rates and poor coagulation.

Table 2. Estimating Alum and Lime Consumption and Costs According to Onsite Measurements

	Alum		Lime	
Flow (mL/d)	Consumption (Kg/d)	Dosage (mg/L)	Consumption (Kg/d)	Dosage (mg/L)
2.75	172	63	42	15
2.75	224	82	27	10
3.41	184	54	42	12
4.17	192	46	45	11
Average Consumption (kg/d)	**193**	**61**	**39**	**12**
Average cost per year for alum and lime				
	R 135 255.00		**17 082.00**	

Inspection of a filter bed directly after manual backwash revealed that the filter media was in a fairly good state, except at the edges of the filter, where it had built up against the filter walls and where a number of mudballs were found, which indicates poor flow distribution adjacent to the walls. The media away from the walls appeared to be clean except for a few millimeters of sludge on the top surface of the bed (typical of filters backwashed without auxiliary backwash). An analysis of the filter effluent turbidity immediately after a manual backwashing revealed very high values (27.5–39 NTU); thereafter a gradual decrease in the turbidity was noted within 4 h (2.33–3.44 NTU) and 6 h (1.98–2.02 NTU). These high turbidities indicated that the volume of backwash was insufficient to flush out all of the floc detached during backwashing.

Disinfection. The chlorine dose rate was manually controlled and set using a rotameter housed in the chlorination room. Like the coagulant doses, the chlorine dose was not ratioed to the plant flow rate. Furthermore, no attempt was made to match the dose to the chlorine demand. During the preliminary plant visits, the dosing rate was set at 100 g/h Cl_2, which translated into applied chlorine doses of 0.6 to 1.3 mg/L at plant flow rates of 2.75–3.97 mL/d. Given the poor quality of the filtrate, these doses were insufficient to establish an adequate residual. It was also noted that a substantial amount of floc had settled in the contact chambers, which could also lead to high consumption of the disinfectant. The dosing rate was subsequently increased to 400 g/h without any improvement in dosing control. Water samples collected at the point of treatment (in-plant reservoir) showed that the free chlorine residual values ranged from 0 to 1.14 mg/L for the period of 5 months. Figure 2 shows the average

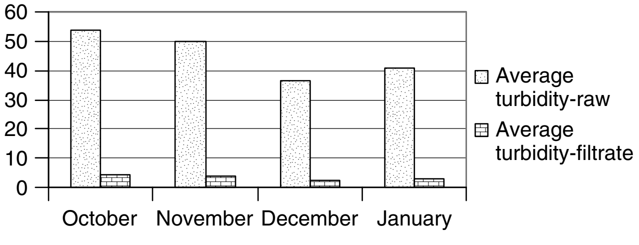

Figure 1. Performance of AWTP for the removal of the turbidity (NTU).

and dead micro- and macro-organisms from the water, is called *schmutzdecke* or dirty skin. Most solid removals in a slow sand filter take place in the *schmutzdecke* layer. The dominant removal mechanisms are both physical and biological. A typical filter cycle may vary from 1 to 6 months (or longer) depending on the source water quality and the filtration rate. Filtration rates range from 0.016 to 0.16 gpm/sq ft (0.04 to 0.40 m/h). Effective sand sizes range from 0.15 to 0.40 mm, sand uniformity coefficients from 1.5 to 3.6, and initial bed depths from 1.5 to 5.0 ft. The sand is supported on graded gravel 6 to 36 inches deep. Slow sand filters are cleaned by scraping *schmutzdecke* and a small amount of sand depth. Usually scraping is done manually but, in some cases, mechanically. The scraped sand is cleaned hydraulically and stockpiled for later reuse.

Rapid Granular Bed Filters

Rapid granular bed filtration consists of passing of pretreated water through a granular bed at rates ranging from 2 to 10 gpm/sq ft (5 to 25 m/h). Flow is typically downward through the bed. During the filtration cycle, solids are removed from the water and accumulate within the voids and on the top surface of the filter medium. This accumulation results in clogging and a gradual increase in head loss. When head loss becomes excessive (generally 8–9 ft), filtrate quality begins to deteriorate, and/or filter cycle reaches a predetermined time limit (usually 3 or 4 days), then rapid filters need cleaning. Dirty/clogged filters may be cleaned by scouring the clogged portion or by reversing the flow through the bed. This application of expanding and washing out trapped particles is called backwashing. Backwashing by water fluidization is frequently assisted by a surface wash or an air scour. The most effective backwash is achieved by simultaneous air scour and subfluidization water backwash. Typical backwash rates range from 15 to 23 gpm/sq ft depending on media sizes. The bed expansion varies from 20% to 50%. The backwash usually lasts from 5 to 15 minutes. The air-scour rate varies from 2 to 4 cu ft/min/sq ft (0.6 to 1.2 cu meter/min/sq meter) (Fig. 1).

Filter Underdrain Systems

Underdrain systems are used to support the filter medium, collect filtered water (in downflow filters), and distribute backwash water (and air, if employed). Four basic types of underdrain systems are commonly used: pipe laterals, blocks, false bottom, and porous bottom. Pipe underdrain systems generally consist of a centrally located pipe to which are attached smaller, equally spaced laterals. The lateral pipes usually have one or two rows of less than one-inch diameter perforations on their bottom sides. The lateral pipes may be fitted with nozzles. The blocks are self-supporting type underdrains. The block underdrain consists of vitrified clay blocks with one-fourth inch diameter dispersion orifices across the top of each block. Support gravel is typically used with this type of underdrain. As a replacement for support gravel, an integral media support (IMS) cap made of plastic beads sintered together may be installed. False-bottom underdrains are made of precast or cast-in-place reinforced concrete supported on concrete sills. This underdrain system consists of uniformly spaced inverted pyramidal depressions. Unglazed porcelain spheres are placed in the depressions to distribute flow. Porous-bottom underdrains constructed of porous aluminum oxide plates have been used in both block and false-bottom configurations. These types of underdrains are constructed of plates mounted on

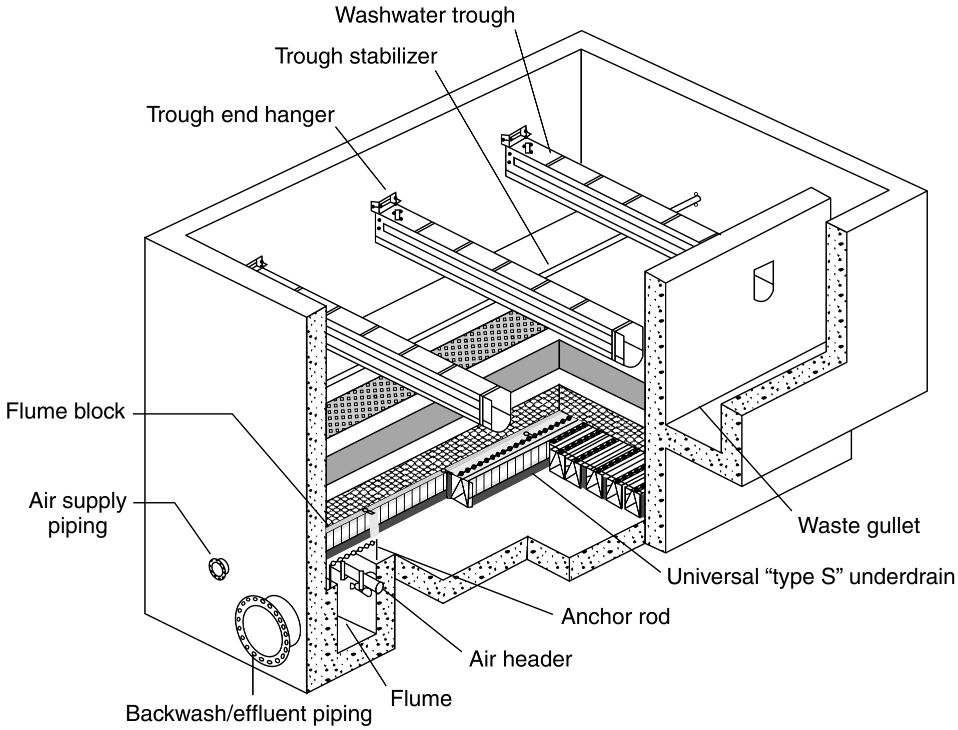

Figure 1. Rapid gravity filter box (*Source*: F.B. Leopold Co.).

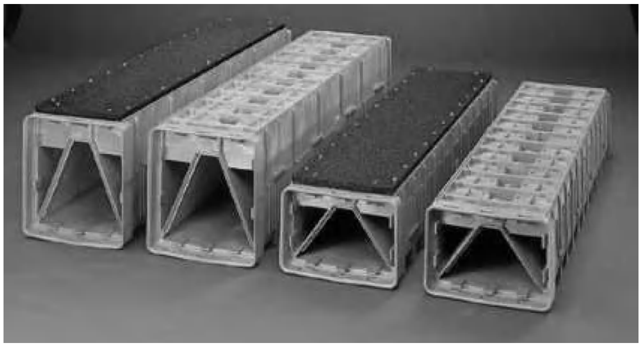

Figure 2. Filter underdrain (*Source*: F. B. Leopold Co.).

concrete or steel piers or on clay tile saddles to form blocks (Fig. 2).

FILTER OPERATION AND CONTROL

The efficiency of a filter is more sensitive to changes in the filtration rate rather than in the actual rate. Therefore, filtration process control is critical to successful operation. Two basic modes of gravity filter control are commonly found: constant rate and declining rate. Constant-rate mode operation of a filter can be achieved in three ways: (1) use of a flow control valve in the filtered water piping; (2) influent flow splitting where the water level over the filter is maintained at a constant level; and (3) influent flow splitting where the water level varies during the filter run. Declining-rate filters, which are most widely designed, are equipped with effluent weirs rather than with rate controllers. Flow is distributed on the basis of the relative conditions of the beds. Common filter problems include inadequate pretreatment or filter washing, gravel bed upset, air binding, restart after shut down, and filter media replacement. These problems lead to operational difficulties like dirty filter media, mudballs, and mineral deposits.

INNOVATIONS IN GRANULAR FILTRATION TECHNOLOGIES

In recent years, direct filtration has received considerable attention and application in treating of drinking water. Direct filtration is not preceded by sedimentation. It offers several advantages over conventional treatment of “good-quality” surface water. Because there is no sedimentation process and a lower coagulant dose, the capital and operating costs are lower compared with those of conventional treatment. Sludge volumes are lower, which results in lower chemical costs for sludge treatment and disposal. Because of increased interest in ozone application in potable water, biological filtration has received noticeable attention and application in recent years. Granular filters become biologically active when ozone is used as a preoxidant. Ozone reacts with organic compounds in water and forms several ozonation byproducts such as aldehydes, carboxylic acids, and keto acids, which are relatively easy to biodegrade. By operating filters in a biological mode, these ozonation byproducts can be effectively removed and in turn reduce the potential for bacterial regrowth in distribution systems and formation of chlorination byproducts. The desire to reduce costs or to treat some waters more effectively is driving the development of new technologies for filtration. Several examples of such proprietary filters include low-head continuous backwash filters, two-stage filtration systems, bag and cartridge filters, moving media filters, and flotation and filtration systems.

SLOW SAND FILTRATION AND THE IMPACT OF *SCHMUTZDECKE*

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INTRODUCTION

The use of sand media to filter drinking water dates to the early nineteenth century; installations in Paisley and Greenock, Scotland are the earliest known successful uses of the technology. The European cholera epidemic of the early 1890s proved conclusively the benefits of filtered water supplies to the health of urban populations (1). Current construction of slow sand filter systems are based on the design refined by Simpson for the London-area Chelsea Water Company in 1829 (2).

Rural areas are the primary benefactors of slow sand technology due to the passive nature of the treatment process and the availability of large tracts of land necessary for filter construction. The lack of a need for constant pumping to maintain the filtration rate through the filter, the ease of operation, and the possibility of using nonmechanical maintenance procedures make slow sand filtration an appropriate technology for small and rural communities (3).

SLOW SAND FILTERS

The source water flows by gravity through the filter column. The supernatant level can be kept constant as the effluent flow rate declines with head loss in the sand media, or the influent may be adjusted for constant flow while the supernatant level rises. The water flows through a layer of sand (0.5–1.0 m), travels through a layer of larger gravel (0.3–0.6 m), and flows out from a perforated pipe or tile underdrain collection grid to the treated water storage and distribution system (Fig. 1).

During slow sand filtration, biomass forms at the sand/water interface (*schmutzdecke*) that provides an effective layer for removing pathogenic micro-organisms. The biomass is formed from populations of algae, diatoms, protozoa, rotifers, and bacteria (4). Also present are extracellular polysaccharides exuded by microbial populations inherent in surface water sources (5), and this polymer formation has been suggested as a source of destabilization for bacteria and clay entering the filter (6).

The importance of *schmutzdecke* on overall filter performance is illustrated by removing it when scraping

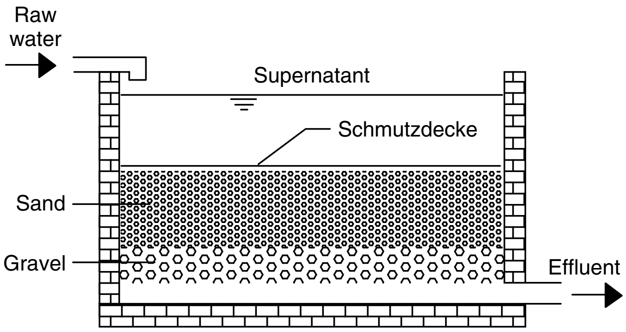

Figure 1. Schematic of a common slow sand filter design.

the top centimeter of media during maintenance; this immediately lessens the head loss caused by biomass growth and returns the flow rate to design levels (0.1–0.2 $m^3/m^2/h$). After removing the *schmutzdecke*, a ripening period is required to allow new biomass to mature. Effluent is wasted until turbidity and biological criteria are within established limits because influent contaminant removal is diminished during the filter ripening period. Efficient filter ripening can be altered by factors such as ambient and source water temperature, aquatic bacterial populations, and available source water nutrient supply (4).

The combination of biological and physical removal mechanisms in slow sand filters, uninterrupted use of slow sand filters during the 2–18-month filtration cycle, proper filter design, and the diligence of operating personnel produces drinking water of excellent quality (Table 1) from raw water sources with low turbidity (7). Source water quality is an important design consideration when communities consider slow sand filtration as a treatment method. The recommended influent turbidity limit for optimum slow sand filter operation is less than 10 nephelometric turbidity units (NTU), and many designers consider source water that regularly exceeds this limit unacceptable for slow sand filter treatment (8). Raw water sources that occasionally exceed turbidity limits are also regarded with apprehension unless the slow sand filter is augmented by a pretreatment method that reduces influent turbidity. Passive pretreatment systems (multistage filtration) that are effective and inexpensive to operate have been developed to mitigate many slow sand filtration deficiencies.

Table 1. Common Treatment Performance of Slow Sand Filters

Parameter	Removal
Color	30–100%
Turbidity	>90%
Fecal coliform	1–3 log units
Total organic carbon	15–25%
Trihalomethane precursors	<25%
Enteric viruses	2–4 log units
Giardia cysts	2–4 log units
Organic matter	60–75% as COD
Heavy metals	30–95%

Research continues toward better understanding of the biological and physical treatment mechanisms of slow sand filtration (9). Combining basic research on solids penetration (10), pathogen removal (11), and computer modeling (12,13) with operational modifications of sand media (14), filtration rates (15), maintenance and cleaning (16), and corrosion control amendments (17) have led to a substantial increase in the understanding and application of slow sand filtration.

SUMMARY

Slow sand filtration is one of the oldest drinking water treatment techniques and is still a viable method of biological water treatment best suited for raw water sources low in turbidity and suspended solids.

BIBLIOGRAPHY

1. Hazen, A. (1913). *The Filtration of Public Water Supplies*, 3rd Edn. John Wiley & Sons, New York.
2. Baker, M. (1948). *The Quest for Pure Water: The History of Water Purification From the Earliest Records to the Twentieth Century*. AWWA, Denver, CO.
3. Visscher, J., Paramasivam, R., Raman, A., and Heijen, H. (1987). *Slow Sand Filtration for Community Water Supply, Planning, Design, Construction, Operation, and Maintenance.* Technical Paper 24, International Water Centre, The Hague, the Netherlands.
4. Huisman, L. and Wood, W. (1974). *Slow Sand Filtration*. World Health Organization, Geneva, Switzerland.
5. Cunningham, A., Characklis, W., Aberdeen, F., and Crawford, D. (1991). Influence of biofilm accumulation on porous media and hydrodynamics. *Environ. Sci. Technol.* **25**: 1305–1311.
6. Bellamy, W., Silverman, G., and Hendricks, D. (1985). Filtration of *giardia* cysts and other substances. *Slow Sand Filtration*, Vol. 2, Report EPA/600/s2-85/026, USEPA.
7. AWWA/ASCE. (1998). *Water Treament Plant Design*, 3rd Edn. McGraw-Hill, New York.
8. AWWARF. (1991). *Manual of Design for Slow Sand Filtration*, D. Hendricks (Ed.). AWWARF and AWWA, Denver, CO.
9. Logsdon, G., Kohne, R., Abel, S., and LaBlonde, S. (2002). Slow sand filtration for small water systems. *J. Environ. Eng. Sci.* **1**: 339–348.
10. Ellis, K. and Aydin, M. (1995). Penetration of solids and biological activity into slow sand filters. *Water Res.* **29**(5): 1333–1341.
11. Calvo-Bado, L. et al. (2003). Spatial and temporal analysis of the microbial community in slow sand filters used for treating horticultural irrigation water. *Appl. Environ. Microbiol.* **69**(4): 2116–2125.
12. Ojha, C. and Graham, N. (1994). Computer-aided simulation of slow sand filter performance. *Water Res.* **28**(5): 1025–1030.
13. Rooklidge, S., Burns, E., and Bolte, J. (in press). Modeling antimicrobial contaminant removal in slow sand filtration. *Water Res.*
14. McMeen, C. and Benjamin, M. (1996). Removal of natural organic matter by slow sand filtration through iron-oxide-coated-olivine. In: *Advances in Slow Sand and Alternative Biological Filtration.* N. Graham and R. Collins (Eds.). John Wiley & Sons, West Sussex, England.

15. Van der Hoek, J., Bonne, P., Kors, L., and Te Welscer, R. (1996). Slow sand filtration: Effects of grain size and filtration rate on operation and performance. In: *Advances in Slow Sand and Alternative Biological Filtration*, N. Graham and R. Collins (Eds.). John Wiley & Sons, West Sussex, England.
16. Kors, L., Wind, A., and van der Hoek, J. (1996). Hydraulic and bacteriological performance affected by resanding, filtration rate and pretreatment. In: *Advances in Slow Sand and Alternative Biological Filtration*, N. Graham and R. Collins (Eds.). John Wiley & Sons, West Sussex, England.
17. Rooklidge, S. and Ketchum, L. (2002). Corrosion control enhancement from a dolomite-amended slow sand filter. *Water Res.* **36**(11): 2689–2694.

MULTISTAGE DRINKING WATER FILTRATION

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INTRODUCTION

Multistage drinking water filtration is a combination of roughing filter and slow sand filter unit processes that broadens the use of these passive treatment methods to include source water whose turbidity is higher than that normally suitable for biological filtration. Slow sand filtration is one of the oldest surface water treatment techniques, but it is easily compromised by source water with high turbidity caused by erosional or meteorologic events in the upstream watershed. By providing roughing filter pretreatment, suspended solids are decreased, and the biological integrity of the slow sand filter is maintained with a concomitant extension of the filtration period.

ROUGHING FILTER PRETREATMENT

Roughing filters are generally designed similarly to slow sand filters, except for larger media grain size and faster filtration rates. Roughing filters are usually composed of individual flow-through filter compartments that contain decreasing sizes of gravel in the direction of flow. The crushed gravel media in the roughing filter provide a large surface area for the flowing water to contact, allowing flocculation from particle collision in the circuitous route through the rock and sedimentation within the interstitial media voids. The addition of roughing filter pretreatment maintains the simplicity of slow sand filtration and achieves suspended solids and turbidity removal acceptable for drinking water.

DYNAMIC ROUGHING FILTERS

Passive filter systems in common use near rivers or canals include dynamic roughing filtration (Fig. 1). This design allows gravity flow from source water through a bed of crushed gravel (6 mm average diameter), and the overflow is wasted back to the river channel. A drawback of the design is the need to remove and clean the gravel media when the filter becomes clogged during high turbidity, and this limits dynamic filtration to raw water sources that experience turbidity peaks of less than a few hours in duration. The substantial filtration rate of 5 m/h in these filters is not designed to alter water quality of low turbidity, but instead it is intended to protect downstream filter systems from intermittent peaks of high solids concentrations, effectively shutting off the water supply as the filter medium clogs. These systems require immediate attention by operating personnel or the flow of water to the final filters will cease, and the resulting loss of supernatant in a slow sand filter may dry out the *schmutzdecke* and drastically reduce its filtration cycle.

VERTICAL ROUGHING FILTERS

Vertical-flow filtration can be used downstream of a dynamic filter to further increase solids removal and protect the slow sand filter from clogging. Modern designs use a minimum of three filter compartments; each subsequent compartment contains smaller sizes of gravel. Media size range from average diameters of 20 mm in the first compartment to 4 mm in the last, and they can operate in either upflow or downflow configurations (Fig. 2). The gravel media are submerged under a supernatant water level, and filtration rates vary from 0.3 to 1.0 m/h. Filter velocities between 0.1 and 0.8 m/h were tested on natural river water in Colombia with an average of 50 nephelometric turbidity units (NTU), and removal efficiencies were between 55% and 45%. Challenge experiments were conducted with turbidities greater than 200 NTU, and removal efficiencies ranged from 70% to 90% (1).

Upflow roughing filters are also equipped with decreasing sizes of gravel in the direction of water flow and have drainage chambers in each filter compartment to facilitate regular cleaning. Filter freeboard must be sufficient to produce gravity hydraulic flushing capable of flow velocities greater than 90 m/h (2). Galvis et al. (3) reported 97% suspended solids removal and 80% turbidity removal for raw water with average suspended solids of 100 mg/L and turbidity of 95 NTU.

HORIZONTAL ROUGHING FILTERS

Horizontal-flow roughing filtration has been a particularly successful pretreatment method for suspended solids removal in rural areas of developing nations that have limited availability of skilled operators (4). Raw water enters the filter by an intake weir and flows horizontally through decreasing sizes of media contained in separate

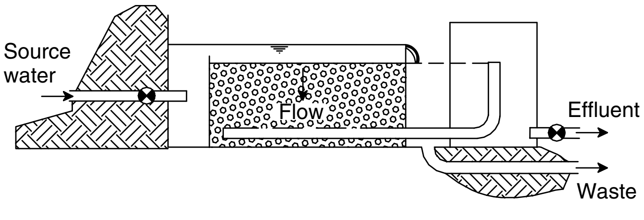

Figure 1. Example of a dynamic roughing filter design.

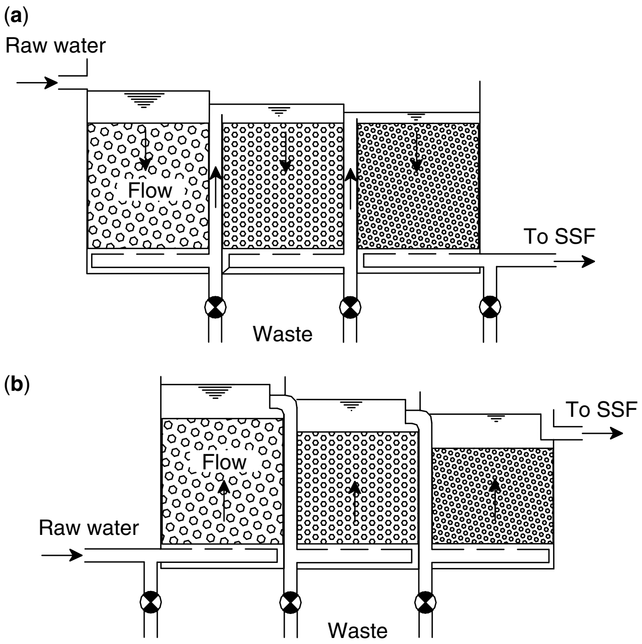

Figure 2. Schematic of downflow (**a**) and upflow (**b**) vertical roughing filters.

compartments (Fig. 3). Flow velocities range from 0.3 to 1.5 m/h, and the media size range and removal efficiencies are similar to vertical-flow filtration. Overall filter length ranges from 5 to 7 m with a filter compartment length ratio of 3:2:1. Typical media depth designs are less than 1 m to facilitate ease of media replacement, and drainage chambers are provided with the same freeboard and flushing velocities as vertical filters. The solids storage capacity for horizontal roughing filters is very large, and adequate filter service life can be years before clogging necessitates media removal (5).

DIRECT ROUGHING FILTRATION

The addition of coagulants to roughing filter influent is regarded as direct roughing filtration. Horizontal roughing filter coagulant injection of 1 mg (Al^{3+})/L as alum decreased raw water influent from 200 NTU to less than 3 NTU at filtration rates of 5–7 m/h (6). Coagulants cause roughing filters to clog much faster than normal (3–5 days), and cleaning process modifications must be designed before this type of treatment can be used reliably in the field. The addition of calcite limestone media in the first compartment of a horizontal roughing filter also aids coagulation, while maintaining the passive nature of the filter system. Source water with 150 NTU clay turbidity was reduced to less than 1 NTU by a limestone-amended multistage filter, and the effluent corrosion control characteristics of neutral pH source water were also enhanced by limestone roughing filter amendments (7).

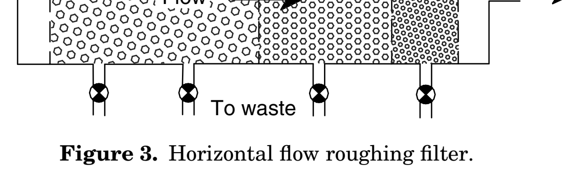

Figure 3. Horizontal flow roughing filter.

SUMMARY

Slow sand filtration is still a viable method of water treatment most suitable for raw water sources low in turbidity and suspended solids. Roughing filter pretreatment prior to slow sand filtration (multistage filtration) has been shown to be an efficient and effective drinking water treatment technique for source water with high turbidity, organic matter, and suspended solids.

BIBLIOGRAPHY

1. Galvis, G., Fernandez, J., and Visscher, J. (1993). Comparative study of different pre-treatment alternatives. *Aqua* **42**(6): 337–346.
2. Wolters, H., Smet, J., and Galvis, G. (1989). Upflow roughing filtration. *Pretreatment Methods for Community Water Supply: An Overview of Techniques and Present Experience*. IRC International Water Centre, The Hague, the Netherlands.
3. Galvis, G., Visscher, J., Fernandez, J., and Beron, F. (1996). *Pre-Treatment Alternatives for Drinking Water Supply Systems*. IRC International Water and Sanitation Centre, The Hague, Netherlands.
4. Wegelin, M. (1996). *Surface Water Treatment by Roughing Filters*. Swiss Centre for Development Cooperation in Technology and Management, Gallen, Switzerland.
5. Collins, M., Westersund, C., Cole, J., and Roccaro, J. (1994). *Evaluation of Roughing Filtration Design Variables*. AWWARF and AWWA, Denver, CO, pp. 77–88.
6. Ahsan, T., Alaerts, G., and Buiteman, J. (1996). Direct horizontal-flow roughing filtration. Part 1: Optimization of process parameters. *Aqua* **45**(5): 262–271.
7. Rooklidge, S. and Ketchum, L. (2002). Calcite-amended horizontal roughing filtration for clay turbidity removal. *J. Water Supply Res. Technol.-Aqua* **51**(6): 333–342.

MULTISTAGE FILTRATION: AN INNOVATIVE WATER TREATMENT TECHNOLOGY

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The technology of multiple stage filtration (MSF) presented here is a combination of coarse gravel prefiltration and slow sand filtration (SSF). This combination allows treating of surface water that has considerable levels of contamination, well above the levels that can be treated by SSF alone. To improve the performance of MSF, other treatment processes such as simple sedimentation, sand traps, and screens can precede MSF technology. Wherever possible, terminal disinfection needs to be included as a safety barrier after MSF.

MSF retains the advantages of SSF in that it is a robust and reliable treatment method that can be maintained by operators who have low levels of formal education. It is much better suited than conventional chemical water treatment to conditions in rural communities and small and medium size municipalities in the South as well as in more remote areas in the North. The article provides a summary description of the components of MSF systems and the findings of recent research. It gives an overview of cost implications and ends with a selection guide.

SELECTION OF MULTISTAGE FILTRATION CRITERIA

Factors for selecting the *best* surface water treatment include the quality of the water sources, the availability of resources (construction material, sand, gravel, chemicals, financial resources, and land), the socioeconomic and cultural conditions of the community, and the level of institutional support. Careful selection of the water treatment technology is crucial to ensuring sustained good quality water at an acceptable cost to users.

MSF alternatives include the dynamic roughing filtration (DyRF) step and SSF alone or in combination with other pretreatment steps. The most common are up-flow roughing filters in layers (URFL) or in series of two or three units (URFS2, URFS3) (see Fig. 1), down-flow roughing filters (DRF), or horizontal-flow roughing filters (HRF). A comparative study showed that URF is technically and economically preferable to DRF and HRF, although these also present good removal efficiencies (1).

The MSF alternatives are similar in their environmental impact and complexity of operation and maintenance. This implies that one can choose among them using three main selection criteria: the sanitary risk of the water source, the treatment efficiency, and the overall cost. Conventional treatment options such as rapid sand filtration of chemically coagulated water often face problems in managing the systems and availability of chemical products. MSF technology, on the other hand, is well received by communities because it is much simpler to administer, operate, and maintain compared to other treatment systems.

Slow Sand Filtration, the Heart of MSF

Slow sand filtration is the heart of MSF technology. It has been recognized as a simple, reliable, and efficient treatment technology and the most effective as a single unit treatment process. An SSF produces an effluent low in turbidity, free of impurities, and even more important, virtually free of bacteria, enteroviruses, and protozoa. Table 1 presents an overview of the removal efficiencies that may be obtained from SSF technology for different parameters of sanitary importance. These efficiencies have been reported for SSF units operating in temperature zones above 5 °C, at flow velocities between 0.04 and 0.20 m^3/m^2h, filter medium depths above 0.5 m, and effective sand grain sizes between 0.15 and 0.30 mm.

The use of SSF technology often has been determined by the availability of good raw quality water resources, as in different areas of Europe and the United State. However, SSF alone is not a feasible solution for more contaminated surface water sources. It is not a panacea for all water quality problems under all circumstances. In general, two situations can be distinguished under which SSF presents limitations.

- Levels of contamination in the raw water that supersede the treatment capacity to comply with the existing norms or that may result in short filter runs. This relates particularly to high quantities of suspended solids, high coliform counts, and large quantities of algae.
- Conditions that inhibit or reduce the efficiency of the treatment process such as low temperature, low nutrient content, and low oxygen level.

Coarse Gravel Filtration

For more contaminated surface water (i.e., turbidity levels higher then 20NTU), it is necessary to apply good pretreatment modalities to condition the water before it enters the SSF units. Commonly used pretreatment systems include simple sedimentation, microscreening, roughing filtration in gravel filters, and, more recently in Europe, also ozone and activated carbon treatment to reduce the levels of organic material.

In the last few decades, the prospect of using SSF technology in rural communities and small/medium size municipalities has increased because of good research

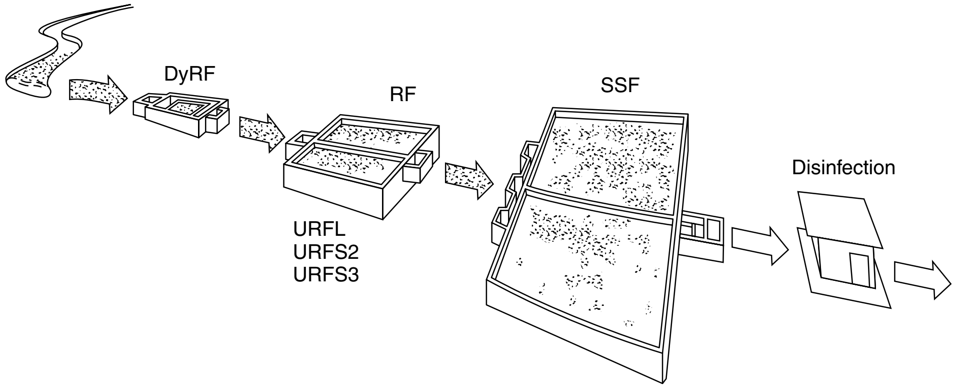

Figure 1. Components of a multistage filtration system.

Table 1. Typical Removal Efficiencies of Conventional SSF Units[a]

Water Quality Parameter	Effluent or Removal Efficiency	Comments
Turbidity	<1 NTU	The level of turbidity and the nature and distribution of particles affect treatment capacity and efficiency
Enterobacteria	90 to 99.9%	Affected by temperature, filtration rate, size, uniformity and depth of sand bed, cleaning operation
Enteroviruses and Giardia/Amoeba cysts	99 to 99.99%	High removal efficiencies, even directly after cleaning (removal of the biomembrane (schmutzdecke))
Cercariae	100%	In good operation and maintenance conditions, virtually complete removal is obtained
True color	25 to 30%	Color associated with organic material and humic acids
TOC	<15–25%	TOC, total organic carbon
AOC	<50%	AOC, biodegradable organic carbon
THM precursors	<25%	Precursors of trihalomethanes
Iron, manganese	30 to 90%	Fe^{2+} levels >1 mg/L reduce filter runs

[a] Reference 1.

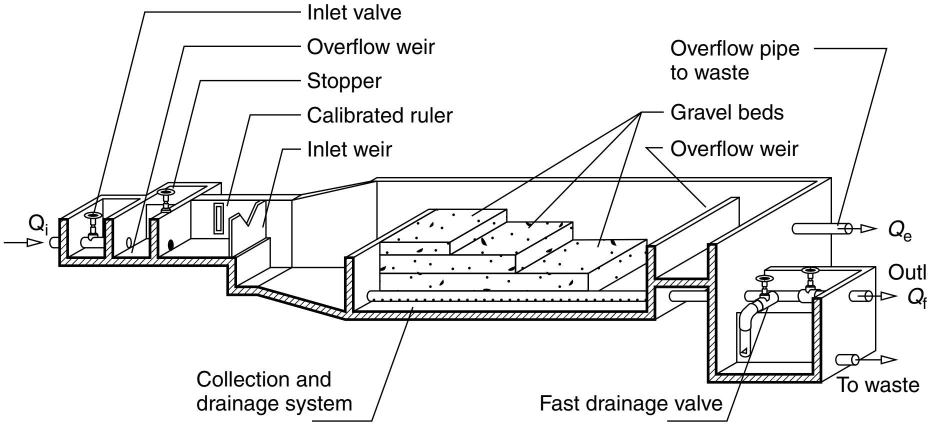

Figure 2. Dynamic roughing filter.

results in roughing filtration (coarse gravel filtration). An important breakthrough in research on pretreatment technology has come from comparative studies of different roughing filtration systems in Colombia (1). Both field testing and full-scale plants were included. The research concluded that for the conditions in Colombia, the combination of DyRF and URF proved to be the best pretreatment option prior to SSF.

PUTTING MSF IN PERSPECTIVE

MSF has advantages similar to SSF in ease of operation and maintenance and production of good water quality. Many rural communities and small/medium size municipalities face problems with conventional surface water treatment using chemicals. MSF technology is then a sustainable and effective treatment alternative (Table 2).

DESCRIPTION OF THE COMPONENTS OF ROUGHING FILTERS

MSF may consist of two or three main filtration stages, depending on the level of contamination of the source. The option with three components, DyRF, URF, and SSF, is indicated in (Fig. 1). In principle, DyRF focuses on reducing suspended solids, particularly removing larger particles and on protecting the subsequent units from high loads of suspended solids. The removal of smaller particles and microorganisms takes place primarily in the next treatment steps. URF can be avoided if good quality surface water is available.

Dynamic Roughing Filters (DyRF) contain a shallow layer of fine gravel in their upper part on top of a layer of coarse gravel that covers the underdrains (total height of the filter bed is about 0.6 m) (see Fig. 2). Water enters the unit and passes through a bed of fine gravel on top of coarse gravel to the drainage system at a filtration rate of some 2 to 3 m^3/m^2h. Moderate levels of suspended solids in the source gradually clog the DyRF. For high suspended solids, clogging happens very quickly. When the gravel bed is completely blocked, raw water will flow over the clogged surface area to waste. In this way, the DyRF acts as a safety valve, and subsequent treatment steps are protected from receiving high suspended solid loads.

Up-flow roughing filters consist of one or more compartments filled with gravel (diameter from 3–24 mm) that reduces in size in the direction of flow. Filtration rates usually range between 0.3 and 0.6 m^3/m^2h (see Fig. 3). A drainage system placed on the bottom of the structure distributes the flow during the filtration period or drains the gravel layers during periods of cleaning and discharges

Table 2. Summary of Considerations for MSF Treatment[a]

Issue	Comment Concerning MSF Treatment
Quality of treated water	It is a good alternative for improving the physical, chemical, and bacteriological quality of the water. In many areas and particularly those that have a less developed infrastructure, MSF may be the only feasible treatment option.
Ease of construction	The relatively simple design facilitates the use of local materials and local skilled manpower. There is no need for special equipment.
Construction cost	Construction in local materials and with local labor reduces the cost. Usually, there is no need for imported materials.
Ease of operation and maintenance	After a short period of training, local operators who have a minimum of formal education can operate and maintain the system.
Cost of operation and maintenance	The cost of operation and maintenance and the requirements in electrical energy are much less than for other systems. There is no need for chemical coagulation products.
Reliability	A low risk of mechanical problems or problems related to changes in raw water quality; in the majority of cases, these can be accommodated without interrupting service.
Cleaning	The cleaning process is simple although laborious but almost always involves low cost, as in most 'potential' countries, labor is relatively cheap.
Requirements of surface area	A conventional chemical and RSF water treatment may require surface areas comparable to an MSF treatment plant.
MSF, the panacea?	There are levels of contamination that interfere with the treatment or that surpass the capacity of MSF.

[a] Reference 1.

Table 3. Performance of MSF Systems in Colombia

Performance Indicator	Raw Water Quality	Efficiency Range	Remarks
Turbidity (NTU)	2–15 NTU and peaks over 180 NTU	83–97% <1 NTU in 65–98% of all samples <5 NTU in 98% of all samples	Lower figure was measured in older MSF system.
Suspended solids, mg/L	2–23 and peaks over 390	0.2–2.8 mg/L	
Fecal coliform density, CFU/100 mL	300–60,000	<25 CFU/100 mL in 97% of all samples	
True color, TCU	5–24 and peaks over 180	<15 TCU in 98% of all samples	
Filter run periods		46–178 days	A short filter run due to algae

the water through the drainage system. The impurities are retained at the bottom, and therefore, it is easy to drain. Two alternatives can be identified: up-flow roughing filters in layers (URFL) when the gravel layers of different size are installed in the same unit (total filter bed height 1.2 m) and up-flow roughing filters in series (URFS) when the gravel layers are installed in two or three different units (each filter bed is about 1.2 m high). (See Table 4.)

Downflow roughing filters in series (DRFS) consist of three compartments of gravel reducing in size (2). The performance of the DRFS is similar to that of the URFS in removal efficiency. Maintenance and cleaning are more difficult than for the URF because the sludge tends to accumulate on the surface and in the deeper layers of the bed.

Horizontal roughing filters (HRF) consist of three compartments separated by perforated walls (3). Their performance is similar to that of the URF, but construction costs are higher (1).

PERFORMANCE OF MSF SYSTEMS

MSF performance data (Table 3) are based on seven community-managed MSF systems in Colombia that were monitored for a 7 years. The systems receive water from catchment areas of low or moderate levels of human intervention.

Based on these effluent water qualities, constant dose disinfection with chlorine, as suggested by WHO (4), functions effectively as a final safety barrier.

The findings show that MSF treatment can adapt itself to the type of raw water and the concentration of contamination. The systems have higher removal efficiencies for water that is higher in contamination. This implies that the barriers become more effective if the water to be treated has a higher risk and still can produce a water at a low sanitary risk level. The results on both pilot and full scale clearly indicate the great potential of MSF technology in reducing the physicochemical and bacteriological risk from surface water sources. Nevertheless, it also shows that the technology is not a panacea and has its limitations. Particularly, for high levels of contamination, MSF systems do not always produce water that meets the required quality, and then extra pretreatment steps may be needed.

MSF systems comply with the multibarrier concept: in general, all treatment steps (barriers) together achieve a removal efficiency that is sufficient to ensure low dose disinfection as a final and efficient safety barrier.

The technology is a reliable alternative for treating water of a low or moderate contamination level such

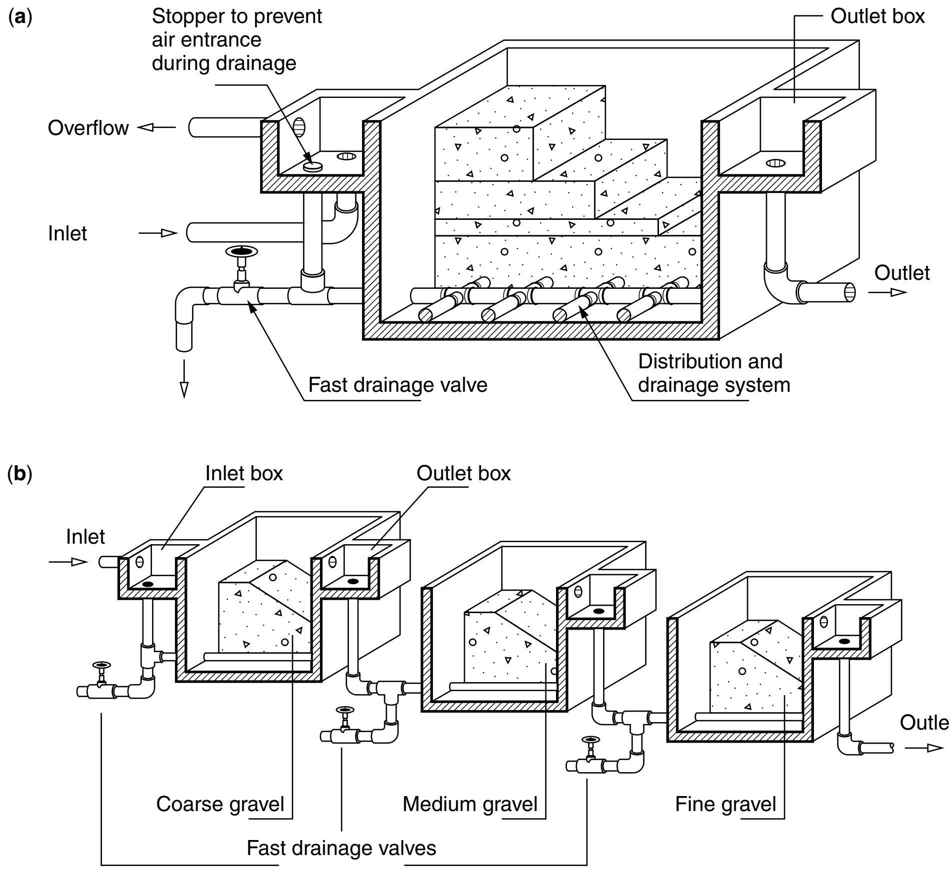

Figure 3. (**a**) Schematic design of an up-flow roughing filter in layers (URFL). (**b**) Schematic design of an up-flow filter in series (URFS).

Table 4. Design Criteria for the MSF Type Designs Used to Establish Construction Volumes for the Cost Model in (Fig. 3)

MSF Component Design Criteria	DyRF	URFL	URFS2	URFS3	SSF
Filtration rate (m^3/m^2h)	2	0.6	0.6	0.6	0.15
Depth of filter medium (m)	0.60	1.2	1.2[a]	1.2[a]	1.05
Filter box height (m)	0.80	1.4	1.4	1.4	2.15
Number of units in parallel	2	2–4	2–4	2–6	4–8
Number of units in series	1	1	2	3	1

[a] Per filter unit.

as received by full-scale plants. However, river water of higher contamination levels can present difficulties. For those conditions, it is essential to study the performance of the MSF system in a pilot plant, before deciding to construct a full-scale plant.

COST ISSUES

Construction costs vary by country. The economy of scale is limited, thus favoring relatively short design periods of some 10 years. Operating and maintenance costs have been estimated on the basis of experience with MSF systems in Colombia. In these plants that are operated under gravity supply, it was found that staff makes up 85% of the cost. Thus, the time involved in the different operating and maintenance tasks are a good basis for assessing the overall cost. The labor requirements for daily and periodic operation and maintenance of MSF systems range between 0.2 and 1.5 equivalent person days per day, depending on the size and composition of the systems. In addition 0.3 equivalent person days are needed for administration, including supervision of the plant operator, planning, customer relations, purchasing, payments, and meetings with sector organizations and local government.

For example, for a system of 10 L/s in Colombia that includes DyRF + URFS2 + SSF, the construction cost would amount to US$ 125,000. The total time required for operation and maintenance of this plant amounts to 1.6 PE (person equivalents per year), 1.0 PE for daily and periodic activities, 0.3 PE for exceptional activities, and 0.3 PE for administration. For 1996, at an average salary of US$150/ month and taking into account the 85% factor, operating and maintenance cost amounted to $(1.6\times150)/0.85 =$ US$ 276/ month.

TECHNOLOGY SELECTION GUIDE

On the basis of the previous considerations, the minimum treatment for surface water of *low sanitary risk*—but requiring more than just disinfection—is a combination of DyRF and SSF. Surface water of a *moderate risk level* requires a URFL or one of the URFS systems in combination with DyRF and SSF. For surface water sources of *high risk levels*, the options of URFS in two or three steps need to be considered in combination with DyRF and SSF.

The findings and design considerations are mainly based on research from Colombia. The biological treatment process involved in MSF technology is important but not easy to predict. In low temperature zones, the efficiencies are lower than indicated here. So, designing MSF under different climatic conditions needs a critical attitude toward design, function and performance. In regions with little experience with MSF technology and/or important uncertainties about the quality of the water sources, it is important to adopt conservative design parameters in the first MSF plants and preferably start with pilot plant experiments to review the functioning of MSF systems under local conditions. A joint learning program, as described by Visscher (5) is recommended. This type of program brings together communities, sector professionals, sector authorities, and other important institutions in the sector, including local universities and research institutions. Together, they review the situation and ensure that the technology can find roots in the new situation.

BIBLIOGRAPHY

1. Galvis, G., Latorre, J., and Visscher, J.T. (1998). *Multi-Stage Filtration, an Innovative Water Treatment Technology*. IRC Technical Paper Series no. 34, The Hague, The Netherlands, IRC International Water and Sanitation Centre; CINARA—Universidad del Valle, Cali, Colombia.
2. Pardon, M. (1987). *Consideraciones, Desarrollo y Evaluación de un Sistema de Tratamiento que Implementa la Filtración Gruesa de Flujo Vertical en Gravas*. Lima, Perú.
3. Wegelin, M. (1986). *Horizontal Flow Roughing Filtration (HRF) Design, Construction and Operation Manual IRCWD. Report No. 06/86.* Duebendorf, Switzerland.
4. WHO. (1996). *Guidelines for Drinking Water Quality: Health Criteria and other Supporting Information*, 2nd Edn. Vol. II. World Health Organization, Geneva, Switzerland.
5. Visscher, J.T. (Ed.). (1997). *Technology Transfer in the Water and Sanitation Sector: A Learning Experience from Colombia*. Technical Paper Series no. 32, The Hague, The Netherlands and CINARA, Cali, Colombia.

PARTICULATE MATTER REMOVAL BY FILTRATION AND SEDIMENTATION

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The settling efficiency for an ideal condition is independent of the depth and dependent on the tank plan or surface area. In reality, depth is important because it can affect flow stability if it is large and scouring if it is small. The basin depth affects flow-through velocity and allows greater opportunity for flocculant particle contact. Conventional settling facilities at larger water treatment plants are often long, narrow (4 or 5 to 1 length to width ratio) rectangular basins that have theoretical detention times in the range of 1.5 to 3 hours at the design flow rate. Most regulatory agencies specify a minimum detention time and a maximum surface overflow rate. Typical sedimentation surface loading rates for long, rectangular tanks and circular tanks using alum coagulation vary from 500 to 1200 gallon per day per square feet (20 to 48 cubic meters per day per square meter). Regulatory agencies sometimes stipulate that their weir rates should not exceed around 20,000 gallons per day per linear foot (250 cubic meters per day per meter) of weir. Flow-through velocities of 2 to 4 ft/min (0.6 to 1.2 m/min) are usually acceptable for basin depths of 7 to 14 ft (2.1 to 4.3 m).

Particulate matter will settle out of a suspension in one of four different ways, depending on the concentration of the suspension and the flocculating properties of the particles. The various settling regimes of particles are commonly referred to as types 1 to 4. In type 1 settling, also called discrete particle settling, particles have little tendency to flocculate upon contact with each other in a dilute suspension. If the particles flocculate, the settling regime in a dilute suspension is identified as type 2 or flocculant settling. In hindered, zone, or type 3 settling, the particle concentration causes interparticle effects, which might include flocculation, to the extent that the rate of settling is a function of solids concentration. Compression or type 4 settling develops under the layers of zone settling. The rate of compression depends on time and the force caused by the weight of solids above. In sedimentation, particulate matter removal is largely governed by types 1 and 2 settling. However, types 3 and 4 regimes are dominant in clarification and thickening processes.

High-rate settlers such as tube or plate settlers are often added to settling basins to improve their efficiency, especially if flows are to be increased beyond original design conditions. The shallow settling depths and the large surface area provided by tube or plate settlers permit effective sedimentation at detention times of several minutes versus several hours in conventional sedimentation basins. The use of tube or plate settlers in new plant construction minimizes settling basin costs by minimizing the basin size necessary to attain a desired level of treatment. They are generally designed to accept overflow rates ranging from 1400 to 4000 gallons per day per sq ft (55 to 160 cubic meters per day per square meter).

In a conventional water treatment process train, filtration follows sedimentation. Filtration is one of the unit processes used in the production of potable water. Particulate matter that is removed by this process includes micro-organisms (bacteria, viruses, and protozoan cysts), clay and silt particles, colloidal and precipitated humic substances and other organic particulates from natural decay of vegetation, precipitates of aluminum or iron coagulation processes, calcium carbonate and magnesium hydroxide precipitates from lime softening, and iron and manganese precipitates.

A number of different types of filters are used in water filtration, and they are described by various classification schemes. Most common filtration technologies used in water supply systems are rapid sand filtration, slow sand filtration, package plants, diatomaceous earth filtration (precoat filtration), membrane filters, and cartridge filters. High-rate granular filters or rapid sand filters are most widely used in conventional treatment and direct filtration. Slow sand filters have been used in water treatment for several decades, but their use in recent decades has declined because of the inherent low filtration rate, large area requirement, and difficulties in filter cleaning. Membrane and cartridge filtration systems are considered emerging technologies. In recent years, some water treatment plants have replaced granular filters with membrane filters. Package plants, slow sand, diatomaceous earth, membrane, and cartridge filters are considered best suited for small water systems [less than 0.44 cubic meter per s (10 MGD)].

Granular medium filtration is a water treatment process that uses a porous medium through which water passes to remove particulates or suspended solids. For granular medium filtration to be effective, pretreatment of source water is required. Chemical destabilization is an essential prerequisite for effective filtration. Chemicals used for particle destabilization are limited primarily to metal salts or cationic polymers as primary coagulants. Pretreatment may also include aeration or introducing an oxidant if water treatment aims to remove iron or manganese. Sometimes a filter aid polymer is added in the influent to the filter to improve particle capture efficiency.

The U.S. Environmental Protection Agency's (USEPA) Surface Water Treatment Rule (SWTR), promulgated on June 29, 1989 (Federal Register 40 CFR Parts 140 and 141), requires community water systems to disinfect all surface waters and requires filtration for most surface water sources. The 1998 Interim Enhanced Surface Water Treatment Rule (IESWTR) requires that surface water or groundwater systems under the influence of surface waters must produce a turbidity less than or equal to 0.3 NTU in 95% of the measurements taken each month. This rule was later extended to smaller systems as part of the Long Term Enhanced Surface Water Treatment Rule (LTESWTR).

Filtration by granular media consists of three principal mechanisms: (1) transport, (2) attachment, and (3) detachment. *Transport* mechanisms move a particle into and through a filter pore so that it comes very close to the surface of the filter medium or existing deposits where *attachment* mechanisms retain the suspended particle in contact with the medium's surface or with previously deposited solids. *Detachment* mechanisms result from the hydrodynamic forces of flow acting so that a certain portion of the previously attached particles, less strongly adhered to others, is detached from the filter medium or previous deposits and is carried further, deep into or through the filter. Important transport mechanisms include screening, interception, inertial forces, sedimentation, diffusion, and hydrodynamic forces. Attachment of particles to the media surfaces is generally governed by physicochemical and molecular forces. Detachment is caused by the impact of arriving particles on unstable deposits and by hydraulic shear stresses without the influence of arriving particles.

The most common types of filter media used in granular bed filters are silica sand, anthracite coal, and garnet. These may be used alone or in dual- or triple-media combinations. Granular-activated carbon (GAC), another type of medium, has been used to reduce taste and odor in granular beds that serve for both filtration and adsorption. A number of properties of a filter medium affect filtration performance and are important in characterizing the medium. Important media properties include size, shape, density, and hardness. The porosity of the granular bed formed by the grains is also an important governing factor in filtration performance. Selection of filter media type and characteristics is based on a number of design decisions concerning source water quality, pretreatment, and desired filtered water quality. Filter media cleaning requirements and underdrain system options depend on filter configuration and filter media selected. Pilot plant studies using alternative filter media and filtration rates can determine the most effective and efficient medium for a particular water.

A slow sand filter generally consists of a watertight basin containing a layer of sand over a layer of gravel. It is operated at very low filtration rates without coagulation in pretreatment. Smaller grain size and lower filtration rate result in removing the solids almost entirely in a thin layer on the top of the sand bed. This layer, composed of dirt and living and dead micro- and macro-organisms from the water, is called *schmutzdecke* or dirty skin. Most of the solid removal in a slow sand filter takes place in the *schmutzdecke* layer. The dominant removal mechanisms are both physical and biological. A typical filter cycle length may vary from 1 to 6 months (or longer) depending on source water quality and filtration rate. Filtration rates range from 0.016 to 0.16 gpm/sq ft (0.04 to 0.40 m/h). Effective sand sizes range from 0.15 to 0.40 mm, sand uniformity coefficients from 1.5 to 3.6, and initial bed depths from 1.5 to 5.0 ft. The sand is supported on graded gravel 6 to 36 inches deep. Slow sand filters are cleaned by scraping the *schmutzdecke* and a small amount of sand depth. Usually, scraping is done manually but, in some cases, mechanically. The scraped sand is cleaned hydraulically and stockpiled for later reuse. Slow sand filters are very effective in removing turbidity, viruses, and bacteria.

Rapid granular bed filtration consists of passing pretreated water through a granular bed at rates ranging from 2 to 10 gpm/sq ft (5 to 25 m/h). Flow is typically downward through the bed. During the filtration cycle, solids are removed from the water and accumulate within the voids and on the top surface of the filter medium. This accumulation results in clogging and a gradual increase in head loss. When head loss becomes excessive (generally 8–9 ft), filtrate quality begins to deteriorate, and/or the filter cycle reaches a predetermined time limit (usually 3 or 4 days), then rapid filters need cleaning. Dirty/clogged filters may be cleared by scouring the clogged portion or by reversing the flow through the bed. This application of expanding and washing out trapped particles is called backwashing. Backwashing by water fluidization is frequently assisted by a surface wash or an air scour. The most effective backwash is achieved by simultaneous air scour and subfluidization water backwash. Typical backwash rates range from 15 to 23 gpm/sq ft depending on media sizes. The bed expansion varies from 20% to 50%. The backwash usually lasts from 5 to 15 minutes. The air-scour rate varies from 2 to 4 cu ft/min/sq ft (0.6 to 1.2 cu meter/min/sq meter). Underdrain systems are used to support the filter medium, collect filtered water (in downflow filters), and distribute backwash water (and air, if employed). The efficiency of a filter is more sensitive to changes in the filtration rate rather than in the actual rate. Therefore, filtration process control is critical to successful operation. Two basic modes of gravity filter control are commonly found, constant rate and declining rate. Common filter problems include inadequate pretreatment or filter washing, gravel bed upset, air binding, restart after shut down, and filter media replacement. These problems lead to operational difficulties like dirty filter media, mud balls, and mineral deposits. Rapid gravity filters that use coagulation and sedimentation normally have 96.9% to 99.9% bacterial and 99.0% virus removal efficiencies. It is not uncommon for a well-operated filter to produce an effluent turbidity of 0.1 NTU (nephelometric turbidity units).

Precoat filters use a thin layer of very fine material such as diatomaceous earth as a filter medium. In precoat filtration, water to be filtered is passed through a uniform layer of the filter medium that has been deposited (precoated) on a *septum*, a permeable material that supports the filter medium. The filter operation is composed of three cycles: (1) precoating, (2) filtering, and (3) cleaning. When the pressure drop through the filter system reaches a point where continued filtration is impractical, the filtration process is stopped. The filter medium and collected dirt are washed off the septum, a new precoat of filter medium is applied, and filtration continues. Diatomaceous filters are effective in removing cysts, algae, and asbestos. These filters are especially suited for low influent turbidity water and are very effective against *Giardia* cysts.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, Inc., New York, NY.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*, American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, Inc., New York, NY.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold Company, New York, NY.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*, John Wiley & Sons, New York, NY.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000). *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

FILTRATION WATER TREATMENT

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All filtration technologies have the same basic objectives: to produce a filtrate that is clear and contains very few particles and to provide a medium-cleaning process so that operation may be continued with the same medium or by replacing the old medium. Particulates that are removed by water filtration process include micro-organisms (bacteria, viruses, and protozoan cysts), clay and silt particles, colloidal and precipitated humic substances and other organic particulates from natural decay of vegetation, precipitates of an aluminum or iron coagulation process, calcium carbonate and magnesium hydroxide precipitates from lime softening, and iron and manganese precipitates.

Rapid gravity filtration consists of passing pretreated water through a granular bed at rates ranging from 2 to 10 gpm/sq ft (5 to 25 m/h) (Fig. 1). Flow is typically downward through the bed. During the filtration cycle, solids are removed from the water and accumulate within the voids and on the top surface of the filter medium. This accumulation results in clogging and a gradual increase in head loss. When head loss becomes excessive (generally 8–9 ft), filtrate quality begins to deteriorate,

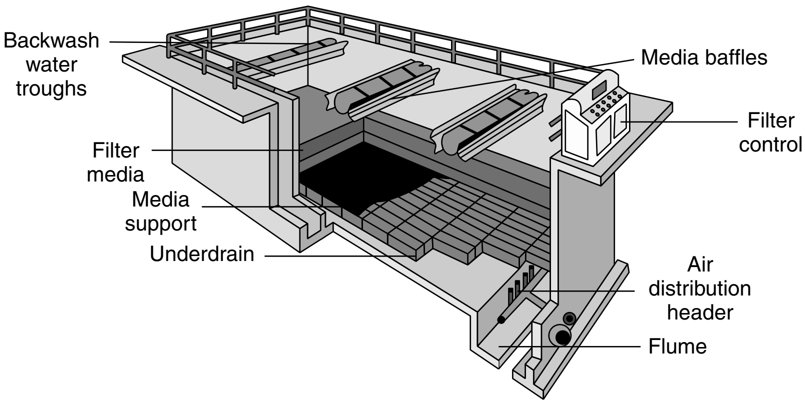

Figure 1. Rapid gravity filter (*Source*: F.B. Leopold Company).

and/or the filter cycle reaches a predetermined time limit (usually 3 or 4 days), then rapid filters need cleaning. Dirty/clogged filters may be cleaned by scouring the clogged portion or by reversing the flow through the bed. This application of expanding and washing out trapped particles is called backwashing. Backwashing by water fluidization is frequently assisted by a surface wash or an air scour. The most effective backwash is achieved by a simultaneous air scour and subfluidization water backwash. Typical backwash rates range from 15 to 23 gpm/sq ft depending on media sizes. The bed expansion varies from 20% to 50%. The backwash duration usually lasts from 5 to 15 minutes. The air-scour rate varies from 2 to 4 cu ft/min/sq ft (0.6 to 1.2 cu meter/min/sq meter).

For rapid gravity filtration to be effective, the source water must be pretreated. Chemical destabilization is an essential prerequisite for effective filtration. Chemicals used for particle destabilization are limited primarily to metal salts or cationic polymers as primary coagulants. Pretreatment may also include aeration or introducing an oxidant if water treatment aims to remove iron or manganese. Sometimes a filter aid polymer is added in the influent to the filter to improve particle capture efficiency. Granular bed filtration consists of three principal mechanisms: (1) transport, (2) attachment, and (3) detachment. *Transport* mechanisms move a particle into and through a filter pore so that it comes very close to the surface of the filter medium or existing deposits where *attachment* mechanisms retain the suspended particle in contact with the medium's surface or with previously deposited solids.

Detachment mechanisms result from the hydrodynamic forces of flow acting so that a certain portion of the previously attached particles, less strongly adhered to others, is detached from the filter medium or previous deposits and carried further, deep into or through the filter.

Important transport mechanisms include screening, interception, inertial forces, sedimentation, diffusion, and hydrodynamic forces. Physicochemical and molecular forces generally govern attachment of particles to media surfaces. Detachment is caused by the impact of arriving particles on unstable deposits and by hydraulic shear stresses without the influence of arriving particles. A number of properties of a filter medium are important in filtration performance and in characterizing the medium. Important media properties include size, shape, density, and hardness. The efficiency of a filter is more sensitive to changes in the filtration rate rather than in the actual rate. Therefore, filtration process control is critical to successful operation.

Several different granular types of filters are classified by various schemes. Filters can be classified by the type of medium (single media, dual media), hydraulic arrangement (gravity or pressure), rate of filtration (rapid or slow), and depth of solids removal (deep or cake). The most common types of filter media used in granular bed filters are silica sand, anthracite coal, and garnet. These may be used alone or in dual- or triple-media combinations. Granular-activated carbon (GAC), another type of medium, has been used in granular beds that serve for both filtration and adsorption to reduce taste and odor.

In recent years, direct filtration has received considerable attention and application in the treating of drinking water. Direct filtration is not preceded by sedimentation. It offers several advantages over conventional treatment of "good-quality" surface water. Because there is no sedimentation process and a lower coagulant dose, the capital and operating costs are lower compared with those of conventional treatment. Sludge volumes are lower, which results in lower chemical costs for sludge treatment and disposal. Because of increased interest in ozone application in potable water, biological filtration has received noticeable attention and application in recent years. Granular filters become biologically active when ozone is used as a preoxidant. Ozone reacts with organic compounds in water and forms several ozonation byproducts such as aldehydes, carboxylic acids, and keto acids, which are relatively easy to biodegrade. By operating filters in the biological mode, these ozonation byproducts can be effectively removed and in turn reduce the potential for bacterial regrowth in distribution systems and formation of chlorination byproducts.

A slow sand filter generally consists of a watertight basin containing a layer of sand over a layer of gravel (Fig. 2). It is operated at very low filtration rates without coagulation in pretreatment. A smaller grain size and lower filtration rate result in solids removal almost entirely in a thin layer on the top of the sand bed. This layer, composed of dirt and living and dead micro- and macro-organisms from the water, is called *schmutzdecke* or dirty skin. Most of the solid removals in slow sand filter take place in the *schmutzdecke* layer. The dominant removal mechanisms are both physical and biological. A typical filter cycle may vary from 1 to 6 months (or longer) depending on the source water quality and the filtration rate. Filtration rates range from 0.016 to 0.16 gpm/sq ft (0.04 to 0.40 m/h). Effective sand sizes range from 0.15

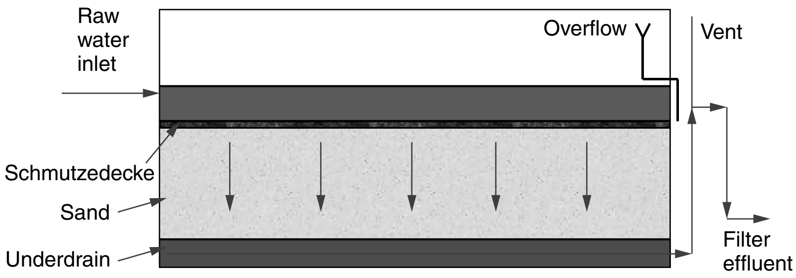

Figure 2. Conventional slow sand filter.

to 0.40 mm, sand uniformity coefficients from 1.5 to 3.6, and initial bed depths from 1.5 to 5.0 ft. The sand is supported on graded gravel 6 to 36 inches deep. Slow sand filters are cleaned by scraping the *schmutzdecke* and a small amount of sand depth. Usually, scraping is done manually but, in some cases, mechanically. The scraped sand is cleaned hydraulically and stockpiled for later reuse.

Rapid rate pressure filters are similar to gravity rapid rate filters, except that the flow enters and exits the filter under pressure (Fig. 3). The filter medium is contained in a steel pressure vessel. The pressure vessel can be vertical or horizontal. Proper backwashing of a pressure filter is more difficult compared with a gravity filter because the filter medium is not conveniently visible to the operator during the backwash operation. Pressure filters tend to be used in small water systems. Many pressure filters are used in industrial water and wastewater filtration. They are also used widely in swimming pool filtration.

Diatomaceous earth filtration, precoat or diatomite, filtration is another water filtration process that works under pressure. It consists of a layer of diatomaceous earth used as a filter medium approximately one-eighth inch thick placed on a septum or filter element. The septum may be placed in a pressure vessel or operated under a vacuum in an open vessel. As the water passes through the filter medium and septum, the suspended particles are captured and deposited. The majority of particles removed by the filters are strained at the surface layer of the filter medium, and some are trapped within the layer. As the filter cycle proceeds, additional filter medium called *body feed* is regularly metered into the influent water in proportion to the solids being removed. Ultimately, a gradually increasing pressure drop through the filter system reaches the point where continued filtration is impractical. The forward filtration process is stopped, the filter medium and collected dirt are washed off the septum, a new precoat of filter medium is applied, and the filtration process continues. Diatomaceous earth filters are widely used in industrial filtration and in swimming pool filtration. They have also been used in municipal potable water treatment, primarily in direct, in-line filtration of high-quality surface water (turbidity 10 NTU or less and acceptable color), and in filtering iron and manganese from groundwater after appropriate pretreatment to precipitate these contaminants. Precoat filters are simple to operate and are effective in removing cysts, algae, and asbestos.

Figure 3. Pressure filter (*Source*: U.S. Filter).

Membrane filtration represents an important set of processes for drinking water treatment. A membrane is a thin layer of natural or synthetic material that can separate substances when a driving force is applied across the membrane. Membranes used for water treatment are commonly made of synthetic organic polymers. Membrane processes for potable water treatment are reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED), ultrafiltration (UF), and microfiltration (MF). Reverse osmosis is used primarily to remove salts from brackish water or seawater. Nanofiltration is used to soften freshwaters and remove disinfection byproduct (DBP) precursors. Electrodialysis is used to demineralize brackish water and seawater and to soften freshwater. Ultrafiltration and microfiltration are used to remove turbidity, pathogens, and other particulates from freshwater (Fig. 4). Membranes are normally classified by solute exclusion size, which is sometimes referred to as *pore size*. Membrane filtration works by passing water at high-pressure through a thin membrane in the form of hollow-fiber or spiral-wound composite sheets. The contaminants are retained on the high pressure side and frequently must be cleaned by reversing the flow and flushing the waste. Periodic chemical cleaning may be required to remove persistent contaminants. Membrane assemblies are contained in pressure vessels or cartridges. Low-pressure membranes in the form of either ultrafiltration (UF) or microfiltration (MF) have become more economical in capital and operating costs and have received increased attention in drinking water application. Fouling of the membrane is the major problem preventing widespread application of this technology.

Cartridge filters traditionally have been applied for point-of-use systems and for pretreatment prior to membrane treatment systems. Composed of membrane, fabric, or string filter media, the filter material is supported by a filter element and housed in a pressure vessel. The application of cartridge filters using either cleanable ceramic or disposable polypropylene cartridge

Figure 4. Microfiltration (MF) system (*Source*: U.S. Filter).

seems to be a feasible method for removing modest levels of turbidity, algae, and microbiological contaminants. As water is filtered through a cartridge filter, the pressure drop increases, which necessitates terminating the filter run. When this process is done, the filter is not backwashed, but the cartridge is thrown away and replaced by a clean filter.

The desire to reduce costs or to treat some waters more effectively is driving the development of new technologies for filtration. Several examples of such proprietary filters include low-head continuous backwash filters, two-stage filtration systems, bag filters, moving media filters, and flotation and filtration systems. A variety of modes of operation are available such as downflow, up-flow, multiple layer, biflow, radial flow, semicontinuous (moving bridge), continuous (media recycle), variable voidage, and pebble matrix.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, Inc., New York, NY.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, Inc., New York, NY.

HDR, Inc. (2001). *Handbook of Public Water System*, 2nd Edn. John Wiley & Sons, New York, NY.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold Company, New York, NY.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York, NY.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000) *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

SYNTHETIC AND NATURAL ORGANIC REMOVAL BY BIOLOGICAL FILTRATION

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Oligotrophy is important because organic substrates are present in drinking water supplies at microgram per liter levels. Most biological processes are aerobic, which means that dissolved oxygen is present and used as the electron acceptor by the bacteria.

The benefits of biological filtration include decreased potential for bacterial regrowth in the water distribution system, reduced chlorination disinfection byproducts (DBPs), reduced chlorine demand, and decreased corrosion potential. So biological filtration is used to achieve three broad goals: (1) biologically oxidize biodegradable components, making the water biologically stable and reducing the need for excess chlorination; this will in turn reduce the formation of DBP compounds, which are known human carcinogens; (2) biodegrade synthetic organic micropollutants that are harmful to human health; and (3) remove nitrate and nitrite via denitrification. In most drinking water treatment, however, the first two goals are the main objectives of biological filtration. Particulate (silt, clay, precipitates) removal does occur in biological filters even though it may not be an intentional goal.

It is well established that ozonation increases the fraction of natural organic material (NOM) that is biodegradable. The effects of ozonation on NOM include formation of hydroxyl, carbonyl, and carboxyl groups; increased polarity and hydrophilicity; loss of double bonds and aromaticity; and a shift in molecular weight distribution toward lower molecular weight compounds. Thus, an increase in biodegradable organic matter (BOM) on ozonation generally enhances biological activity considerably in filters, after ozonation. Often, biological filtration can reduce BOM concentration to approximately preozonation levels, although this depends on the specifics of biological filters and water quality parameters, and the composition of BOM may be different after biological filtration. Currently identified ozonation byproducts such as aldehydes, carboxylic acids, and keto acids are biodegraded by biological filters that have more than 75% removal efficiency. Several synthetic organic compounds (SOCs) are also substantially biodegraded by the biological filtration process. In particular, phenol, chlorinated phenols, and chlorinated benzenes show significant percentage removals immediately or after a short acclimation period. In general, SOCs that are built on an aromatic structure should be most susceptible to biodegradation, and halogenated aliphatics should be more resistant to biodegradation.

READING LIST

Ahmad, R., Amirtharajah, A., Al-Shawwa, A., and Huck, P. (1998). Effects of backwashing on biological filters. *J. American Water Works Assoc.* **12**: 62–73.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, Inc., New York, NY.

Bouwer, E.J. and Crowe, P.B. (1988). Biological processes in drinking water treatment. *J. American Water Works Assoc.* **9**: 82–91.

Hozalski, R.M., Goel, S., and Bouwer, E.J. (1995). TOC removal in biological filters. *J. American Water Works Assoc.* **12**: 40–54.

Mallevialle, J., Suffet, I.H., and Chan, U.S. (Eds.). (1992). *Influence and Removal of Organics in Drinking Water*. CRC Press, Inc., Boca Raton, FL.

Manem, J.A. and Rittman, B.E. (1992). Removing trace-level organic pollutants in a biological filter. *J. American Water Works Assoc.* **4**: 152.

Rittman, B.E. and Snoeyink, V.L. (1984). Achieving biologically stable drinking water. *J. American Water Works Assoc.* **10**: 106.

Rittman, B.E. and Huck, P.M. (1989). Biological treatment of public water supplies. *Crit. Rev. Environ. Cont.* **19**: 119–184.

Urfer, D., Huck, P.M., Booth, S.D.J., and Coffey, B.M. (1997). Biological filtration for BOM and particle removal: A critical review. *J. American Water Works Assoc.* **12**: 83–98.

GRANULAR BED AND PRECOAT FILTRATION

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Various filtration processes are used in potable water treatment. Granular bed and precoat filtration processes are described in this article, and focus is on descriptions of these processes and their particle removal efficiencies. Filtration processes are some of the major tools that are used to minimize microbial pathogens in drinking water, so the descriptions of their removal efficiencies contained herein emphasize their removal of microbes. This type of efficiency is characterized by a term called log removal, which is defined as log C_o/C, where C_o and C are the pathogen concentrations in a filter's inlet and outlet flows, respectively. Thus, a 1-log removal is equivalent to 90% removal. Current drinking water regulations target log removals of pathogens. Filter performance is also based on the amount of turbidity in the filtered water. Turbidity is a measure of water clarity. Turbidity reduces the aesthetic acceptability of drinking water and also shields pathogens from disinfectants that are added downstream of filters.

GRANULAR BED FILTRATION

In this process, water passes through a filter containing a bed of granular material. Particles are removed by different mechanisms, depending, primarily, on the filter medium used and the hydraulic filtration rate. The term "particles," used herein, refers to any particulate contaminants in water. These include very fine inanimate and biological objects and microbial pathogens. Granular filtration can be classified as slow sand filtration or high-rate granular filtration. Slow sand filters are operated at filtration rates of less than 0.4 m/h; the filtration rates for high-rate filters are typically 5 to 25 m/h. The design/operating criteria and particle removal mechanisms for slow sand filtration and high-rate filtration are considerably different, so each process is described in a separate subsection.

Slow Sand Filtration

Slow sand filtration was first developed in England about 200 years ago to protect drinking water consumers from microbe-related health risks. Detailed design guidelines for slow sand filters are available (1). A slow sand filter consists of a layer of sand supported on a graded gravel layer. The gravel layer surrounds a system of perforated pipes that collect the filtered water. The gravel keeps the sand from entering the pipe perforations and, thereby, being lost from the filter. Water passes through the sand and gravel by gravity, normally without being pretreated, and as it does, the sand removes particles. Biological and physicochemical removal mechanisms are believed to be involved (2,3). Specifically, these may include biological action (e.g., ciliate protozoa on the sand grains acting as bacterial predators), particle attachment to the sand grains (e.g., the extracellular macromolecules of microbial particles attaching to the sand grains) and physical straining between sand grains.

The predominant removal location is a thin layer at the top of the sand bed. This biologically active layer is termed the *schmutzdecke*. It contains living and dead micro- and macroorganisms. As filtration progresses, materials removed and biological growths on the sand grains increase the loss of hydraulic head as the water passes from above to below the sand layer. When the head loss reaches a predetermined limit, normally from 1 to 2 m, the filter is removed from service. Before being returned to service, the filter is cleaned usually by scraping about 2 cm of accumulated material and sand from the top layer of the sand bed, which is nominally the *schmutzdecke*. The typical time period between cleanings (called a filter run) varies from 1 to 6 months, depending on the inlet water characteristics and filtration rate. After the sand bed depth is reduced to the lowest acceptable value by multiple scrapings, replacement of the entire sand bed is necessary.

Pretreatment is normally not required for slow sand filtration. However, if the source water has a high concentration of suspended particles, physical pretreatment processes, such as roughing filters or microstrainers, may be employed to prevent rapid clogging of the sand and, thus, maintain reasonable filter run periods.

Virus removal by slow sand filters can range from slightly better than 1 log to as much as 5 logs (4). Fairly good removal of bacteria and protozoa can also be achieved by slow sand filtration. During a pilot-scale study, a new filter removed 0.82 logs of total coliform bacteria and greater than 1.7 logs of *Giardia* (5). After 2 weeks, a microbiological population was established within the sand bed, the removal of total coliforms increased to 4 logs, and no *Giardia* were detected in the filtered water. The calculated reduction of *Giardia* was greater than 2.6 logs.

In a full-scale study at three slow sand filtration plants in Idaho, no *Giardia* were detected in the filtered water at two of the three plants (6). For the one positive sample found at the third plant, 1-log removal of *Giardia* was achieved. In the same study, removal of total coliforms and fecal coliforms varied from 0.81 to 2.30 logs and from 0.29 to 0.52 logs, respectively. These ranges in removal efficiency were influenced by inlet water quality, filtration rate, and media size and depth. Removing *Cryptosporidium* by slow sand filtration is often more difficult than removing *Giardia*. In a full-scale study conducted in British Columbia, the average removal of *Giardia* was 1.16 logs, whereas it was only 0.28 logs for *Cryptosporidium* (7).

The reduction of turbidity by slow sand filtration may be site-specific. Turbidity removal in a pilot study was 1.66 logs or better after the filter was operated for 2 days (8). However, only 0.14 to 0.22 log removal of turbidity was found in another study, even though the reduction of *Giardia* in the same study was as high as 4 logs (5). The authors concluded that this was due to the fine clay particles in the inlet water to the filter. In a full-scale study, between 0 to 0.43 log removal of turbidity was reported (6). This low removal was due to the fine particles in the inlet water and to the large fraction (4% by weight) of fines in the sand medium used in the study.

Under proper design and operating conditions, slow sand filtration can provide a high degree of protection against microbial pathogens. This includes effective removal of viruses, bacteria, and protozoa. If the inlet water is of high quality, pretreatment is normally not required. The construction, operating, and maintenance costs of slow sand filtration are low. However, land requirements are high. This technology is therefore attractive for small systems that treat high-quality surface water.

High-Rate Filtration

High-rate granular filtration is the most widely used filtration process in drinking water treatment. A comprehensive review of this process is available (9). Filter media types include monomedia (typically silica sand but also anthracite coal), dual media (usually anthracite coal over silica sand), and trimedia (commonly anthracite coal over silica sand over garnet). Granular activated carbon is used when both particle removal and adsorption of dissolved organic compounds are desired.

Particle removal by high-rate granular filtration is a physicochemical process that involves two sequential steps, transport and attachment. Particles are initially transported from suspension to within a very close distance of filter media grains, and then attachment of particles to the media grains occurs (10). The transport step depends on the physical–hydrodynamic properties of the system. Process variables such as the size and density of particles, size and depth of filter media, and filtration rate affect transport efficiency. Attachment is controlled by the surface and solution chemistry of the filter media and particle suspension (11). Unfavorable interactions between the particles and the filter media must be avoided so that the particles can attach to the media. Chemical coagulation prior to filtration is used to overcome any unfavorable interactions between the particles and the filter media, and it is the single most important factor in determining filtration efficiency. Optimum coagulation, which is typically defined as the minimum coagulant dose required to achieve the best filtered water quality, should be provided. Without proper chemical coagulation, high-rate filtration works as a simple straining process and is not effective for particle removal.

Depending on the degree of pretreatment of the water before it is applied to the filters, granular filtration can be operated in three different treatment modes: conventional, direct, and in-line. Conventional treatment, appropriate for most source waters, consists of adding coagulant chemicals in rapid mixing basins, flocculation in slow mixing basins, and particle removal in sedimentation basins and filters. When sedimentation is omitted, the treatment mode is termed “direct filtration.” If both flocculation and sedimentation are omitted, the term “in-line filtration” is used. Direct or in-line filtration is used for source waters of consistently good quality, such as those of low turbidity and low color.

Particle removal by high-rate granular filtration occurs within the depth of the granular media (depth filtration) rather than only at the top of the filter media (cake filtration). A filter is cleaned when, during operation, the hydraulic head lost across the filter medium or the filtered water quality reaches unacceptable levels. The cleaning consists of surface washing and backwashing the filter medium. Surface washing is used to break up the mat of particles that has accumulated near the surface of the medium. This is achieved by directing water jets downward toward the filter medium’s surface or causing air bubbles to rise upward through the medium. Backwashing is achieved by a reverse flow of water applied below the medium and rising through the medium bed to flush the particles that have accumulated at the surface and within the filter bed out of the medium and the filter.

After backwashing, filters exhibit an initial period of poor performance (termed the ripening period) before achieving good filtered water quality. The passage of particles during the ripening period can be formidable. The ripening period can last from less than an hour to several hours. Different methods are used to minimize this impact, such as wasting the initial filtered water (filter -to-waste), limiting the initial filtration rate until the filtrate quality is acceptable (slow start), placing the filter in operation after a period of inactivity following backwashing (delayed start), or adding coagulant or polymer chemicals to the backwash water supply.

The importance of chemical pretreatment to removal efficiency by high-rate granular filtration has been emphasized in numerous studies. Without adding any chemicals, the average log removal of *Giardia* was 0.60 logs for conventional treatment and 0.44 logs for in-line filtration in a pilot study (12). In optimum chemical pretreatment, the removal increased to 1.70 logs for conventional treatment and 1.19 logs for in-line filtration. Results from a 2-year study indicated that maintaining optimum coagulation conditions to produce low filtered water turbidity (0.1 to 0.2 NTU) provided effective removal of *Giardia* and *Cryptosporidium* (13). Under optimum coagulation conditions, the average removal of *Giardia* was 3.3 logs or better, and the average removal of *Cryptosporidium* was 2.3 logs or better.

Results from a full-scale study confirmed that a properly operated conventional treatment plant provided a substantial barrier to microbial pathogens (14). Dual media filters were used in this plant. Coagulation was provided using alum and activated silica. Prechlorination was applied at a dosage of 1 mg/L. *Giardia* was detected in only 1 of 32 filtered water samples, and the mean removal was 3.6 logs by sedimentation and filtration. *Cryptosporidium* was detected in 7 of 32 filtered water samples, and the mean removal was 2 logs. *Clostridium perfringens* was detected in 9 of 33 filtered water samples, and the mean removal was 4.4 logs. No human enteric viruses were detected in 32 filtered water samples where the mean removal was 3.1 logs. *Somatic coliphage* was detected in 24 of 32 filtered water samples whose a mean removal was 3.5 logs.

Under proper design and operating conditions, high-rate granular filtration can act as a consistent and effective barrier to pathogenic microbes (15). Providing effective chemical pretreatment is the single most important factor in enhancing treatment efficiency. It is expensive, if not impossible, to remove microbes effectively without the proper chemistry provided by optimum coagulation.

Precoat Filtration

Precoat filtration was originally developed by the United States Army during World War II. The objective was a portable device to remove *Entamoeba histolytica*, a protozoan parasite prevalent in the Pacific war zone, from potable water. Precoat filtration is now accepted by the U.S. Environmental Protection Agency as a filtration technique for potable water treatment. A detailed design and operation manual for precoat filtration has been published (16).

In precoat filtration, water is forced by pressure or pulled by vacuum through a uniform, thin layer of filtering material precoated onto a permeable, rigid supporting structure (septum). As water passes through the precoat filter medium (filter cake) and septum, particles whose sizes are larger than the pore size of the filter medium are strained and removed. Typical filtration rates for this process are about 2.5 to 7 m/h.

During filtration, a slurry (called the body-feed solution) containing the coating material is often continuously added at the filter inlet to maintain filter cake permeability. As the filter cake thickness builds due to captured particles and the added precoat, the hydraulic head lost across the filter cake increases to a level impractical for further filtration. The filter cake is then removed from the support septum and disposed of. The filter is then cleaned and precoated with a new layer of coating materials, and a new filter run is started.

Precoat materials include diatomaceous earth (DE) and perlite; DE is more commonly used in drinking water treatment. DE is composed of fossilized skeletons of microscopic water plants called diatoms and is almost pure silica. Perlite originates as rock formed by the solidification of magma, is composed primarily of alumina silicate, and processed into a fine granular material for use as precoat. The primary removal mechanism of precoat filtration is straining, so its removal efficiency depends to a great extent on the pore size of the coating materials. The median pore size is called the media grade. Diatomite grades used for drinking water treatment have a median pore diameter of about 3 to 17 μm. Other important factors that influence the removal efficiency are chemical pretreatment of the filter medium, filtration rate, and body-feed rate. To maintain reasonable filter run time, the inlet water must be of high quality. Inlet water turbidity levels of less than 10 NTU are desirable, or pretreatment of the source water should be considered.

A pilot study showed complete removal of *Giardia* by both coarse and fine grades of DE in filtration across a wide range of operating conditions (17). Removal of *Cryptosporidium* by a bench-scale DE filter ranged from 3.60 to 6.68 logs, depending on the media grade and filtration rate (18). In a pilot-plant study, complete removal of *Giardia* and 3-log removal of *Cryptosporidium* by DE filtration were reported (19). Based on the results from another pilot-scale study, 6-log removal of *Cryptosporidium* was achieved by DE filtration at rates from 2.5 to 5 m/h (20). In most of the runs, the turbidity level decreased from about 1 NTU in the inlet water to less than 0.1 NTU in the outlet water.

Precoat filtration can remove protozoan parasites very effectively, but chemical pretreatment of coating media with aluminum or iron coagulants or cationic polymers is required to remove submicron-sized microbes such as viruses and some bacteria. In a pilot study, removal of coliforms by untreated DE was about 0.36 logs (19). The removal increased to 0.82 logs for DE coated with an alum dosage of 0.001 g/g DE and to 2 logs with an alum dosage of 0.003 g/g DE. This enhancement was probably due to the enmeshment of the bacteria on the aluminum precipitates. A similar beneficial effect was observed by coating the DE with cationic polymers. When the DE was coated with a polymer dosage of 0.0035 g/g DE, the removal of coliforms was greater than 3.3 logs. The authors concluded that this could be due to increased density of positively charged sites on the polymer-coated DE for adsorption of negatively charged coliforms. An enhancement in virus removal by chemical pretreatment of filter cake has been reported (21). The removal of bacteriophage T2 and poliovirus was about 1 log for an uncoated filter cake. When the filter cake was coated with ferric hydrate or polyelectrolytes, the removal increased to more than 1.7 logs.

Under proper design and routine operating conditions, precoat filtration can remove protozoan parasites such as *Cryptosporidium* and *Giardia* very effectively. Precoat filters can also be effective in removing submicron-sized microbes including viruses and some bacteria, provided that chemical pretreatment of the coating materials is employed.

BIBLIOGRAPHY

1. Hendricks, D. (1991). *Manual of Design for Slow Sand Filtration*. American Water Works Association Research Foundation, Denver, CO.

2. Weber-Shirk, M.L. and Dick, R.I. (1997). Biological mechanisms in slow sand filters. *Journal of American Water Works Association* **89**(2): 72–83.
3. Weber-Shirk, M.L. and Dick, R.I. (1997). Physical-chemical mechanisms in slow sand filters. *Journal of American Water Works Association* **89**(2): 87–100.
4. Ellis, K.V. (1985). Slow sand filtration. *Critical Reviews in Environmental Control* **15**(4): 315–354.
5. Bellamy, W.D., Silverman, G.P., Hendricks, D.W., and Logsdon, G.S. (1985). Removing *Giardia* cysts with slow sand filtration. *Journal of American Water Works Association* **77**(2): 52–60.
6. Tanner, S.A. and Ongerth, J.E. (1990). Evaluating the performance of slow sand filters in northern idaho. *Journal of American Water Works Association* **82**(12): 51–61.
7. Fogel, D. et al. (1993). Removing *Giardia* and *Cryptosporidium* by slow sand filtration. *Journal of American Water Works Association* **85**(11): 77–84.
8. Cleasby, J.L., Hilmoe, D.J. and Dimitracopoulos, C.J. (1984). Slow sand and direct in-line filtration of a surface water. *Journal of American Water Works Association* **76**(12): 44–55.
9. Cleasby, J.L. and Logsdon, G.S. (1999). Granular bed and precoat filtration. In: *Water Quality & Treatment*, R.D. Letterman (Ed.). McGraw Hill, Inc., New York, pp. 8.1–8.99.
10. Yao, K.M., Habibian, M.T., and O'Melia, C.R. (1971). Water and waste water filtration: Concepts and applications. *Environmental Science and Technology* **5**(11): 1105–1112.
11. Tobiason, J.E. and O'Melia, C.R. (1988). Physicochemical aspects of particle removal in depth filtration. *Journal of American Water Works Association* **80**(12): 54–64.
12. Ongerth, J.E. (1990). Evaluation of treatment for removing *Giardia* cysts. *Journal of American Water Works Association* **82**(6): 85–96.
13. Nieminski, E.C. and Ongerth, J.E. (1995). Removing *Giardia* and *Cryptosporidium* by conventional treatment and direct filtration. *Journal of American Water Works Association* **87**(9): 96–106.
14. Payment, P. et al. (2000). *An Epidemiological Study of Gastrointestinal Health Effects of Drinking Water*. AWWA Research Foundation and American Water Works Association, Denver, CO.
15. Au, K.-K. and LeChevallier, M.W. (2002). Removal of pathogenic microbes by granular high-rate filtration. In: *Encyclopedia of Environmental Microbiology*. G. Bitton (Ed.). John Wiley & Sons, New York, pp. 2707–2713.
16. *American Water Works Association*, Precoat Filtration. AWWA Manual M30, Denver, CO, (1995).
17. Langé, K.P., Bellamy, W.D., Hendricks, D.W., and Logsdon, G.S. (1986). Diatomaceous earth filtration of *Giardia* cysts and other substances. *Journal of American Water Works Association* **78**(1): 76–84.
18. Ongerth, J.E. and Hutton, P.E. (1997). DE filtration to remove *Cryptosporidium*. *Journal of American Water Works Association* **89**(12): 39–46.
19. Schuler, P.F. and Ghosh, M.M. (1990). Diatomaceous earth filtration of cysts and other particulates using chemical additives. *Journal of American Water Works Association* **82**(12): 67–75.
20. Ongerth, J.E. and Hutton, P.E. (2001). Testing of diatomaceous earth filtration for removal of *Cryptosporidium* oocysts. *Journal of American Water Works Association* **93**(12): 54–63.
21. Brown, T.S., Malina, J.F., Jr., and Moore, B.D. (1974). Virus removal by diatomaceous-earth filtration-part 2. *Journal of American Water Works Association* **66**(12): 735–738.

FLOCCULATION

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The flocculation process aggregates destabilized particles into larger and more easily settleable flocs. The coagulation process destabilizes particles through chemical reactions between the coagulant and the suspended colloids, but flocculation is the transport step that causes the necessary collision between destabilized particles. The purpose of the flocculation process is to promote the interaction of particles and to form aggregates that can be efficiently removed in the subsequent separation processes such as sedimentation, flotation, and coarse bed filtration. In practice, flocculation is accomplished by providing a gentle mixing phase that follows the rapid dispersion of coagulants.

There are three major mechanisms of flocculation: perikinetic, orthokinetic, and differential settling. In perikinetic flocculation, the aggregation of particles occurs as a result of random thermal motion (Brownian diffusion) caused by continuous bombardment by surrounding fluid molecules. The driving force for this type of particle movement is the thermal energy of the fluid. This is significant for particles that are 1 to 2 microns in size. In orthokinetic flocculation, the aggregation of particles is caused by induced velocity gradients in the fluid. The suspended particles follow the streamlines at different velocities and eventually lead to interparticle contacts. The velocity gradient is related to the energy dissipated into the water (via mixing). Flocculation by differential settling occurs when particles have unequal settling velocities, and their alignment in the vertical direction makes them tend to collide when one overtakes on other. This collision occurs in sludge blanket or solids contact clarifiers where differential and fluctuating velocities can lead to particle collision and aggregation. In water treatment, the predominant mechanism is orthokinetic flocculation.

In systems that are mixed (velocity gradients are induced), the velocity of the fluid varies both spatially and temporally. The spatial changes in the velocity are termed the *velocity gradient*, G. The unit of velocity gradient is $\sec^{-1}$. In water treatment plants, mean velocity gradients of 10 to 100 $\sec^{-1}$ are typical for flocculation. Flocculation usually follows a rapid mixing process in conventional treatment plants. Flocculation is a time-dependent process that directly affects clarification efficiency by providing multiple opportunities for particles suspended in water to collide through gentle and prolonged agitation. Most water treatment plants provide 20 to 30 min of flocculation time (at 20 °C). An increase in flocculation time does not improve flocculation significantly. The optimum flocculation conditions are those that rapidly form flocs large enough to be separated by settling, flotation, or filtration leaving no residual primary particles or small aggregates. However, rates of flocculation that are too high cause floc breakup. Thus, a balance must be achieved between the velocity gradient G and the flocculation time t, one compensating for the other. In some cases, flocculation is characterized by the dimensionless product Gt (sometimes called the Camp number). Based on observational data from water utilities in the United States, the optimal value of Gt is set between the limits of 10^4 and 10^5. It is desirable to compartmentalize the flocculation process by dividing the basin into two or more defined compartments or stages. Compartments prevent short-circuiting and permit defined zones of reduced energy input or tapered flocculation. Studies have shown that tapered flocculation at a diminishing velocity gradient is more efficient than uniform velocity flocculation.

Flocculation can be achieved by hydraulic methods or mechanical devices. Hydraulic methods are used most often in small plants. Mechanical flocculators cover a broad range of configurations. Mechanical flocculators are preferred by most design engineers in the United States because of their flexibility in varying G values and because they cause low head loss. Mechanical flocculators can be divided into two major types: (1) shaft with turbine or propeller type blades and (2) paddle type with either horizontal or vertical shafts. Turbines can have flat or curved blades that are connected to a disk or shaft (Fig. 1). Propellers are shaped like ships' screws. The blades are mounted on a vertical or inclined shaft. The paddle type consists of blades attached directly to vertical or horizontal shafts (Figs. 2 and 3). In some flocculators, moving blades (rotors) may be complemented by stationary blades (stators) that oppose rotational movement of the entire mass of water within the treatment unit and help suppress vortex formation. Paddles are rotated at slow to moderate speeds of 2 to 15 rpm. The currents generated by them are both radial and tangential. The type of mechanical flocculators influences the shape of flocculation compartments. Vertical flocculators are often associated with square compartments, whereas the horizontal shaft, reel, or paddle flocculators are associated with rectangular compartments. Between each zone or stage of mechanical flocculation, baffles are designed to prevent short-circuiting. Vertical flocculators are more applicable to high-energy flocculation such as direct filtration.

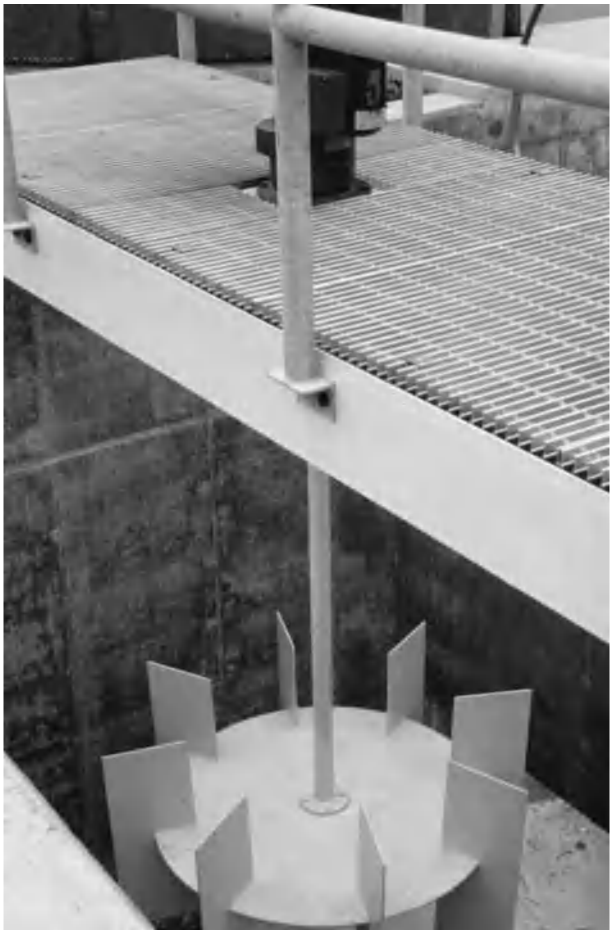


Figure 1. Flat blade turbine type flocculator (*Source*: Dorr Oliver Eimco).

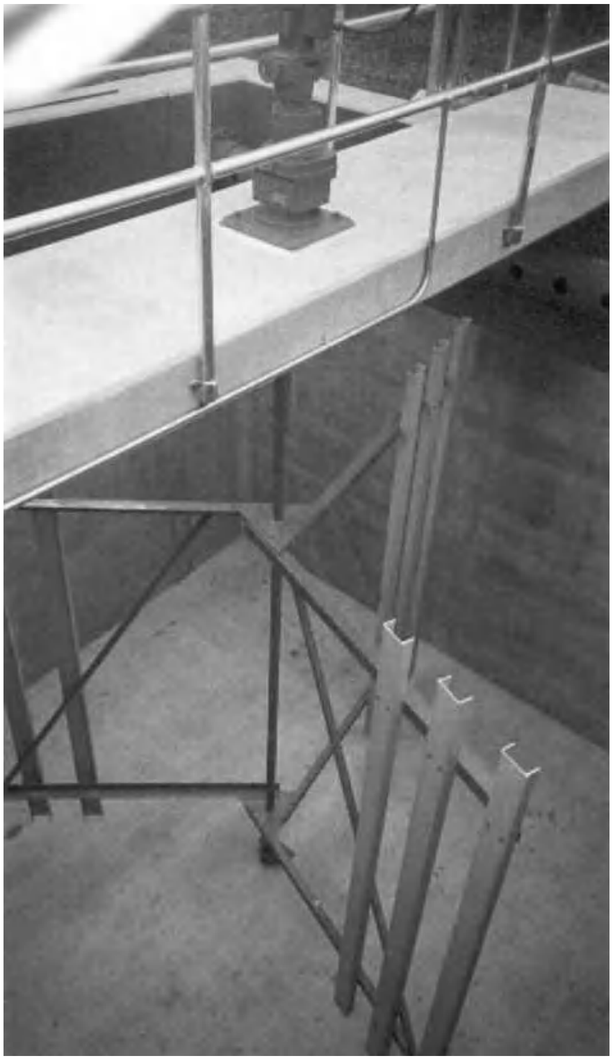
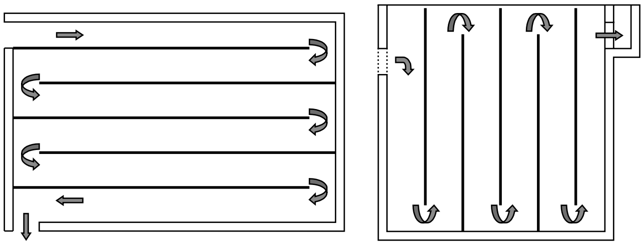


Figure 2. Vertical shaft paddle flocculator (*Source*: Walker Process Equipment, a Division of McNish Corporation).

Hydraulic flocculation methods are simple and effective, especially if flows are relatively constant. Hydraulic flocculation is achieved in baffled channel basins. They can be horizontally baffled (around-the-end flow) or

Figure 3. Horizontal shaft paddle flocculator (*Source*: Walker Process Equipment, a Division of McNish Corporation).



Around-the-end flow type baffled channel (plan)

Over-and underflow type baffled channel (section)

Figure 4. Hydraulic or baffled channel flocculation.

vertically baffled (over- and underflow) channels (Fig. 4). The velocity gradients are purposely intensified in these channels by enforced changes in the direction of flow. When designed properly, baffle channels perform well and exhibit good plug flow characteristics. However, they have two disadvantages: there is a significant head loss across the tank, and the mixing intensity is a function of plant flow rate. Some new water treatment plants in the United States have used a combined system of hydraulic and mechanical flocculation. It offers a large reduction in mechanical flocculator units, so there is a saving in capital and maintenance costs and increased reliability.

Some other types of flocculators are not commonly used in water treatment. Contact flocculation (gravel-packed filter) requires minimal maintenance because it has no moving parts. This type of flocculation system depends on plant flow rate and requires minimal variation in flow rate and water temperature for adequate mixing intensity. Contact flocculation also requires frequent backwashing. Contact flocculation may be applicable for difficult high-suspended-solids water or water with low total dissolved solids that may not respond readily to metal ion coagulants. Diffused air or water jet agitation is used as an auxiliary or temporary flocculation. This system is characterized by a high rate of energy consumption and is an inefficient flocculation process.

Several manufacturers provide proprietary designs that incorporate rapid mixing, flocculation, and settling in one unit, which is sometimes called a solids contact reactor unit. These units perform best in waters that can develop a dense, fast-settling floc, but the process may be difficult to control in some waters. These units have an option for sludge recirculation. Recirculating water treatment sludge may improve efficiency and reduce chemical requirements. The walking beam is another kind of proprietary flocculator. Walking beam flocculators are driven in the vertical direction in reciprocating fashion. The unit contains a series of cone-shaped devices on a vertical rod. The cone devices impart energy to the water as they move up and down, thereby creating velocity gradients.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, New York.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, New York.

Fair, G.M., Geyer, J.C., and Okun, D.A. (1968). *Waste and Wastewater Engineering*. John Wiley & Sons, New York.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold, New York.

HDR Engineering, Inc. (2001). *Handbook of Public Water Systems*, 2nd Edn. John Wiley & Sons, New York.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

FLUORIDATION

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Fluoridation of water supplies has been a controversial subject for more than 60 years. Much of the debate is concerned with questions of safety, but recently questions have been also raised about the efficacy of fluoridation. More than 35,000 papers on fluoridation have been published in the years since fluoride supplementation was first proposed as a safe and effective way of decreasing tooth decay. The overwhelming conclusion is that fluoride is safe and cost-effective.

TOOTH DECAY

Tooth decay is the most common disease of all humanity. It is the principal cause of tooth loss from early childhood through middle age. And decay continues to be a major problem as we age, particularly root decay which seriously affects the elderly due to receded gums and a general decrease in the amount of saliva. Dental decay not only affects the general health by interfering with the ability to eat and digest certain foods, but it also impacts an individual's emotional and social well-being. Recent surveys have found that more than 94% of adults have had decayed teeth, and 22.5% had root surface decay. In 1997, the United States spent more than $50.6 billion on dental care.

HISTORY OF WATER FLUORIDATION

In 1892, Sir Crichton-Browne advocated augmenting the common diet of his era with fluoride to reduce decay (1). Not until the 1950s, however, did years of research pay off, and it was unequivocally determined that when water contains approximately 1 part of fluoride per million parts of water (1 ppm) which is equivalent to 1 milligram of fluoride per liter of water (1 mg/L), decay rates are reduced by up to 60%. In the 1940s, there was substantial resistance to adding fluoride to community water supplies, even though people had been drinking naturally occurring fluoridated water containing several times the 1-ppm level of fluoride for a lifetime without any negative side effects (2).

The most famous study of the effects of fluoridation was done in the 1940s in Newburgh and Kingston, New York. These cities are located 35 miles apart near the Hudson River; both had populations of about 30,000 and were also similar in their demographics. Newburgh's water supply was fluoridated, and Kingston's was not. After 10 years, the study found that there were no medical differences between the two groups except for the fact that Newburgh's children had almost 60% fewer cavities (2). Many studies have confirmed these findings in the years since.

FLUORIDE

Fluoride is one of the earth's most common elements and is therefore present in variable amounts in all water supplies. It is also found in most plants and animals that we eat. The fluoride concentrations in water supplies within the United States vary from 0.1 to 10 mg/L (3). Ocean water also contains fluoride at concentrations of 1.0 to 1.5 mg/L. This causes a fairly uniform level of fluoride in all seafood.

Fluoride is classified by the National Academy of Sciences as an essential nutrient (4). Unlike many other essential elements that are found in food, water consumption is the most practical, consistent and effective method of fluoride application to the teeth. In growing children, fluoride will be incorporated throughout the entire hard structure (enamel and dentin) of the teeth. This continues until around age 50 when it appears that the spaces available to fluoride in the tooth's structure will be filled. In adults, fluoride will continue to be absorbed by the enamel surface, lending the teeth temporary but substantial resistance to decay. Fluoride is easily absorbed into the blood stream from the gastrointestinal tract and reaches a peak concentration within 20–60 minutes. This level declines rapidly due to the uptake of fluoride by the hard tissues and the removal of fluoride by the kidneys. Approximately 50% of the fluoride that is absorbed is incorporated in the body's teeth and bones within 24 hours.

Table 1. Supplemental Fluoride Dosage (Milligrams of Fluoride per Day)[a]

	Concentration of Fluoride in Water (parts/million)		
Age (years)	0.0 to 0.3	0.3 to 0.6	Over 0.6
Birth to six months	None	None	None
Six months to three years	0.25	None	None
Three to six years	0.50	0.25	None
Six to sixteen years	1.0	0.50	None

[a] Reference 6.

The amount of decay reduction caused by fluoridation of local water supplies has decreased during the last 40 years probably because of improved dental hygiene and widespread use of fluoride toothpaste. This increase in fluoride availability has led to a reduction in the dose of fluoride supplementation recommended for children living in non-optimally fluoridated communities (Table 1). In 1991, it was found that fluoride reduces the incidence of cavities 20% to 40% in children and 15% to 35% in adults (5).

THE SAFETY OF FLUORIDE

In 1970, the World Health Organization (WHO) issued a report, "Fluorides and Human Health," that had taken years of research to compile. The WHO wanted to evaluate impartially the vast number of scientific studies of fluoridation that had been published. These papers included population studies, experimental research, animal studies, human autopsy studies, clinical trials, and X-ray research. The WHO expert panel concluded that there was no reliable evidence that drinking water fluoridated at the recommended levels caused any ill health effects. In 1975, the WHO stated, "The only sign of physiological or pathological change in life-long users of optimally fluoridated water supplies .... is that they suffer less from tooth decay" (3).

Fluoride ingested through community water systems has a large margin of safety. It has never been shown that fluoride intake at 1 ppm has any negative effect on disease or death rates. Numerous studies performed before and after supplemental fluoridation have shown no changes in death rates from cancer, heart disease, intracranial lesions, nephritis, cirrhosis, or from any other cause. In addition, the normal disease and death rates of more than 7 million Americans who have lived for generations where the natural fluoride concentration was 2 to 10 mg/L (1 mg/L is the recommended dose), is compelling evidence of fluoridation's safety. Two extensive studies have established that there is no link between fluoridation and Down's syndrome, cleft palate, heart abnormalities, clubfoot, and other common birth defects.

Antifluoridationists have long claimed that fluoride use leads to an increase in cancer rates. Consumer's Union characterized this accusation as "absurd." It has been shown that fluoride has no mutagenic effect in studies of cattle (7) or mice (8). This makes sense because fluoride is not in the class of electrophilic compounds that can interact with DNA, nor is it likely that the small tissue levels of fluoride present due to fluoridated water supplies could interfere with DNA replication.

It has also been proven that fluoride does not cause allergic reactions. The executive committee of the American Academy of Allergy has stated, "There is no evidence of allergy or intolerance to fluorides as used in fluoridation of community water supplies."

The effect of fluoridated water on kidney function has been thoroughly investigated, and here again no ill effects have been shown. No kidney changes were detected in a population exposed for a lifetime to water supplies that have fluoride levels of 8 mg/L (1).

Opponents of fluoridation also routinely claim that it causes coronary artery disease. They use data on heart disease rates from Antigo, Wisconsin, to support this claim. Antigo did show increased death rates from heart disease in the period since fluoride was introduced to its water supply in 1949. But, in that same period, the percentage of elderly people living in Antigo doubled, due to longer life spans. Actually, the segment of the population 75 years old or older increased 106% (2). The higher death rates from heart disease amongst the elderly were never factored into the interpretation of the Antigo death-rate data. When this factor is taken into account, the alleged deleterious effect of fluoride disappears. Unfortunately, the population of Antigo believed the scare tactics and false claims of the antifluoridationist movement and voted to end the fluoridation of their water supply. After only 4 years, the decay rates in permanent teeth of second graders rose 183%. A year later, Antigo voted to reinstate fluoridation (2).

FLUORIDE SAFETY MARGINS

Food and water account for 1.2 to 2.6 mg of fluoride ingestion per day. Urban air usually contains less than 1 $\mu g/m^3$, an insignificant amount. The margin of safety for fluoride is very large, and toxic effects have not been demonstrated at levels far higher than one could receive in a lifetime of exposure to drinking water containing 8 times the recommended level of 1 ppm. The acute lethal dose for a 150 lb. (70 kg) man is 5 to 10 g of sodium fluoride or 2.3 to 4.5 g of fluoride (9). Chronic overexposure to fluoride at levels over 1 ppm before age 8 can lead to discoloration of the enamel, ranging from barely detectable white flecks to large brown areas. Known as enamel fluorosis, this solely cosmetic problem can be achieved only by ingesting high amounts of fluoride, not by topical application.

THE COST OF FLUORIDATING WATER SYSTEMS

Fluoride protection obtained through community water treatment costs approximately 50 ¢ per person per year (10). This saves an estimated $75 in dental treatment costs (11). The National Preventive Demonstration Program monitored nearly 30,000 children, ages 5 to 14, for 4 years and found that the most cost-effective method of decay prevention was to drink fluoridated water from birth and have sealants applied as needed (12).

THE ANTIFLUORIDATIONIST MOVEMENT

The water supply of the developed world is slowly becoming entirely fluoridated, although overcoming the misinformation promoted by those opposed to fluoridation is a long and difficult process. The resistance to this overwhelmingly endorsed public health benefit tells us a great deal about the psychology of fear, the strength of rumor, and the loss of trust in government and industry. William T. Jarvis, Ph.D., the Executive Director of the National Council Against Health Fraud, has stated,

> These charges seem to grow out of a mentality of distrust. Antifluoridation groups are led by many of the same people who oppose immunization, pasteurization, sex education, mental health programs, and other public health advances. Most are closely connected with sellers of alternatives to medically accepted products and services. The so-called "health food" industry justifies its existence by declaring that our conventional sources of food, water, and health care are misguided.

No studies will satisfy those who are opposed to fluoridation. A vociferous minority, made up mostly of food faddists, cultists, chiropractors, and people who misunderstand what fluoridation is, has developed effective ways of stopping fluoride from being adjusted to optimum levels in water. "Lifesavers Guide to Fluoridation," a pamphlet by John Yiamouyiannis, Ph.D., is often distributed in communities that are considering fluoridation. It cites 250 references as proof that fluoride is dangerous. However, in 1988, experts from the Ohio Department of Health published "Abuse of the Scientific Literature in an Antifluoridation Pamphlet." This review traced the references and found that almost half had no relevance to community water fluoridation and that many others actually supported fluoridation but were selectively misquoted and misrepresented.

In 1990, an article in *Newsweek* magazine implied that fluoridation was ineffective and unsafe. The article was a response to the unauthorized and premature release of data from an experiment at the National Institute of Environmental Health Science. The experiment exposed rats and mice to high doses of fluoride. A thorough review of the experiments by a U.S. Public Health Service expert panel concluded that the data were insignificant and that fluoridation posed no risk of cancer or any other disease. Dr. Stephen Barrett, a leading consumer health advocate, called the *Newsweek* article "the most irresponsible analysis of a public health topic ever published by a major national news outlet."

Fluoride has been a favorite target of those who want to frighten the public into believing that our health system is dangerous and uncaring. They continue to undermine the significant health advances that have been made by public health measures, modern agriculture, and industry. As Consumers Union has concluded,

> The simple truth is that there's no "scientific controversy" over the safety of fluoridation. The practice is safe, economical, and beneficial. The survival of this fake controversy represents one of the major triumphs of quackery over science in our generation (2).

FLUORIDATION RATES AROUND THE WORLD

Tooth decay, or caries, is the most prevalent disease of all humanity, more common than the common cold (13). The cost of tooth decay in human suffering as well as economic expenditures is also enormous, accounting for many billions of dollars. Yet, as we enter the twenty-first century, only a small percentage of the world's population can easily drink fluoridated water. In addition, the majority of bottled water is not fluoridated, and many types of home water filtering devices actually remove the fluoride that may be in the water.

In the United States, 62.2% of the population has access to public water supplies that are optimally fluoridated (14). More than 360 million people worldwide in approximately 60 countries also drink fluoridated water. Dr. C. Everett Kopp, the former Surgeon General of the United States has stated, "Fluoridation is the single most important commitment that a community can make to the oral health of its citizens." It is imperative to continue to fluoridate water systems throughout the world.

BIBLIOGRAPHY

1. Richmond, V.L. (1985). Thirty years of fluoridation. *Amer. Jour. Clinical Nutrition* **41**: 129–138.
2. Anon. (July, August, 1978). Fluoridation: a two-part report. *Consumers Reports*.
3. World Health Organization. (1970). *Fluorides and Human Health*. Monograph 59, Geneva. World Health Organization.
4. National Academy of Sciences. (1980). *National Research Council Food and Nutrition Board. Recommended Daily Allowances*, 9th Edn. Washington, DC, pp. 156–59.
5. *American Dental Association* (1991). Facts about Fluoride.
6. Barrett, S., Jarvis, W.T., Kroger, M., and London, W.M. (1997). *Consumer Health: A Guide to Intelligent Decisions*, 6th Edn. Brown & Benchmark, p. 121.
7. Leonard, A., Deknudt, G.H., Decat, G., and Leonard, E.D. (1977). Cytogenic investigations of leucocytes of cattle intoxicated with fluoride. *Toxicology* **7**: 239–42.
8. Japello, G. and Lia, J.S. (1974). Sodium fluoride as potential mutagen in mammalian egg. *Arch. Environ. Health* **29**: 230–35.
9. Ripa, L., DePaola, P., Horowitz, H., Nowak, A. et al. (1986). *A Guide to the Use of Fluorides for the Prevention of Dental Caries*. American Dental Assoc.
10. Barrett, S., Jarvis, W.T., Kroger, M., and London, W.M. (1997). *Consumer Health: A guide to intelligent Decisions*, 6th Edn. Brown & Benchmark, Madison, WI.
11. Centers for Disease Contol. (1992). Fluoridation of community water systems. *JAMA* **267**: 3264–3265.
12. Weisfeld, V.D. (Ed.). *Preventing tooth decay: Results from a four-year national study. Special Report Number Two, 1983*. Robert Wood Johnson Foundation, Princeton, NJ.
13. Schissel, M.J. and Dodes, J.E. (1999). *Healthy Teeth: A User's Manual*. St. Martin's/Griffin, New York.
14. *American Dental Association*. (1999). Fluoridation Facts. Council on Access, Prevention and Interprofessional Relations, Chicago, IL.

GIARDIASIS

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GIARDIA LAMBLIA

Giardia lamblia is an intestinal flagellated protozoan, which infects the intestinal tract of a wide range of mammals, including humans. Two forms of this protozoan exist, a highly resistant cyst and a motile, feeding trophozoite. Cysts may be found in freshwater surface water supplies as a result of contamination from sewage and animal waste runoff. Trophozoites of this obligate parasite do not typically survive outside the host and are therefore not the major mode of transmission. The cyst form is capable of surviving for long periods of time in cool water supplies and has been responsible for major waterborne outbreaks in the United States.

LIFE CYCLE AND MORPHOLOGY

The life cycle of *Giardia lamblia* begins with the ingestion of the cyst form, which reaches the small bowel, and in response to the low pH, encysts into the motile, feeding trophozoite form. Using flagella and the ventral disk, the trophozoite moves from the small intestine to the duodenum and jejunum where it attaches to the intestinal epithelium. Trophozoites do not seem to penetrate the epithelium and may remain attached to the mucosal surface until it sloughs off the tip of the villus approximately every 72 hours (1). The trophozoites are pear-shaped and have a concave ventral disk, which they use for attachment. They have four pairs of flagella, two nuclei, two axonemes, and two median bodies and are 10 to 20 μm long and 5 to 15 μm wide (see Fig. 1).

Trophozoites encyst as they move down through the colon. During encystation, flagella are retracted, the cytoplasm becomes condensed, and the cyst wall is secreted. This process of encystation is a key step in the life cycle of *Giardia* that allows the organism to survive between hosts outside the human body. The cysts can survive for 3 months in water at 4 °C (2). They are usually oval-shaped and contain four nuclei, axonemes, and median bodies. They measure 11 to 14 μm in length and 7 to 10 μm wide (see Fig. 2).

CLINICAL DISEASE

The cyst form is infectious, and an inoculum of 10 to 100 cysts is required to infect humans (1,3). The incubation time to infection ranges from 12 to 20 days before the acute stage begins, which lasts only a few days. The organisms are present in the duodenal mucosa, but they do not cause

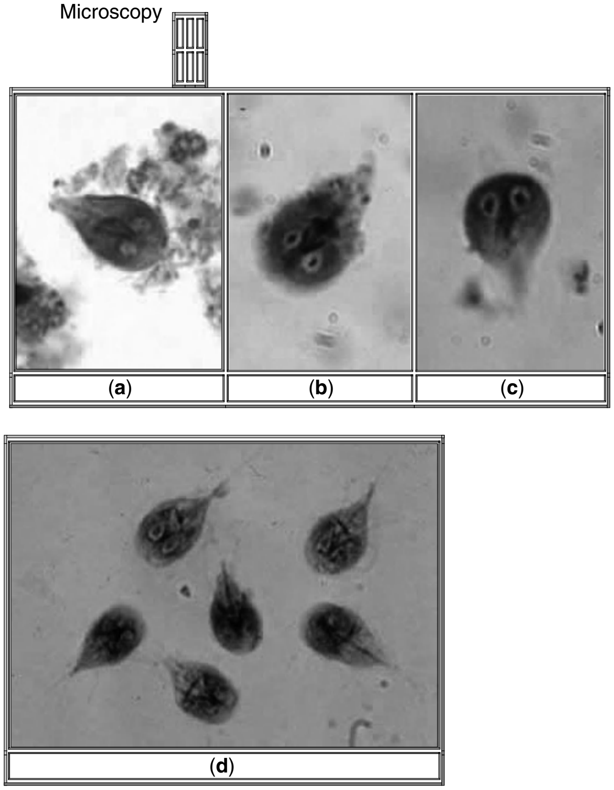

Figure 1. Three trophozoites of *Giardia intestinalis*, stained with trichrome (**a**) and stained with iron hematoxylin (**b** and **c**). Each cell has two nuclei with a large, central karyosome. Cell size: 9 to 21 μm in length. Trophozoites in culture (**d**). Photographs are courtesy of Centers for Disease Control & Prevention National Center for Infectious Diseases Division of Parasitic Diseases DPDx Laboratory Identification of Parasites of Public Health Concern.

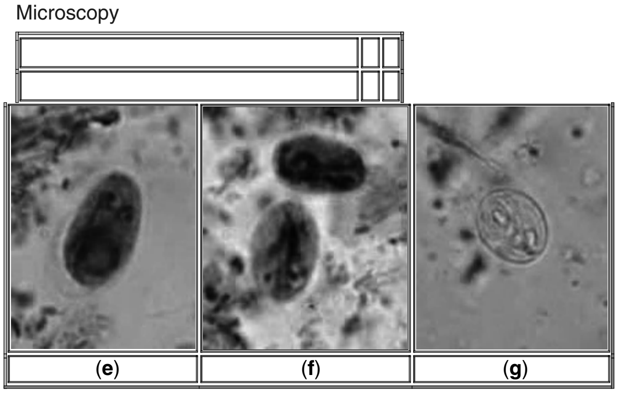

Figure 2. Cysts of *Giardia intestinalis*, stained with iron-hematoxylin (**e, f**) and in a wet mount (**g**) from a patient seen in Haiti). Size: 8 to 12 μm in length. These cysts have two nuclei each (more mature ones will have four). Photographs are courtesy of Centers for Disease Control & Prevention National Center for Infectious Diseases Division of Parasitic Diseases DPDx Laboratory Identification of Parasites of Public Health Concern.

pathology, as they do not penetrate the mucosa. Symptoms of the acute phase can include nausea, anorexia, fever, chills, and a sudden onset of explosive, foul-smelling diarrhea. Stools may have increased amounts of fecal fat and mucus, but no blood is present. Fat absorption may be disrupted because of the presence of trophozoites coating the mucosal lining. Rapid multiplication of trophozoites by binary fission creates a barrier between the intestinal epithelial cells and the lumen causing interference with nutrient absorption (1).

A chronic phase may follow the acute phase and induces symptoms of brief, recurrent diarrhea followed by normal stools or even constipation. Antigenic variation is a factor in the development of this chronic stage as certain surface antigens may allow the organism to survive better in the intestinal tract. Some other patients are asymptomatic and continue to pass cysts in stools.

Giardiasis occurs often in patients with hypogammaglobulinemia, but it has not become the problem it was expected to in AIDS patients. AIDS patients do not seem to be more susceptible to *Giardia* than do healthy people, and when cases occur, treatment is available and effective for this protozoan (1).

In summary, giardiasis causes infection ranging from an asymptomatic carrier state to severe malabsorption syndrome. Factors contributing to the variation in the effects of exposure include the strain of *Giardia,* dose, age of the host, and immune system function of the host.

DIAGNOSIS

Cysts and trophozoite forms are recovered by performing either a flotation or sedimentation procedure to concentrate them from fecal samples. Diagnosis is achieved by demonstrating either form in feces. Once the fecal sample is concentrated, a trichrome stain may be performed to enhance visualization of trophozoite and cyst forms. Fecal concentrates may be examined directly for cyst forms with iodine to enhance visualization. Direct fluorescent antibody (FA) or enzyme-linked immunosorbent assay (ELISA) techniques that incorporate monoclonal antibody-based reagents are also instruments for rapid diagnosis (1).

TREATMENT

Once an infection is diagnosed, treatment is recommended for all cases of *Giardia* for several reasons. First, the infection may cause subclinical malabsorption. The symptoms may be periodic, and if a carrier state develops, asymptomatic carriers are potential sources of infection for others with whom they may come in contact. The treatment of choice is metronidazole for all cases except during pregnancy. Other drugs are available and have been used by infected persons successfully, including paromomycin and tinidazole.

EPIDEMIOLOGY AND PREVENTION

Transmission of viable cyst forms can occur through many modes, including the ingestion of contaminated food or water, direct contact with an infected person such as children in day care centers, any group of people living in close quarters, or through oral/anal sexual practices, especially in male homosexuals. Areas with poor sanitation, such as those that travelers and/or campers may encounter, have resulted in giardiasis being referred to as "traveler's diarrhea." Also, some occupations increase the likelihood of exposure, including sewage and irrigation workers and clinical laboratory workers handling fecal samples. Waterborne outbreaks have occurred in the United States and have been associated with hikers and campers drinking stream water that was contaminated with fecal material from animal reservoirs, such as beavers.

Increased susceptibility has been demonstrated in patients with decreased gastric acidity and with malnutrition in young children in developing countries. The disease is more prevalent in children than in adults and is now reportable to the State Public Health Department and the Centers for Disease Control only in those patients aged 5 years and younger in the United States. The total cases reported in 2002 in the United States was 16,124 (4). Epidemics among adults in this country are seen in association with fecally contaminated food or water. Dogs, cats, and other animals can also carry *Giardia* infection.

To prevent transmission of this disease, personal hygiene must be addressed in all patient populations. Improved sanitation measures can be effective in controlling the person-to-person spread of infection. Travelers are advised to avoid drinking from local water supplies when traveling to foreign countries and to limit intake to bottled water. Iodine disinfection of drinking water as well as the use of filtration systems may serve to allow the decontamination of water sources for campers and travelers.

BIBLIOGRAPHY

1. Garcia, L. S. and Bruckner, D. (2002). *Diagnostic Medical Parasitology*, 4th Edn. American Society for Microbiology (ASM) Press, Washington, DC.
2. Olson, M.E., Goh, J., Phillips, M., Guselle, N., and McAllister, T. (1999). *Giardia* cyst and *Cryptosporidium* oocyst survival in water, soil and cattle feces. *J. Environ. Qual.* **28**: 1991–1996.
3. AWWA (American Water Works Association). (1999). *Waterborne Pathogens, Manual of Water Supply Practices*. AWWA M48 177–182.
4. MMWR (Morbidity and Mortality Weekly Report). (2003). Selected notifiable disease reports, United States, comparison of provisional 4-week totals October 11, 2003, with historical data. **52**(41): 998–1005.

GRAVITY SEPARATION/SEDIMENTATION

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Gravity separation or sedimentation is the step in conventional water treatment systems that follows flocculation and precedes filtration. Its purpose is to enhance the filtration process by removing particulate matter. Sedimentation requires that the water flow through a basin at a slow enough velocity to permit the particulate matter to settle to the bottom of the basin before the water exits the basin. The equipment required for this process includes a settling basin of rectangular, square, or circular configuration. The basin includes provisions for inlet and outlet structures and a sludge collection system. In addition, sedimentation systems are optionally equipped with tube or plate settlers to improve performance.

The settling velocity of particles or particulate matter is governed by particle size, shape, density, and water viscosity (which varies with temperature). Stokes' law describes the terminal velocity of discrete spherical particles in a laminar flow regime. In an ideal upflow rectangular settling tank (Figs. 1 and 2), all particles that have a settling velocity greater than the liquid upflow velocity will be captured. This upflow velocity is more commonly called the hydraulic overflow rate or surface loading rate. The surface overflow rate is the primary design parameter for sizing sedimentation basins. This rate is defined as the rate of inflow (Q) divided by the tank surface or floor area (A). Units are typically rated in gallons per day per square foot, gallons per minute per square foot, or cubic meter per hour per square meter. Design hydraulic overflow rates vary with the nature of the settling solids, water temperature, and the hydraulic characteristics of the sedimentation basin.

The settling efficiency for an ideal condition is independent of the depth and dependent on the tank plan

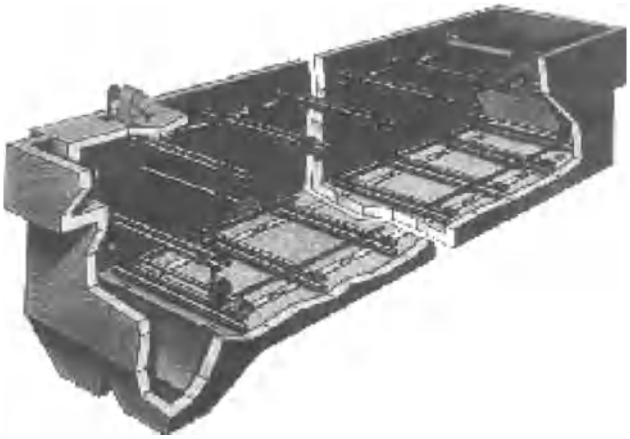

Figure 1. Rectangular sedimentation tank (*Source*: U.S. Filter).

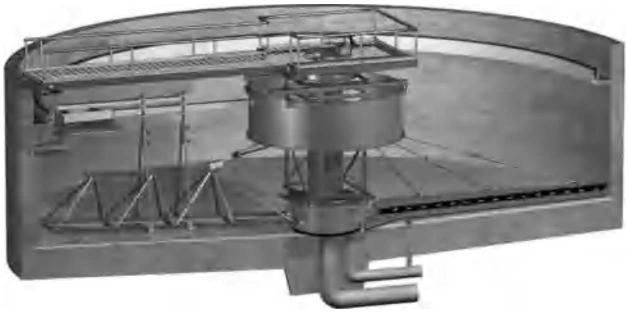

Figure 2. Circular sedimentation tank (*Source*: U.S. Filter).

or surface area. In reality, depth is important because it can affect flow stability if it is large and scouring if small. The basin depth affects flow-through velocity and plays a role in allowing greater opportunity for flocculant particle contact. Conventional settling facilities provided at larger water treatment plants are often long, narrow (4 or 5 to 1 length to width ratio) rectangular basins whose theoretical detention times are in the range of 1.5 to 3 hours at the design flow rate. Most regulatory agencies specify a minimum detention time and a maximum surface overflow rate. Typical sedimentation surface loading rates for long, rectangular tanks and circular tanks using alum coagulation vary from 500 to 1200 gallons per day per square feet (20 to 48 cubic meters per day per square meter). Regulatory agencies sometimes stipulate that weir rates should not exceed around 20,000 gallons per day per linear foot (250 cubic meters per day per meter) of weir. Flow-through velocities of 2 to 4 ft/min (0.6 to 1.2 m/min) are usually acceptable for basin depths of 7 to 14 ft (2.1 to 4.3 m).

Particulate matter settles out of a suspension in one of four different ways, depending on the concentration of the suspension and flocculating properties of the particles. The various settling regimes of particles are commonly referred to as types 1 to 4. In type 1 settling, also called discrete particle settling, the particles have little tendency to flocculate on contact with each other in a dilute suspension when settling. If the particles flocculate, the settling regime in a dilute suspension is identified as type 2 or flocculant settling. In hindered zone, or type 3 settling, the particle concentration causes interparticle effects, which might include flocculation, to the extent that the rate of settling is a function of solids concentration. Compression or type 4 settling develops under the layers of zone settling. The rate of compression depends on time and the force caused by the weight of solids above. In sedimentation, particulate matter removal is largely governed by types 1 and 2 settling. However, types 3 and 4 regimes are dominant in clarification and thickening processes.

High-rate settlers such as tube or plate settlers are often added to settling basins to improve their efficiency, especially if flows are to be increased beyond original design conditions (Figs. 3 and 4). The shallow settling depths and the large surface area provided by tube or plate settlers permit effective sedimentation at detention times of several minutes versus several hours in conventional sedimentation basins. The use of tube or plate settlers in new plant construction minimizes settling basin costs by minimizing the basin size necessary to attain a desired level of treatment. They are generally designed to accept overflow rates ranging from 1400 to 4000 gallons per day per sq foot (55 to 160 cubic meters per day per square meter).

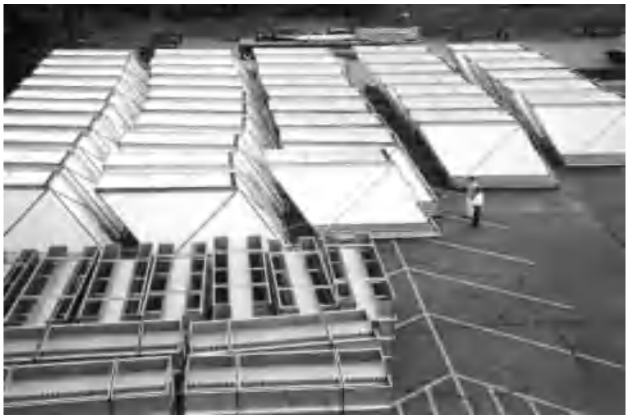

Figure 3. Plate settlers for installation (*Source*: U.S. Filter).

Figure 4. Installed plate settlers (*Source*: U.S. Filter).

In wastewater practice, sedimentation tanks are used in primary and in secondary treatment. They are called primary and secondary clarifiers. For sludge treatment, thickeners are used whose design is also based on sedimentation principles. However, the dominant settling regimes in wastewater treatment are clarification and thickening.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*, 3rd Edn. McGraw-Hill, New York.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*, 5th Edn. McGraw-Hill, New York.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold, New York.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000). *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

WATER HAMMER

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Water hammer refers to fluctuations caused by a sudden increase or decrease in flow velocity. These pressure fluctuations can be severe enough to rupture a water main. Potential water hammer problems should be considered when pipeline design is evaluated, and a thorough surge analysis should be undertaken, in many instances, to avoid costly malfunctions in a distribution system. Every major system design change or operation change—such as the demand for higher flow rates—should include consideration of potential water hammer problems. This phenomenon and its significance to both the design and operation of water systems is not widely understood, as evidenced by the number and frequency of failures caused by water hammer.

WHAT IS WATER HAMMER?

Water hammer (or hydraulic shock) is the momentary increase in pressure, which occurs in a water system when there is a sudden change of direction or velocity of the water. When a rapidly closed valve suddenly stops water flowing in a pipeline, pressure energy is transferred to the valve and pipe wall. Shock waves are set up within the system (Fig. 1). Pressure waves travel backward until encountering the next solid obstacle, then forward, then back again (Fig. 2). The pressure wave's velocity is equal to the speed of the sound; therefore it "bangs" as it travels back and forth, until dissipated by friction losses. Anyone who has lived in an older house is familiar with the "bang" that resounds through the pipes when a faucet is suddenly closed. This is an effect of water hammer.

A less severe form of hammer is called surge, a slow motion mass oscillation of water caused by internal pressure fluctuations in the system. This can be pictured as a slower "wave" of pressure building within the system. Both water hammer and surge are referred to as transient pressures. If not controlled, they both yield the same results: damage to pipes, fittings, and valves, causing leaks and shortening the life of the system. Neither the pipe nor the water will compress to absorb the shock.

INVESTIGATING THE CAUSES OF WATER HAMMER

A water transport system's operating conditions are almost never at a steady state. Pressures and flows change continually as pumps start and stop, demand fluctuates, and tank levels change. In addition to these normal events, unforeseen events, such as power outages and equipment malfunctions, can sharply change the operating conditions of a system. Any change in liquid flow rate, regardless of the rate or magnitude of change, requires that the liquid be accelerated or decelerated from its initial flow velocity. Rapid changes in flow rate require large forces that are seen as large pressures, which cause water hammer.

Entrained air or temperature changes of the water also can cause excess pressure in the water lines. Air trapped in the line will compress and will exert extra pressure on the water. Temperature changes will actually cause the water to expand or contract, also affecting pressure. The maximum pressures experienced in a piping system are frequently the result of vapor column separation, which is caused by the formation of void packets of vapor when pressure drops so low that the liquid boils or vaporizes. Damaging pressures can occur when these cavities collapse.

The causes of water hammer are varied. There are, however, four common events that typically induce large changes in pressure:

1. Pump startup can induce the rapid collapse of a void space that exists downstream from a starting pump. This generates high pressures.
2. Pump power failure can create a rapid change in flow, which causes a pressure upsurge on the suction side and a pressure downsurge on the discharge side. The downsurge is usually the major problem. The pressure on the discharge side reaches vapor pressure, resulting in vapor column separation.
3. Valve opening and closing is fundamental to safe pipeline operation. Closing a valve at the downstream end of a pipeline creates a pressure wave that moves toward the reservoir. Closing a valve in less time than it takes for the pressure surge to travel to the end of the pipeline and back is called "sudden valve closure." Sudden valve closure will change velocity quickly and can result in a pressure surge. The pressure surge resulting from a sudden valve opening is usually not as excessive.
4. Improper operation or incorporation of surge protection devices can do more harm than good. An example is oversizing the surge relief valve or improperly selecting the vacuum breaker-air relief valve. Another example is to try to incorporate some means of preventing water hammer when it may not be a problem.

FINDING PRACTICAL SOLUTIONS

The surge pressure must be incorporated with the operating pressure in the design of the pipe. The recommendations and requirements regarding allowances for surge pressure are given in the American Water Works (AWWA) standards and manuals for water supply practice, and vary depending on the type of pipe used. The following tools reduce the effects of water hammer.

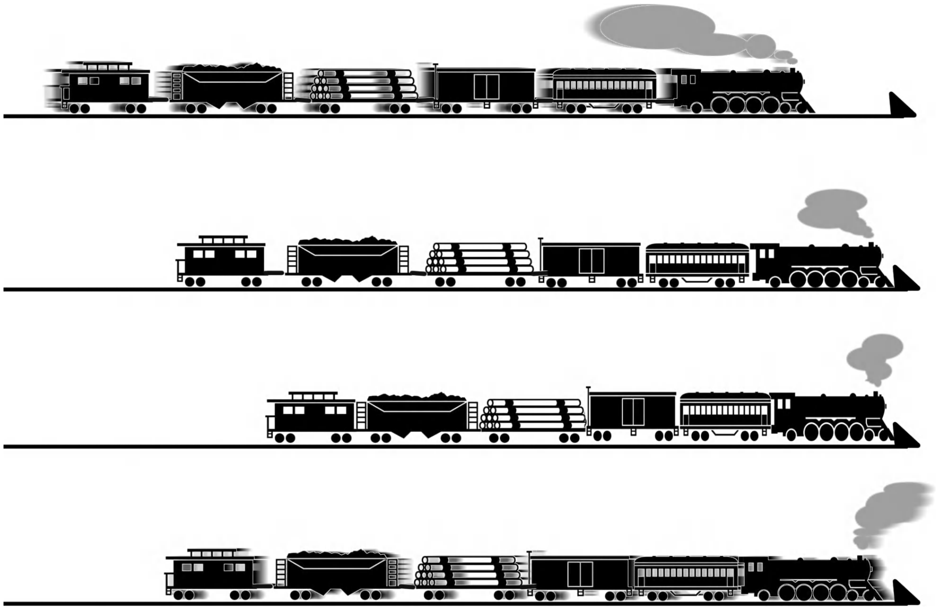


Figure 1. Illustration of water hammer. A column of water acts like a freight train suddenly stopping when an outlet valve is suddenly closed. *Source*: Pickford, John. 1969. *Analysis of Water Surge.* Gordon and Breach Science Publishers.

VALVES

Water hammer often damages centrifugal pumps when electrical power fails. In this situation, the best form of prevention is to have automatically-controlled valves, which close slowly. (These valves do the job without electricity or batteries. The direction of the flow controls them.) Closing the valve slowly can moderate the rise in the pressure when the downsurge wave—resulting from the valve closing—returns from the reservoir.

Entrained air or temperature changes of the water can be controlled by pressure relief valves, which are set to open with excess pressure in the line and then closed when pressure drops. Relief valves are commonly used in pump stations to control pressure surges and to protect the pump station. These valves can be an effective method of controlling transients. However, they must be properly sized and selected to perform the task for which they are intended without producing side effects.

If pressure may drop at high points, an air and vacuum relief valve should be used. All downhill runs where pressure may fall very low should be protected with vacuum relief valves. Vacuum breaker-air release valves, if properly sized and selected, can be the least expensive means of protecting a piping system. A vacuum breaker valve should be large enough to admit sufficient quantities of air during a downsurge so that the pressure in the pipeline does not drop too low. However, it should not be so large that it contains an unnecessarily large volume of air, because this air will have to be vented slowly, increasing the downtime of the system. The sizing of air release valves is, as mentioned, critical.

PUMP

Pump startup problems can usually be avoided by increasing the flow slowly to collapse or flush out the voids gently. Also, a simple means of reducing hydraulic surge pressure is to keep pipeline velocities low. This not only results in lower surge pressures, but results in lower drive horsepower and, thus, maximum operating economy.

SURGE TANK

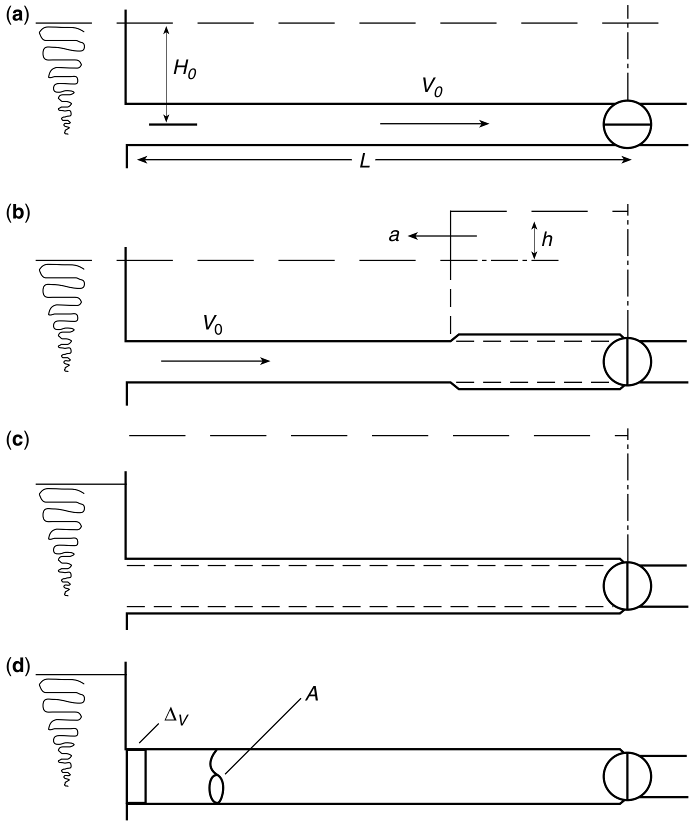
In long pipelines, surge can be relieved with a tank of water directly connected to the pipeline called a “surge tank.” When surge is encountered, the tank will act to relieve the pressure, and can store excess liquid, giving the flow alternative storage better than that provided by expansion of the pipe wall and compression of the fluid. Surge tanks can serve for both positive and negative pressure fluctuations. These surge tanks can also be designed to supply fluid to the system during a downsurge, thereby preventing or minimizing vapor column separation. However, surge tanks may be an expensive surge control device.

AIR CHAMBER

Air chambers are installed in areas where water hammer is encountered frequently, and are typically seen behind sink and tub fixtures. Shaped like thin, upside-down bottles with a small orifice connection to the pipe, they are air-filled. The air compresses to absorb the shock, protecting the fixture and piping.

CONCLUSION

Water hammer will continue to challenge engineers, operators, and managers of water systems because it is associated with systems that cannot be exactly defined due to the size and length of the water distribution system with ondulating profile or the lack of definition of the system components such as valves or pumps. There is a need for a more practical approach while research continues



(a)
Valve in open position.

(b)
Valve is shut. A pressure wave moves upstream with velocity "a". At the same time water still enters the pipe with velocity V_0.

(c)
Wave front continues upstream until it reaches the end taking time L/a to reach there. The time 2*L*/a is known as the "period" of the pipe μ.

(d)
If the total quantity of water that enters the pipe during this time 1/2 μ is ΔV then because it is moving with velocity V_0, $\Delta V = 1/2\ V_0 A\mu$. This whole extra volume of water is occupying the space ($A \times L$) where *A* is the cross section of the pipe. The resulting increase in pressure or "water hammer" pressure is $P = K\,\frac{\Delta V}{\Delta L}$

Figure 2. Sudden valve closing. *Source*: Pickford, John. 1969. *Analysis of Water Surge.* Gordon and Breach Science Publishers.

to provide better descriptions of the physics of water hammer and for useful computational solutions including those basics.

WHERE CAN I FIND MORE INFORMATION?

Kroon, J. R., M. A. Stoner, and W. A. Hunt. 1984. "Water Hammer: Causes and Effects." *Journal of the American Water Works Association.* 76: 39–45.

National Drinking Water Clearinghouse. 2001. "Ask the Experts." *On Tap.* Vol. 1, Issue 3: 10–11.

Parmakian, J. 1963. *Waterhammer Analysis*. Dover Publications.

Sharp, B.B. and D. B. Sharp. 1996. *Water Hammer: Practical Solutions.* New York: Halsted Press.

Weis, F. 1996. "Dispelling Common Misconceptions about Water Hammer." *Water Engineering and Management.* 143: 24–30.

Wood, D. J. 2002. SURGE2000 Software. (Modeling water hammer in pipes and a wide range of hydraulic and surge protection devices are addressed). Civil Engineering Software Center, University of Kentucky Lexington, KY.

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HEALTH EFFECTS OF COMMONLY OCCURRING DISINFECTION BYPRODUCTS IN MUNICIPAL WATER SUPPLIES

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Disinfectants, such as chlorine, chlorine dioxide, chloramine, and ozone, have been used in drinking water treatment plants throughout the world to disinfect source waters containing disease-causing pathogens. The noteworthy biocidal properties of the disinfectants are somewhat offset by the formation of disinfection byproducts (DBPs) through reactions between the disinfectants and the dissolved organic and inorganic chemicals in raw water.

From the present knowledge of occurrence and health effects, the DBPs of most interest are halomethanes, including trihalomethanes (THMs), haloacetic acids (HAAs), bromate, chlorate, and chlorite, followed by haloacetonitriles, haloacetaldehydes, haloketones, and halonitromethanes (1). In addition, a number of epidemiological studies exist that indicate an association between chronic ingestion of drinking water containing DBPs and increased risk of rectal, bladder, or colon cancer in humans (2–5), but these studies cannot provide information on whether the observed health effects are because of one or more of the hundreds of other DBPs that are also present in drinking water.

Health effects on humans (if available) and animals including general, immunological, neurological, reproductive, and developmental toxicity; mutagenicity [based on the *Salmonella typhimurium* assay (6)]; and carcinogenicity associated with oral exposure to some commonly occurring DBPs are summarized in the sections below. A majority of the health effects observed in these studies were because of exposure to single chemicals at dose levels much above those typically found in drinking water. Hence, health effects associated with drinking water, which typically contains mixtures of DBPs, may be different from those mentioned below.

HALOMETHANES

Data on the health effects of non-THMs are available to a limited extent in the literature. However, THMs, which have been fairly well studied in the literature, are known to induce cytotoxicity in the liver and kidneys of rodents, and to cause cancer in the liver, kidneys, and the large intestine. Most THMs do not induce reproductive or developmental toxicity. In addition, halomethanes are considered to be weak mutagens. Health effects of halomethanes are summarized below.

Chloromethane

Although inhalation of chloromethane may cause damage to the lung and kidneys, no data are currently available for carcinogenic, reproductive, developmental, neurological, and immunotoxicity endpoints because of oral exposures in humans or animals. Chloromethane tested positive for mutagenicity in the *Salmonella typhimurium* assay (7).

Bromomethane

As in the case of chloromethane, direct inhalation of bromomethane may cause seizures and kidney and nerve damage (8). No data exist on health effects because of human oral exposure in the literature. However, limited evidence exists that chronic exposure to bromomethane may occasionally lead to neoplasia in the forestomach at high concentrations in rats (9). At concentrations of 0.4 mg/kg/day (~40 mg/L) or less, no evidence existed of significant adverse effects in rats (9). Bromomethane tested positive in the *Salmonella* mutagenicity assay (10).

Bromochloromethane

No data on the health effects of oral exposure to bromochloromethane in humans or animals are available in the literature. The only studies that were available in the literature were the *Salmonella* mutagenicity results, which were consistently positive for bromochloromethane (11).

Dibromomethane

No data on the health effects of oral exposure to dibromomethane in humans or animals are available in the literature. Various studies showed a positive response for mutagenicity as measured by the *Salmonella typhimurium* assay (12).

Chloroform

Limited data are available in the literature on death because of oral exposure to pure chloroform in both humans (13) and animals (14–17). Various studies have indicated the liver and kidney as the primary target organs of chloroform toxicity and have observed reversibility in toxic effects on cessation of exposure in both humans (13,18,19) and animals (20,21). However, the doses required to cause toxicity in the liver and kidney were high for both humans and animals. No indications of renal effects were observed in humans (22) and animals (21) because of ingestion of low doses of chloroform. No studies existed on the effect of chloroform exposure on immunological effects in the humans, whereas a few studies documented a reduction in immunity levels in animals exposed to chloroform (23,24). With respect to neurological effects, humans exposed to high concentrations of chloroform immediately fell into a deep coma (13,19), whereas the central nervous system was affected in animals (25,26). An epidemiologic study on drinking water consumption by the population of a small town in northern New Jersey between 1985 and 1988 noticed low birth weight among term babies (27). However, in addition to predominant amounts of chloroform in the drinking water, other THMs were also present in the town's water supply. An equivalent study on animals demonstrated increased resorptions among fetuses at high doses of chloroform in drinking water (20). Other epidemiologic studies have suggested an association between cancer in humans and consumption of chlorinated drinking water predominantly containing chloroform (28–31). However, no concrete evidence exists linking chloroform specifically to the increased incidence of cancer in those studies. In experiments with animals, chloroform has been reported to be carcinogenic in several chronic animal bioassays, with significant increases in the incidence of liver tumors in male and female mice and significant increases in the incidence of kidney tumors in male rats and mice (32,33).

Bromodichloromethane

No studies on the human health effects of bromodichloromethane because of oral exposure were available in the literature. In animals with acute exposures to bromodichloromethane, typical pathological changes observed include fatty infiltration of liver and hemorrhagic lesions in kidney, adrenals, lung, and brain (26). Animals orally exposed to bromodichloromethane show liver and kidney damage followed by death within 2 weeks. Typical signs include increased liver weight, pale discoloration of liver tissue, increased levels of hepatic tissue enzymes in serum, decreased levels of secreted hepatic proteins in blood, and focal areas of inflammation or degeneration (24,34–36). Rats and mice administered oral doses of 150 to 600 mg/kg often displayed acute signs of central nervous system depression, including lethargy, labored breathing, sedation, and flaccid muscle tone, but the signs were reversible several hours after cessation of exposure (25,34,37,38). Ruddick et al. (36) reported fetal and maternal toxicity effects on rats exposed to bromodichloromethane during gestation. With respect to cancer, several epidemiological studies have indicated that an association may exist between ingestion of chlorinated drinking water containing bromodichloromethane and increased risk of cancer in humans (4,5,39), but those studies could not assign the cause of cancer specifically to bromodichloromethane. However, chronic oral studies in animals provide evidence of liver and kidney tumors because of bromodichloromethane exposure (34,40,41).

Dibromochloromethane

No studies exist on human health effects because of oral exposure of dibromochloromethane in the literature. Significant increases in animal mortality have been reported because of acute, subchronic, and chronic oral exposure to dibromochloromethane in the literature (16,26,38,42,43). Typical sites of toxicity in animals exposed to dibromochloromethane include the central nervous system, liver, and kidney (26,43). Oral exposure to dibromochloromethane results in an accumulation of fat in the liver, hepatocyte vacuoles, alterations in serum cholesterol levels, and decreases in serum triglyceride levels followed by liver necrosis at higher doses (16,24,43,44). In addition, tubular regeneration and mineralization leading to nephrosis has been observed in both rats and mice (43). A few studies have examined the potential association between adverse human reproductive outcomes, including spontaneous abortions, stillbirths, and preterm delivery, and the consumption of municipal drinking water containing a mixture of THMs (27,45–53), but they have not been able to implicate dibromochloromethane specifically to the reproductive effects. However, animal studies show an association between reproductive effects and dibromochloromethane in drinking water at high doses. For example, female mice exposed to dibromochloromethane experienced a marked reduction in fertility, with significant decreases in litter size, body weight of the dam and the litter, gestational survival, and postnatal survival (54). Various studies have reported increased incidences of hepatocellular adenomas and carcinomas in mice exposed to dibromochloromethane [summarized in (43)], leading the EPA to classify the chemical as a possible human carcinogen (55).

Bromoform

Several studies in the literature have documented deaths of children because of accidental overdoses of bromoform (when used as a sedative) leading to severe central nervous system depression and respiratory failure (56–58). As in the case of dibromochloromethane, the central nervous system and the liver seem to be the primary sites for bromoform-induced toxicity in animals, leading to liver necrosis and slight nephrosis at higher doses (16,24,43,44). Animal studies that examined the potential of bromoform to induce histological alterations and impair reproductive function indicate that the chemical does not induce any reproductive or developmental effects (59,60). With respect to cancer, an increased incidence of tumors and neoplastic lesions in the large intestines after oral administration of bromoform in rats and intraperitoneal administration in mice was observed, leading the EPA to classify the chemical as a probable human carcinogen (61).

Iodinated THMs

Recently, several iodinated THMs, such as dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane, and iodoform, have been identified in finished water at a few water treatment plants across the United States (1). No human or animal toxicity information on any of the iodinated THMs are available in the literature except for a positive response in the *Salmonella* mutagenicity assay and a negative response for carcinogenicity in mice for iodoform (62).

HALOACETIC ACIDS

Most haloacetic acids of concern have carcinogenic, reproductive, and developmental effects, whereas neurotoxic effects are significant when high doses are used for therapeutic purposes. Carcinogenic effects seem to be limited to the liver at high doses. The health effects of the HAAs are summarized below.

Chloroacetic Acid

Acute exposure of chloroacetic acid by humans may lead to interference with essential enzyme systems in the body, leading to intestinal perforation and peritonitis (63). Rodents exposed to chloroacetic acid orally or by gavage exhibited neurological dysfunction, damage to the respiratory tract including inflammation of the lung and nasal mucosa, metaplasia of the olfactory epithelium, and squamous cell hyperplasia of the forestomach (33,64). In addition, chronic exposure to chloroacetic acid via gavage resulted in myocarditis and mortality because of myocardial failure in rats and hepatic vacuolar degeneration in mice (33,64). No information on the reproductive or developmental effects of chloroacetic acid in animals or humans is available in the literature. With respect to cancer, no significant increase in tumor incidences were reported in studies involving rats and mice exposed to chloroacetic acid (64). In addition, chloroacetic acid was not mutagenic in the *Salmonella typhimurium* assay (64).

Bromoacetic Acid

No studies exist on human health effects because of oral exposure to bromoacetic acid in the literature. Acute exposure of rats to bromoacetic acid lead to various clinical symptoms including excess drinking water intake, hypomobility, labored breathing, and diarrhea (65). No adverse reproductive effects were observed in a spermatotoxicity study involving male rats (65), but developmental effects were observed at high doses in rats (66). Carcinogenic effects of bromoacetic acid have not been evaluated, but the chemical was found to be positive for mutagenicity in the *Salmonella typhimurium* assay (67).

Dichloroacetic Acid

Dichloroacetic acid has been shown to have some beneficial effects in curing a variety of metabolic diseases in humans (68–72). No evidence exists of adverse effects because of acute exposures or exposures at low concentrations in humans. However, limited human experiments coupled with animal studies have indicated that dichloroacetic acid is neurotoxic to humans (70,73). Animals exposed to dichloroacetic acid have been shown to produce developmental, reproductive, neural, and hepatic effects at high doses. Short-term exposure to dichloroacetic acid produced hind-limb paralysis at the highest dose in rats, whereas a significant increase occurred in relative liver and kidney weights and histopathological changes in the brain and testes of dogs (74,75). Reproductive effects include testicular toxicity manifested by distorted sperm heads, fused sperm, and reduced sperm counts in rats exposed to high doses of dichloroacetic acid (75,76), whereas a degeneration of the testicular epithelium and syncytial giant cell formation was noticed in dogs, even at low doses (74). Developmental effects include soft tissue abnormalities in the fetus, interventricular septal defects between the aorta and right ventricle, and urogenital defects in rats (77,78). With respect to cancer, dichloroacetic acid has been shown to be a very effective inducer of hepatic adenomas and carcinomas in both mice and rats at high doses (79–83), thus prompting the EPA to classify the chemical as possibly carcinogenic to humans (84).

Bromochloroacetic Acid

No studies exist on human health effects because of oral exposure to bromochloroacetic acid in the literature. No treatment-related differences in body weight, food and water consumption, clinical observations, or mortality were reported in rats exposed to bromochloroacetic acid for 14 days (85). However, mice showed liver effects including hepatomegaly, glycogen accumulation, and cytomegaly (86). No reproductive, developmental, or embryo toxicity effects were observed in rats treated with low doses of bromochloroacetic acid in a 35-day study (85). However, bromochloroacetic acid at high doses (>600 ppm) produced a consistent decrease in water consumption in both sexes of rats and affected reproductive function in females of both rats and mice (87,88). No data on carcinogenicity were available in the literature; however, bromochloroacetic acid was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (89).

Dibromoacetic Acid

Acute exposures of high doses of dibromoacetic acid by rats lead to several clinical symptoms including excess drinking water intake, hypomobility, labored breathing, diarrhea, and ataxia (65). In addition, histopathological examination of epididymal sperm in surviving animals showed the presence of misshapen and degenerating sperm, and abnormal retention of spermatids (65,90). Male mice exposed to dibromoacetic acid showed an increase in absolute and relative liver weights at doses greater than 125 mg/kg/d (91), whereas female mice showed body weight gain, decrease in thymus weights at 236 mg/kg/d, and increased liver and kidney weights at all tested doses (92). Reproductive effects because of dibromoacetic acid exposure in male rats include adverse effects on caput-sperm count, sperm morphology, and sperm motility, but only marginal changes in reproductive organ weights (90) and decreased fertility as measured by the number of copulations, number of litters, and number of implants and fetuses per litter (93). Immunological effects because of dibromoacetic acid exposure in animals include changes in spleen cell numbers and spleen cell populations, as well as alteration in natural killer cell activity and an antibody-forming cell response to sheep erythrocytes (92). No data on carcinogenicity were available in the literature; however, dibromoacetic acid was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (93).

Trichloroacetic Acid

Acute exposures to trichloroacetic acid by humans can cause severe burning in the mouth, pharynx, and abdomen, and low blood pressure followed by vomiting and diarrhea (94). Animals exposed to high doses of trichloroacetic acid showed liver and kidney effects, including significant increases in relative kidney weight and hepatic peroxisomal beta oxidation activity, and focal areas of hepatocellular hypertrophy and narcosis (95). At lower doses typical of concentrations in drinking water, trichloroacetic acid has been shown to seriously impair water and food consumption (79,81,96,97) and cause liver effects (79,97–99) in experimental animals. Trichloroacetic acid has also been shown to produce reproductive and developmental effects at very high doses in experimental animals, but no effects have been observed at drinking water concentration levels (100–102). With respect to cancer, trichloroacetic acid induces hepatocellular carcinomas, dose-related increases in the incidence of malignant tumors, and precancerous lesions when administered in drinking water to male B6C3F1 mice (79,82,103), but not in rats (104). In addition, trichloroacetic acid has been shown to be negative for mutagenicity in the *Salmonella typhimurium* assay (105).

Bromodichloroacetic Acid

No studies exist on the health effects on humans, and limited studies exist on the health effects on animals, because of oral exposure to bromodichloroacetic acid in the literature. Narotsky et al. (87) reported no maternal toxicity but some developmental toxicity (reduced pup weights) in mice at the highest dose tested. In the only other study (unpublished) available, Bull reported the observance of liver and lung tumors in mice exposed to bromodichloroacetic acid (106). In addition, bromodichloroacetic acid was shown to be weakly positive for mutagenicity in the *Salmonella typhimurium* assay (107).

Dibromochloroacetic Acid

No studies exist on the health effects on humans, and one short-term reproductive and developmental study exists on animals, because of oral exposure to dibromochloroacetic acid in the literature. Results from the reproductive study on rats indicate that although dibromochloroacetic acid produced consistent decreases in food and water consumption in both sexes at doses above 1000 ppm, it did not result in any female reproductive toxicity or any visceral malformation or variations in any pups (108).

Tribromoacetic Acid

No studies exist on the health effects on humans, and one short-term reproductive and developmental study exists on animals, because of oral exposure to tribromoacetic acid in the literature. Results from this reproductive study indicate that tribromoacetic acid at up to 400 ppm marginally reduced water consumption, but it did not affect reproductive function or produce general toxicity in rats of either sex (109). In addition, tribromoacetic acid was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (110).

HALOACETONITRILES

The toxicological effects of haloacetonitriles have not been well studied to date. Although very limited studies exist on the carcinogenicity of this group of chemicals, results of *Salmonella typhimurium* mutagenicity assays are available in the literature. The known health effects of haloacetonitriles are summarized below.

Chloroacetonitrile

No human health studies because of oral chloroacetonitrile exposure are available in the literature. Among the haloacetonitriles, chloroacetonitrile was shown to be metabolized to cyanide in rats and excreted as thiocyanate to the greatest extent (111). Chloroacetonitrile was shown to induce cytotoxic effects and oxidative stress in cultured rat gastric epithelial cells *in vitro* (112). In rat studies, slight decreases in maternal weight gain occurred during the treatment period and in the birth weights of pups born to rats given 55-mg/kg chloroacetonitrile orally on gestation days 7–21 (113). No other evidence of developmental or reproductive effects was reported in the literature. The IARC evaluated the carcinogenic potential of chloroacetonitrile and concluded that inadequate evidence exists for classification purposes, and they were hence assigned to group 3: The agent is not classifiable as to its carcinogenicity to humans (113,114). In addition, chloroacetonitrile was shown to be negative for mutagenicity in the *Salmonella typhimurium* assay (115).

Bromoacetonitrile

No human health studies because of oral bromoacetonitrile exposure are available in the literature. Rats exposed to high doses of bromoacetonitrile (>500 ppm) in drinking water resulted in significant reductions in body weight and reductions in feed and water consumption (116). At lower doses, study results indicated that a significant aversion to bromoacetonitrile in the water existed and suggested that the chemical may be a possible mild renal toxicant at 100 ppm as evidenced by an increase in blood urea nitrogen, and a potential reproductive toxicant at the same dose as evidenced by increased post-implantation loss (116). No studies on the carcinogenicity potential of bromoacetonitrile are available in the literature. However, bromoacetonitrile was shown to be negative for mutagenicity in the *Salmonella typhimurium* assay (117).

Dichloroacetonitrile

No human health studies because of oral dichloroacetonitrile exposure are available in the literature. In rats exposed to dichloroacetonitrile in corn oil by gavage, increased mortality was observed at 33-mg/kg/d dose, whereas decreased body weight, lower organ weight, and organ-to-body weight ratios were observed for spleen and gonads at higher doses (118). However, no serum chemistry changes indicative of adverse effects were seen at sublethal doses (118). Reproductive effects in rats because of dichloroacetonitrile exposure by gavage during gestation include significantly reduced percentage of females delivering litters, increased resorption rates, reduced mean birth weight of pups, and reduced maternal weight gain (119). Developmental effects in rats exposed to dichloroacetonitrile resulted in soft tissue anomalies, including an intraventricular septal defect in the heart, hydronephrosis, fused ureters and cryptorchidism, and skeletal abnormalities such as fused and cervical ribs (120). The IARC evaluated the carcinogenic potential of dichloroacetonitrile and concluded that inadequate evidence exists for classification purposes, and they were hence assigned to group 3: The agent is not classifiable as to its carcinogenicity to humans (113,114). However, dichloroacetonitrile was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (121).

Bromochloroacetonitrile

No human health effect studies because of oral bromochloroacetonitrile exposure are available in the literature. In rats exposed to bromochloroacetonitrile in corn oil by gavage, reduced mean birth weight of pups and reduced postnatal weight gain were observed to a much lesser extent than rats exposed to dichloroacetonitrile (119). Christ et al. (122) reported maternal toxicity and urogenital, skeletal malformations at doses above 65 mg/kg/d and total litter loss at 45 mg/kg/d in rats, whereas lower doses resulted in shorter fetal crown-rump lengths, reduced fetal weights, and increased frequency of cardiovascular malformations. Female mice treated with bromochloroacetonitrile showed a significant increase in the incidence of lung adenomas; however, the authors cautioned that a large variation in background incidence of lung tumors was also observed in the same species (123). However, bromochloroacetonitrile was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (124).

Dibromoacetonitrile

No human health effect studies because of oral dibromoacetonitrile exposure are available in the literature. In rats exposed to dibromoacetonitrile in corn oil by gavage, increased mortality was observed at 45-mg/kg/d dose (118). However, no serum chemistry changes indicative of adverse effects were seen at sublethal doses (118). Reproductive effects in rats exposed to dibromoacetonitrile were similar to effects observed in rats exposed to bromochloroacetonitrile (119). In addition, exposure to dibromoacetic acid reduced water consumption in male and female rats exposed to doses greater than 50 ppm; however, no other reproductive effects were observed in the animals (125). Female mice treated with dibromoacetonitrile showed only a marginal increase in the incidence of lung adenomas (123). In addition, dibromoacetonitrile was shown to be weakly positive for mutagenicity in the *Salmonella typhimurium* assay (126).

Trichloroacetonitrile

No human health effect studies because of oral trichloroacetonitrile exposure are available in the literature. Reproductive effects in rats because of trichloroacetonitrile exposure by gavage during gestation include a significantly reduced percentage of females delivering litters, increased resorption rates, reduced mean birth weight of pups, and reduced maternal weight gain (119). Developmental effects observed in rats include embryolethality with doses as low as 7.5 mg/kg/d and soft tissue abnormalities, including fetal cardiovascular anomalies and cardiovascular and urogenital malformations with a 15-mg/kg/d dose (127). Female mice treated with trichloroacetonitrile showed a significant increase in the incidence of lung adenomas; however, the authors cautioned that a large variation in background incidence of lung tumors was also observed in the same species (123). In addition, trichloroacetonitrile was shown to be weakly positive for mutagenicity in the *Salmonella typhimurium* assay (128).

HALOACETALDEHYDES AND HALOKETONES

Trichloroacetaldehyde is the most common haloacetaldehyde found in drinking water. Other acetaldehydes and haloketones found at low concentrations include dichloroacetaldehyde, bromochloroacetaldehyde and tribromoacetaldehyde, chloropropanone, and di-, tri-, and tetrahalopropanones. Limited toxicity data are available for the halogenated aldehydes and ketones other than trichloroacetaldehyde. Chloroacetaldehyde exposure causes hematological effects (129) and liver tumors (130) in rats. Exposure of mice to 1,1-dichloropropanone resulted in liver toxicity (131). Some halogenated aldehydes and ketones are potent inducers of mutations in bacteria (132–139). Other halogenated aldehydes, e.g., 2-chloropropenal, have been identified as tumor initiators in the skin of mice (131). The haloketones have not been tested for carcinogenicity in drinking water. However, 1,3-DCPN acted as a tumor initiator in a skin carcinogenicity study in mice (131). The health effects of trichloroacetaldehyde are summarized below.

Trichloroacetaldehyde Monohydrate

The primary effect seen with ingestion of trichloroacetaldehyde monohydrate or chloral hydrate in humans is central nervous system depression, the basis of its use in therapeutics (140–142). At high doses, chloral hydrate produces cardiac arrhythmias (141–144) and liver damage (140,145), whereas at lower doses, high incidences of direct hyperbilirubinemia were observed in newborns (146). In animals, hepatocellular necrosis has been observed in rats dosed with 1200-mg/L chloral hydrate (147), whereas mice displayed hepatomegaly at a dose of 144-mg/kg/d chloral hydrate (148). In a reproductive study, Klinefelter et al. (149) observed a significant decrease in the percentage of motile sperm in rats exposed to 188-mg/kg/d chloral hydrate, whereas Saillenfait et al. (101) observed developmental effects *in vitro* using a rat whole-embryo culture system. A chronic bioassay in female mice showed a slight increase in the severity grade of hyperplasia and a slight increase in the incidence of adenoma in the pituitary gland pars distalis at the highest exposure tested, whereas some evidence existed that chloral hydrate causes hepatocellular tumors in male mice (150). As a result of a lack of human carcinogenic studies and inadequate animal studies, the EPA has classified chloral hydrate as a Group C or possible human carcinogen (151). In addition, chloral hydrate was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (152).

MISCELLANEOUS CHEMICALS

Many other DBPs that are found in low concentrations can be found in drinking water. DBPs whose health effects have been summarized below include MX, chloropicrin, and the inorganic chemicals bromate, chlorate, and chlorite.

MX (3-Chloro-4-(Dichloromethyl)-5-Hydroxy-2(5H)-Furanone)

No human health effect studies because of oral MX exposure are available in the literature. In acute animal studies, mice that died within 24 hours of receiving a dose of 128 mg/kg MX were found to have enlarged stomachs with moderate hemorrhagic areas in the forestomach (153). In a second study, very limited mortality was observed in mice administered a dose of 144 mg/kg (154). Other effects observed in the study included focal epithelial hyperplasia in the stomach, vacuolation of the superficial villus epithelium in the duodenum and jejunum, increased numbers of mitotic figures in the liver, and some cytotoxicity in the urinary bladder (154). Meier et al. (155) observed reduced hepatic levels of catalase, cytochrome P450 reductase, aminopyrine demethylase, and aromatic hydrocarbon hydroxylase, thereby leading to potential modifications of metabolism of various xenobiotics and endogenous biochemicals in rats exposed to 64-mg/kg/d MX for 14 days. Vaittinen et al. (156) observed some lethality, hypersalivation, wheezing respiration, emaciation, tangled fur, increased water consumption, decreased body weights and food consumption, elevated plasma cholesterol, increased relative weights in the liver and kidneys, and increased urine excretion in rats dosed with 75-mg/kg/d MX for 14 weeks. MX administered to rats in drinking water for 104 weeks showed dose-dependent increases in tumors of the lung, mammary gland, hematopoietic system, liver, pancreas, adrenal gland, and thyroid (157). In addition, chloral hydrate was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (158).

Chloropicrin

Humans exposed orally to chloropicrin produced severe nausea, vomiting, colic, diarrhea, respiratory problems, and sometimes death (159,160). Health effects in rats orally exposed to chloropicrin include significantly reduced mean body and thymus weights and death because of pulmonary complications at high doses and dose-related histological changes in the stomach including forestomach inflammation, necrosis, acantholysis, hyperkeratosis, and ulceration (161). Oral developmental and reproductive animal studies were not available in the literature, but an inhalational study on rats and rabbits reported developmental toxicity in both species manifested as reduced fetal body weight, and maternal toxicity manifested in rats by mortality, reduction in body weight gain, and, in rabbits, by mortality, abortion, and inhibition of body weight gain and food consumption (162). In cancer studies involving rats and mice, proliferative lesions of the squamous epithelium of the forestomach, including carcinoma, papilloma, acanthosis, and hyperkeratosis, were observed in the dosed animals (163). However, owing to the short survival time of the dosed animals, conclusive evidence of carcinogenicity could not be established (163). However, chloropicrin was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (164).

Chlorite

No treatment-related effects were observed in humans exposed to rising doses of chlorite in drinking water (165). Short-term toxicity studies in rats, mice, cats, and monkeys indicated oxidative stress and signs of hemolytic anemia with decreases in red blood cell count, hemoglobin concentration, and hematocrit (166–171). The study results also indicated that although the changes in the blood parameters decreased in severity with duration of exposure, signs of oxidative stress remained elevated. Reproductive and developmental effects because of 100-mg/kg/d chlorite exposure include reduced conception rate and number of pups alive at weaning in mice (172) and vaginal and urethral bleeding, decreased body weight and food consumption, and mortality in rats (173,174). However, no effects were observed in animals dosed with chlorite at drinking water concentration levels. Chronic oral studies in rats showed no evidence of carcinogenicity (175), whereas mouse studies showed an increase in liver and lung tumors in male mice (176,177). However, the relatively short study duration and high mortality in the controls made the study interpretation difficult, leading the EPA to classify chlorite as a Group D chemical: not classifiable as to human carcinogenicity because of inadequate data (151). However, chlorite was shown to be positive for mutagenicity in the *Salmonella typhimurium* assay (178).

Chlorate

There have been a few reports of chlorate poisoning with evidence of oxidative damage to erythrocytes, methemoglobin formation, and hemolytic anemia in humans (179–182). In animals, high acute doses of 1000 mg/kg/d or higher induced methemoglobinemia and discoloration of the kidneys in dogs (183,184), but no consistent effects were noted in rats exposed to 10-mg/kg/d chlorate for 12 months (168). In an NTP study on reproductive and developmental effects because of chlorate exposure, transient changes in maternal food intake, urinary color, and/or output were noted at >100 mg/kg/d, but clear evidence of maternal toxicity was observed only at doses greater than 475 mg/kg/d in the screening study (185). In addition, chlorate did not cause any significant treatment-related developmental toxicity under the conditions of this study. In the lone cancer study available in the literature, a statistically insignificant increase in incidence of renal cell tumors in the N-ethyl-N-hydroxyethylnitrosamine-initiated rats treated with sodium chlorate was observed, but no effect was observed with potassium chlorate (186). In addition, chlorite was shown to be negative for mutagenicity in the *Salmonella typhimurium* assay (187).

Bromate

Clinical signs of bromate poisoning in humans include anemia, hemolysis, renal failure, and hearing loss (188,189). Acute toxic effects of bromate in rats, mice, and hamsters include suppressed locomotor activity, ataxia, tachypnoea, hypothermia, diarrhea, lacrimation and piloerection, hyperemia of the stomach, congestion of lungs, and damage to renal tubules including necrosis in the proximal tubular epithelium (189). Elevated levels of glutamate-oxalate transaminase, glutamate-pyruvate transaminase, lactate dehydrogenase, alkaline phosphatase, and blood urea nitrogen were observed in blood samples of rats exposed to bromate for 13 weeks (189,190). An NTP study on reproductive and developmental toxicity in rats indicated no reproductive effects in females but suggested that bromate may be a selective male reproductive toxicant at 250-ppm dose or higher (191). Cancer studies on rats indicated tumors at multiple sites including the kidney, thyroid, and the peritoneum (175,176,192), leading the EPA to classify bromate as a probable human carcinogen (193). However, bromate was shown to be weakly positive for mutagenicity in the *Salmonella typhimurium* assay (178).

MODELED TOXICITY ESTIMATES

Quantitative structure activity relationships (QSARs) may be used to estimate toxicities of many DBPs that lack experimental data in the literature. Commercial QSAR software packages such as DEREK (LHASA Ltd., Leeds, UK), CASE and MULTICASE (MultiCase Inc., Cleveland, OH), COMPACT (School of Biological Sciences, University of Surrey, UK), HazardExpert (Compudrug Ltd., Budapest, Hungary), ONCOLOGIC (Logichem Inc., Boyertown, PA), and TOPKAT (Accelrys Inc., Birmingham, MA) are able to predict the toxicities of a wide variety of chemicals for a number of health endpoints. In this section, TOPKAT has been used to estimate various toxicological endpoints for DBPs of health concern. Table 1 lists the rodent carcinogenicity based on the weight of evidence, Salmonella mutagenicity, rat developmental toxicity, lethal dose that causes 50% mortality in a rat study population, and the lowest dose that causes an adverse effect in rats. The procedure for estimating the endpoints using TOPKAT and its potential limitations are listed in Venkatapathy et al. (195) and Moudgal et al. (196,197).

BIBLIOGRAPHY

1. Weinberg, H.S., Krasner, S.W., Richardson, S.D., and Thruston, Jr., A.D. (2002). The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study. National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA. EPA Report EPA/600/R-02/068.
2. Cantor, K.P., Hoover, R., Hartge, P. et al. (1987). Bladder cancer, drinking water source, and tap water consumption: A case-control study. *J. Natl. Cancer Inst.* **79**: 1269–1279.
3. Crump, K.S. (1983). Chlorinated drinking water and cancer: The strength of the epidemiologic evidence. In: *Water Chlorination: Environmental Impact and Health Effects*. Jolley, R.L., Brungs, W.A., Cotruvo, J.A. et al. (Eds.). *Vol. 4, Book 2. Environment, Health, and Risk*. Ann Arbor Science Publishers, Ann Arbor, MI, pp. 1481–1491.
4. Kanarek, M.S. and Young, T.B. (1982). Drinking water treatment and risk of cancer death in Wisconsin. *Environ. Health Perspect.* **46**: 179–186.
5. Marienfeld, C.J., Collins, M., Wright, H. et al. (1986). Cancer mortality and the method of chlorination of public drinking water: St. Louis City and St. Louis County, Missouri. *JEPTO* **7**: 141–158.
6. Mortelmans, K. and Zeiger, E. (2000). The Ames Salmonella/microsome mutagenicity assay. *Mutat. Res.* **455**(1–2): 29–60.
7. du Pont de Nemours. (1977). Mutagenic activity of methane, chloro- in the Salmonella/microsome assay. E.I. du Pont de Nemours and Company, Haskell Laboratory Report, Wilmington, DE.
8. ATSDR. (1992). *Toxicological Profile for Bromomethane*. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.
9. Danse, L.H., van Velson, F.L., and van der Heljden, C.A. (1984). Methylbromide: Carcinogenic effects in the rat forestomach. *Toxicol. Appl. Pharmacol.* **72**: 262–271.
10. Voogd, C.E., Knaap, A.G.A.C., Van der Heijden, C.A., and Kramers, P.G. (1982). Genotoxicity of methylbromide in short-term assay systems. *Mutat. Res.* **97**: 233.
11. Simmon, V.F. and Tardiff, R.G. (1978). Mutagenic activity of halogenated compounds found in chlorinated drinking water. *Water Chlorination: Environ. Health Eff. Proc. Conf.* **2**: 417–431.
12. Thier, R. et al. (1996). Human glutathione S-transferase T1-1 enhances mutagenicity of 1,2-dibromoethane, dibromomethane and 1,2,3,4-diepoxybutane in Salmonella typhimurium. *Carcinogenesis* **17**(1): 163–166.

Table 1. Toxicity Estimate of DBPs of Health Concern Using TOPKAT

DBP	Carcinogenicity[a]	Mutagenicity[b]	DTP[c]	LD$_{50}$[d]	LOAEL[e]
Halomethanes					
Chloromethane	Positive	Positive	Negative	1500	65.4
Bromomethane	Positive	Positive	Negative	622.9	71.2
Bromochloromethane	Negative	Positive	Ind[*]	1300	26
Dibromomethane	Positive	Positive	Positive	465.2	89.1
Chloroform	Positive	Negative	Negative	536.5	57.1
Bromodichloromethane	Positive	Negative	Negative	954.3	14
Dibromochloromethane	Positive	Negative	Negative	914.5	12.1
Bromoform	Positive	Positive	Negative	308.9	99.4
Dichloroiodomethane	Positive	Negative	Negative	1200	23.8
Bromochloroiodomethane	Negative	Negative	Negative	1600	4.7
Dibromoiodomethane	Positive	Positive	Negative	521.8	38.9
Chlorodiiodomethane	Positive	Negative	Negative	1300	34.1
Bromodiiodomethane	Positive	Positive	Negative	603.6	66.3
Iodoform	Negative	Positive	Negative	481.2	496.7
Carbon tetrachloride	Positive	Negative	Ind	2700	820.7
Tribromochloromethane	Positive	Negative	Negative	4500	158.5
Haloacetic acids					
Monochloroacetic acid	Negative	Negative	Positive	195.6	14.3
Monobromoacetic acid	Negative	Positive	Positive	1400	15.3
Dichloroacetic acid	Negative	Negative	Negative	1100	5.9
Bromochloroacetic acid	Negative	Positive	Negative	652.8	2.7
Dibromoacetic acid	Negative	Positive	Negative	867.3	19.9
Trichloroacetic acid	Ind	Negative	Positive	263.5	60.3
Bromodichloroacetic acid	Negative	Negative	Positive	164	28.8
Dibromochloroacetic acid	Negative	Ind	Positive	134.4	29
Tribromoacetic acid	Ind	Negative	Positive	162.9	62.3
Haloacetonitriles					
Chloroacetonitrile	Negative	Positive	Positive	194.5	0.645
Bromoacetonitrile	Negative	Positive	Positive	1100	0.6989
Dichloroacetonitrile	Positive	Positive	Positive	526.9	0.287
Bromochloroacetonitrile	Negative	Positive	Negative	305.1	0.0932
Dibromoacetonitrile	Positive	Positive	Positive	425.8	0.9403
Trichloroacetonitrile	Positive	Positive	Positive	757.7	4.5
Haloacetaldehydes					
Dichloroacetaldehyde	Negative	Positive	Negative	685.6	5.8
Bromochloroacetaldehyde	Negative	Positive	Negative	399	2.2
Trichloroacetaldehyde	Positive	Positive	Positive	966.1	72.2
Tribromoacetaldehyde	Positive	Ind	Positive	589.5	63.4
Haloketones					
Chloropropanone	Positive	Positive	Positive	283.6	47.5
1,1-Dichloropropanone	Positive	Positive	Negative	886.2	17.7
1,3-Dichloropropanone	Negative	Positive	Positive	70.5	77.3
1,1-Dibromopropanone	Positive	Positive	Negative	669	57.2
1,1,1-Trichloropropanone	Positive	Positive	Positive	511.5	169.2
1,1,3-Trichloropropanone	Negative	Positive	Negative	323.6	11.5
1-Bromo-1,1-dichloropropanone	Negative	Positive	Positive	312.1	89.7
1,1,1-Tribromopropanone	Positive	Positive	Positive	286.1	138.4
1,1,3-Tribromopropanone	Negative	Positive	Negative	2200	25.6
1,1,3,3-Tetrachloropropanone	Negative	Negative	Negative	1600	36.3
1,1,3,3-Tetrabromopropanone	Negative	Positive	Negative	596.5	62.6
Halonitromethanes					
Bromonitromethane	Negative	Positive	Positive	1500	0.8421
Dichloronitromethane	Negative	Negative	Negative	323.1	0.647
Dibromonitromethane	Negative	Positive	Negative	258.4	2.2
Chloropicrin	Ind	Ind	Positive	345.6	14.3

[a] Carcinogenicity based on Weight of Evidence characterization (194).

[b] Ames Mutagenicity.

[c] Developmental Toxicity Potential.

[d] Rat oral lethal dose (LD50) that causes mortality in 50% of an exposed population.

[e] Rat oral lowest observed adverse effect level—lowest dose that causes an adverse effect in an exposed population.

[*] Model was unable to determine positive or negative response unequivocally.

13. Schroeder, H.G. (1965). Acute and delayed chloroform poisoning. *Br. J. Anaesth.* **37**: 972–975.
14. Torkelson, T.R., Oyen, F., and Rowe, V.K. (1976). The toxicity of chloroform as determined by single and repeated exposure of laboratory animals. *Am. Ind. Hyg. Assoc. J.* **37**: 697–705.
15. Smyth, H.F., Jr., Carpenter, C.P., Weil, C.S. et al. (1962). Range-finding toxicity data: List VI. *Am. Ind. Hyg. Assoc. J.* **23**: 95–107.
16. Chu, I., Villeneuve, D.C., Secours, V.E. et al. (1982). Trihalomethanes: II. Reversibility of toxicological changes produced by chloroform, bromodichloromethane, chlorodibromomethane and bromoform in rats. *J. Environ. Sci. Health B.* **17**: 225–240.
17. NCI. (1976). Report on carcinogenesis bioassay of chloroform. Carcinogenesis Program, National Cancer Institute, Bethesda, MD.
18. Wallace, C.J. (1950). Hepatitis and nephrosis due to cough syrup containing chloroform. *Calif. Med.* **731**: 442–443.
19. Piersol, G.M., Tumen, H.J., and Kau, L.S. (1933). Fatal poisoning following the ingestion of chloroform. *Med. Clin. N. Am.* **17**: 587–601.
20. Thompson, D.J., Warner, S.D., and Robinson, V.B. (1974). Teratology studies on orally administered chloroform in the rat and rabbit. *Toxicol. Appl. Pharmacol.* **29**: 348–357.
21. Larson, J.L., Wolf, D.C., and Butterworth, B.E. (1993). Acute hepatotoxic and nephrotoxic effects of chloroform in male F-344 rats and female B6C3Fl mice. *Fundam. Appl. Toxicol.* **20**(3): 302–315.
22. De Salva, S., Volpe, A., Leigh, G. et al. (1975). Long-term safety studies of a chloroform-containing dentifrice and mouth-rinse in man. *Food Cosmet. Toxicol.* **13**: 529–532.
23. Chu, I., Villeneuve, D.C., Secours, V.E. et al. (1982). Toxicity of trihalomethanes: I. The acute and subacute toxicity of chloroform, bromodichloromethane, chlorodibromomethane and bromoform in rats. *J. Environ. Sci. Health B.* **17**: 205–224.
24. Munson, A.E., Sain, L.E., Sanders, V.M. et al. (1982). Toxicology of organic drinking water contaminants: Trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane. *Environ. Health Perspect.* **46**: 117–126.
25. Balster, R.L. and Borzelleca, J.F. (1982). Behavioral toxicity of trihalomethane contaminants of drinking water in mice. *Environ. Health Perspect.* **46**: 127–136.
26. Bowman, F.J., Borzelleca, J.F., and Munson, A.E. (1978). The toxicity of some halomethanes in mice. *Toxicol. Appl. Pharmacol.* **44**: 213–215.
27. Bove, F.J., Fulcomer, M.C., Klotz, J.B. et al. (1995). Public drinking water contamination and birth outcomes. *Amer. J. Epidemiol.* **141**(9): 850–862.
28. Alavanja, M., Goldstein, I., and Susser, M. (1978). A case control study of gastrointestinal and urinary tract cancer mortality and drinking water chlorination. In: *Water Chlorination, Environmental Impact and Health Effects*. Jolley, R.J., Gorchen, H., Hamilton, D.H., Jr. (Eds.). Ann Arbor Science Publications, Ann Arbor, MI, 395–409.
29. Cantor, K.P., Hoover, R., Mason, T.J. et al. (1978). Associations of cancer mortality with halomethanes in drinking water. *J. Natl. Cancer Inst.* **61**: 979–985.
30. Suarez-Varela, M.M. and Gonzalez, A.L. (1994). Chlorination of drinking water and cancer incidence. *J. Environ. Path. Toxicol. Onocol.* **13**(1): 39–41.
31. Young, T.B., Kanarek, M.S., and Tsiatis, A.A. (1981). Epidemiologic study of drinking water chlorination and Wisconsin female cancer mortality. *J. Natl. Cancer Inst.* **67**: 1191–1198.
32. U.S. EPA. (1994). Final Draft for the Drinking Water Criteria Document on Trihalomethanes. Prepared for Health and Ecological Criteria Division, Office of Science and Technology, Washington, DC. Under EPA Contract No. 68-C2-0139 by Clement International Corporation.
33. U.S. EPA. (1998). National primary drinking water regulations: Disinfectants and disinfection byproducts. Final Rule. *Fed. Reg.* **63**(241): 69406–69407.
34. NTP. National Toxicology Program. (1987). Toxicology and Carcinogenesis Studies of Bromodichloromethane (CAS No. 75-27-4) in F344/N Rats and B6C3F, Mice (Gavage Studies). NIH Publication No. 88–2537, TR-321, Research Triangle Park, NC.
35. Condie, L.W., Smallwood, C.L., and Laurie, R.D. (1983). Comparative renal and hepatotoxicity of halomethanes: ‘bromodichloromethane, bromoform, chloroform, dibromochloromethane and methylene chloride. *Drug Chem. Toxicol.* **6**: 563–578.
36. Ruddick, J.A., Villenueve, D.C., and Chu, I. (1983). A teratological assessment of four trihalomethanes in the rat. *J. Environ. Sci. Health B.* **18**: 333–349.
37. Aida, Y., Takada, K., Momma, J. et al. (1987). Acute and subacute toxicities of three trihalomethanes in rats (I). *J. Toxicol. Sci.* **12**: 585.
38. Chu, I., Secours, V., Marino, I. et al. (1980). The acute toxicity of trihalomethanes in male and female rats. *Toxicol. Appl. Pharmacol.* **52**: 351–353.
39. Gottlieb, M.S., Carr, J.K., and Morris, D.T. (1981). Cancer and drinking water in Louisiana: Colon and rectum. *Int. J. Epidemiol.* **10**: 117–125.
40. Tumasonis, C.F., McMartin, D.N., and Bush, B. (1985). Lifetime toxicity of chloroform and bromodichloromethane when administered over a lifetime in rats. *Ecotoxicol. Environ. Safety.* **9**: 233–240.
41. Dunnick, J.K., Eustis, S.L., and Lilja, H.S. (1987). Bromodichloromethane, a trihalomethane that produces neoplasms in rodents. *Cancer Res.* **47**: 5189–5193.
42. Hewitt, W.R., Brown, E.M., and Plaa, G.L. (1983). Acetone-induced potentiation of trihalomethane toxicity in male rats. *Toxicol. Lett.* **16**: 285–296.
43. NTP. (1985). Toxicology and Carcinogenesis Studies of Chlorodibromomethane (CAS No. 124-48-1) in F344/N Rats and B6C3F, Mice (Gavage Studies). Technical report series no. 282. NIH Publication No. 88–2538, Research Triangle Park, NC.
44. Aida, Y., Takada, K., Uchida, O. et al. (1992). Toxicities of microencapsulated tribromomethane, dibromochloromethane and bromodichloromethane administered in the diet to Wister rats for one month. *J. Toxicol. Sci.* **17**(3): 119–133.
45. Bove, F.J., Fulcomer, M., Klotz, J.B. et al. (1992). *Population-Based Surveillance and Etiological Research of Adverse Reproductive Outcomes and Toxic Wastes*. Report on phase 1V-B: Public drinking water contamination and birthweight, and selected birth defects. A case control study. New Jersey Department of Health, Trenton, NJ.
46. Bove, F., Shim, Y., and Zeitz, P. (2002). Drinking water contaminants and adverse pregnancy outcomes: A review. *Environ. Health Perspect.* **110**(Suppl 1): 61–74.

47. Dodds, L., King, W., Woolcott, C. et al. (1999). Trihalomethanes in public water supplies and adverse birth outcomes. *Epidemiology*. **10**(3): 233–237.
48. Kramer, M.D., Lynch, C.F., Isacson, P. et al. (1992). The association of waterborne chloroform with intrauterine growth retardation. *Epidemiology*. **3**: 407–413.
49. Mills, C.J. et al. (1998). Workshop report on health risks of drinking water chlorination by-products: Report of an expert working group, *Chronic Diseases in Canada*. **19**(3).
50. Nieuwenhuijsen, M.J., Toledano, M.B., Eaton, N. et al. (2000). Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: A review. *Occup. Environ. Med.* **57**(2): 73–85.
51. Savitz, D.A., Andrews, K.W., and Pastore, L.M. (1995). Drinking water and pregnancy outcome in central North Carolina: Source, amount, and trihalomethane levels. *Environ. Health Perspect.* **103**(6): 592–596.
52. Waller, K., Swan, S.H., Delorenze, G. et al. (1999). Trihalomethanes in drinking water and spontaneous abortion. *Epidemiology* **10**(2): 203–204.
53. Mills, W.B., Lew, C.S., and Loh, J.Y. (1998). Predictions of potential human health and ecological risks from power plant discharges of total residual chlorine and chloroform into rivers. *Environ. Sci. Technol.* **32**: 2162–2171.
54. Borzelleca, J.F. and Carchman, R.A. (1982). Effects of Selected Organic Drinking Water Contaminants on Male Reproduction. U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC. EPA 600/l-82-009. NTIS No. PB82-259847.
55. IRIS. (2004). Dibromochloromethane. U. S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/iris/subst/0222.htm.
56. Dwelle, E.H. (1903). Fatal bromoform poisoning. *JAMA* **41**: 1540.
57. Kobert, R. (1906). *Lehrbuch der Intaxikationen. II band. Spezieller teil*. Verlag Von Ferdinand Enke, Stuttgart, Germany, pp. 914–916.
58. von Oettingen, W.F. (1955). The Halogenated Aliphatic, Olefinic, Cyclic, Aromatic, and Aliphatic-aromatic Hydrocarbons Including the Halogenated Insecticides, their Toxicity and Potential Dangers. U.S. Department of Health, Education and Welfare, Public Health Service, Washington, DC, pp. 65–67.
59. NTP. (1989). Toxicology and Carcinogenesis Studies of Tribromomethane (Bromoform) (CAS No. 75-25-2) in F344/N Rats and B6C3F1 Mice (Gavage Studies). Technical report series no. 350. NIH Publication No. 88–2805, Research Triangle Park, NC.
60. NTP. (1989). Bromoform: Reproduction and Fertility Assessment in Swiss CD-1 Mice When Administered by Gavage. Report to National Toxicology Program. NTP-89-068. NTIS No. PB89-169254, Research Triangle Park, NC.
61. IRIS. (2004). Bromoform. U. S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/iris/subst/0214.htm.
62. NCI. (1978). Bioassay of Iodoform for Possible Carcinogenicity. Carcinogenesis Program, National Institute of Health, Bethesda, MD, NCI-CG-TR-110.
63. HSDB. Hazardous Substances Data Bank. (2004). U.S. Department of Health and Human Services. National Toxicology Information Program, National Library of Medicine, Bethesda, MD. Available at http://toxnet.nlm.nih.gov/.
64. NTP. (1992). Toxicology and Carcinogenesis Studies of Monochloroacetic Acid. (CAS no. 79-11-8) in F344/N Rats and B6C3F1 Mice (Gavage Studies). Department of Health and Human Services, Public Health Service, National Institutes of Health. NTP TR 396, Beltsville, MD.
65. Linder, R.E. et al. (1994). Acute spermatogenic effects of bromoacetic acids. *Fundam. Appl. Toxicol.* **22**: 422–430.
66. Randall, J.L. et al. (1991). Developmental effects of 2-bromoacetic acid in the Long Evans rat. *Teratology* **43**(5): 454.
67. NTP. National Toxicology Program. (2000). Water disinfection byproducts (bromoacetic acid). Available at http://ntpserver.niehs.nih.gov/htdocs/Results_Status/Resstatb/M920034.html.
68. Crabb, D.W., Yount, E.A., and Harris, R.A. (1981). The metabolic effects of dichloroacetate. *Metabolism* **30**: 1024–1039.
69. Coude, F.X. et al. (1978). Dichloroacetate as treatment for congenital lactic acidosis. *N. Engl. J. Med.* **299**: 1365–1366.
70. Stacpoole, P.W. (1989). The pharmacology of dichloroacetate. *Metabolism* **38**: 1124–1144.
71. Stacpoole, P.W. and Greene, Y.J. (1992). Dichloroacetate. *Diabetes Care* **15**: 785–791.
72. Toth, P.P. et al. (1993). Transient improvement of congenital lactic acidosis in a male infant with pyruvate decarboxylase deficiency treated with dichloroacetate. *J. Pediatr.* **123**: 427–430.
73. Moore, G.W. et al. (1979). Reduction of serum cholesterol in two patients with homozygous familial hypercholesterolemia by dichloroacetate. *Atherosclerosis* **33**: 285–293.
74. Cicmanec, J.L., Condie, L.W., Olson, G.R., and Wang, S.R. (1991). 90-day toxicity study of dichloroacetate in dogs. *Fundam. Appl. Toxicol.* **17**: 376–389.
75. Katz, R. et al. (1981). Dichloroacetate, sodium: 3-month oral toxicity studies in rats and dogs. *Toxicol. Appl. Pharmacol.* **57**: 273–287.
76. Toth, G.P. et al. (1992). Adverse male reproductive effects following subchronic exposure of rats to sodium dichloroacetate. *Fundam. Appl. Toxicol.* **19**: 57–63.
77. Epstein, D.L. et al. (1992). Cardiopathic effects of dichloroacetate in the fetal Long-Evans rat. *Teratology*. **46**: 225–235.
78. Smith, M.K., Randall, J.L., Read, E.J., and Stober, J.A. (1992). Developmental toxicity of dichloroacetate in the rat. *Teratology*. **46**: 217–223.
79. Bull, R.J. et al. (1990). Liver tumor induction in B6C3F1 mice by dichloroacetate and trichloroacetate. *Toxicology*. **63**: 341–359.
80. Daniel, F.B. et al. (1992). Hepatocarcinogenicity of chloral hydrate, 2-chloroacetaldehyde, and dichloroacetic acid in male B6C3F1 mouse. *Fundam. Appl. Toxicol.* **19**: 159–168.
81. DeAngelo, A.B., Daniel, F.B., Stober, J.A., and Olson, G.R. (1991). The carcinogenicity of dichloroacetic acid in the male B6C3F1 mouse. *Fundam. Appl. Toxicol.* **16**: 337–347.
82. Herren-Freund, S.L., Pereira, M.A., Khoury, M.D., and Olson, G. (1987). The carcinogenicity of trichloroethylene and its metabolites, trichloroacetic acid and dichloroacetic acid, in mouse liver. *Toxicol. Appl. Pharmacol.* **90**: 183–189.
83. Pereira, M.A. (1996). Carcinogenic activity of dichloroacetic acid and trichloroacetic acid in the liver of female B6C3F1 mice. *Fundam. Appl. Toxicol.* **31**: 192–199.
84. IRIS. (2004). Dichloroacetic acid. U. S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/iris/subst/0654.htm.
85. NTP. National Toxicology Program. (1998). Bromochloroacetic Acid: Short Term Reproductive and Developmental

Toxicity Study When Administered to Sprague-Dawley Rats in the Drinking Water. Final report. R.O.W. Sciences, Inc. R.O.W. Sciences Study No. 7244-301; NTP/NIEHS No.: NO1-ES-75409; NTP-RDGT No.:1998, 96-001, Gaithersburg, MD.

86. Bull, R.J. and DeAngelo, A.B. (1995). *Carcinogenic Properties of Brominated Haloacetates—Disinfection by-products in Drinking Water: Critical Issues in Health Effects Research*. International Life Sciences Institute, Washington, DC, p. 29.
87. Narotsky, M.G., Best, D.S., Rogers, E.H., and Hunter, E.S. (2001). Developmental effects of disinfectant by-products bromoform, bromodichloromethane, bromodichloroacetic acid, and bromochloroacetic acid in mice. *Teratology* **63**(6): 279.
88. Wolfe, G.W., Kaiser, L.B., Mowry, R.N., Klinefelter, G., Hunter, E.S., and Chapin, R.E. (1998). Final Report on the Short Term Reproductive and Developmental Toxicity of Bromochloroacetic Acid (CAS #5589-96-8) Administered in Drinking Water to Sprague-Dawley Rats. NTIS Technical Report (NTIS/PB98-172414) (NTP/RDGT-96001), p. 222.
89. NTP. National Toxicology Program. (2000). Water disinfection byproducts (bromochloroacetic acid). Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatw/M980085.html.
90. Linder, R.E. et al. (1994). Spermatotoxicity of dibromoacetic acid in rats after 14 daily exposures. *Reprod. Toxicol.* **8**(3): 251–259.
91. Parrish, J.M. et al. (1996). Haloacetate-induced oxidative damage to DNA in the liver of male B6C3F1 mice. *Toxicology*. **110**: 103–111.
92. NTP. National Toxicology Program. (White, K.L. and Munson, J.A.). (1999). Immunotoxicity of Dibromoacetic Acid in Female B6C3F1 Mice. Final report, Medical College of Virginia, Richmond, VA.
93. NTP. National Toxicology Program. (2000). Water disinfection byproducts (dibromoacetic acid). Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatw/M960093.html.
93. Linder, R.E. et al. (1995). Dibromoacetic acid affects reproductive competence and sperm quality in the male rat. *Fundam. Appl. Toxicol.* **28**: 9–17.
94. Dreisbach, R.H. (1977). *Handbook of Poisoning*, 9th Edn. Lange Medical Publications, Los Altos, CA.
95. ACGIH. (1991). *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th Edn. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.
96. Davis, M.E. (1990). Subacute toxicity of trichloroacetic acid in male and female rats. *Toxicology* **63**: 63–72.
97. Mather, G.G., Exon, J.H., and Koller, L.D. (1990). Subchronic 90 day toxicity of dichloroacetic and trichloroacetic acid in rats. *Toxicology* **64**: 71–80.
98. Goldsworthy, T.L. and Popp, J.A. (1987). Chlorinated hydrocarbon-induced peroxisomal enzyme activity in relation to species and organ carcinogenicity. *Toxicol. Appl. Pharmacol.* **88**: 225–233.
99. Sanchez, I.M. and Bull, R.J. (1990). Early induction of reparative hyperplasia in the liver of B6C3F1 mice treated with dichloroacetate and trichloroacetate. *Toxicology* **64**: 33–46.
100. Cosby, N.C. and Dukelow, W.R. (1992). Toxicology of maternally ingested trichloroethylene (TCE) on embryonal and fetal development in mice and of TCE metabolites on *in vitro* fertilization. *Fundam. Appl. Toxicol.* **19**: 268–274.
101. Saillenfait, A.M., Langonne, I., and Sabate, J.P. (1995). Developmental toxicity of trichloroethylene, tetrachloroethylene and four of their metabolites in rat whole embryo culture. *Arch. Toxicol.* **70**: 71–82.
102. Smith, M.K., Randall, J.L., Read, E.J., and Stober, J.A. (1989). Teratogenic activity of trichloroacetic acid in the rat. *Teratology* **40**: 445–451.
103. Daniel, F.B. et al. (1993). Toxicity of 1,1,1-trichloro-2-propanone in Sprague-Dawley rats. *J. Toxicol. Environ. Health.* **39**: 383–393.
104. DeAngelo, A.B., Daniel, F.B., Most, B.M., and Olson, G.R. (1997). Failure of monochloroacetic acid and trichloroacetic acid administered in the drinking water to produce liver cancer in male F344/N rats. *J. Toxicol. Environ. Health.* **52**: 425–445.
105. IARC. (1995). Dry Cleaning, Some Chlorinated Solvents and Other Industrial Chemicals. Lyon, International Agency for Research on Cancer (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 63).
106. Mills et al. (2000).
107. NTP. National Toxicology program. (1998). Water disinfection byproducts (bromodichloroacetic acid). Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/ResstatB/M970039.html.
108. NTP. (2000). Short Term Reproductive and Developmental Toxicity Study of Dibromochloroacetic Acid (CAS No. 5278-95-5) Administered to Sprague-Dawley Rats in the Drinking Water NTP Study Number: RDGT98001. NTIS # PB2000-103420.
109. NTP. (1998). Short Term Reproductive and Developmental Toxicity of Tribromoacetic Acid (CAS No. 75-96-7) Administered in Drinking Water to Sprague-Dawley Rats. NTP Study Number: RDGT94009. NTIS#: PB98-165111.
110. NTP. National Toxicology Program. (1997). Water disinfection byproducts (Tribromoacetic acid). Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatt/M940117.html.
111. Lin, E.L., Daniel, F.B., Herren-Freund, S.L., and Pereira, M.A. (1986). Haloacetonitriles: metabolism, genotoxicity, and tumor-initiating activity. *Environ. Health Perspect.* **69**: 67–71.
112. Mohamadin, A.M. and Abdel-Naim, A.B. (1999). Chloroacetonitrile-induced toxicity and oxidative stress in rat gastric epithelial cells. *Pharmacol. Res.* **40**(4): 377–383.
113. IARC. (1999). Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. World Health Organization, International Agency for Research on Cancer, Geneva, 1972-PRESENT. V71, p. 1327.
114. IARC. (1991). Chlorinated Drinking-water; Chlorination By-products; Some Other Halogenated Compounds; Cobalt and Cobalt Compounds. Lyon, International Agency for Research on Cancer (IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Volume 52).
115. NTP. National Toxicology program. (1981). Chloroacetonitrile. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/ResstatC/10979-X.html.
116. NTP. (1997). Short Term Reproductive and Developmental Toxicity of Bromoacetonitrile (CAS No. 590-17-0) Administered in Drinking Water to Sprague-Dawley Rats. NTP Study Number: RDGT94013. NTIS # PB97-167084.
117. NTP. National Toxicology program. (1982). Bromoacetonitrile. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatb/10972-V.html.

118. Hayes, J.R., Condie, L.W., and Borzelleca, J.F. (1986). Toxicology of haloacetonitriles. *Environ. Health Perspect.* **69**: 183–202.
119. Smith, M.K. et al. (1987). Developmental toxicity of halogenated acetonitriles: Drinking water by-products of chlorine disinfection. *Toxicology* **46**: 83–93.
120. Smith, M.K., Randall, J.L., Stober, J.A., and Read, E.J. (1989). Developmental toxicity of dichloroacetonitrile: A by-product of drinking water disinfection. *Fundam. Appl. Toxicol.* **12**: 765–772.
121. NTP. National Toxicology program. (1981). Dichloroacetonitrile. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatd/10989-F.html.
122. Christ, S.A., Read, E.J., Stober, J.A., and Smith, M.K. (1995). The developmental toxicity of bromochloroacetonitrile in pregnant Long-Evans rats. *Int. J. Environ. Health Res.* **5**(2): 175–188.
123. Bull, R.J. and Robinson, M. (1985). Carcinogenic activity of haloacetonitrile and haloacetone derivatives in the mouse skin and lung. In: *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Jolley, R.L. et al. (Eds.), Vol. 5. Lewis Publishers, Chelsea, MI, pp. 221–227.
124. Bull, R.J. et al. (1985). Evaluation of mutagenic and carcinogenic properties of brominated and chlorinated acetonitriles byproducts of chlorination. *Fundam. Appl. Toxicol.* **5**(6 Part 1): 1065–1074.
125. NTP. (1997). Reproductive Toxicity of Dibromoacetonitrile (CAS No. 3252-43-5) Administered to Sprague-Dawley Rats in the Drinking Water. NTP Study Number: RDGT94014. NTIS # PB97-143127.
126. NTP. National Toxicology program. (1982). Dibromoacetonitrile. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatd/10985-P.html.
127. Smith et al. (1988).
128. NTP. National Toxicology program. (1981). Trichloroacetonitrile. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatt/11036-S.html.
129. Lawrence, W.H., Dillingham, E.O., Turner, J.E., and Autian, J. (1972). Toxicity profile of chloroacetaldehyde. *J. Pharm. Sci.* **61**: 19–25.
130. van Duuren, B.L. et al. (1979). Carcinogenicity of halogenated olefinic and aliphatic hydrocarbons in mice. *J. Natl. Cancer Inst.* **63**: 1433–1439.
131. Robinson, M., Bull, R.J., Olson, G.R., and Stober, J. (1989). Carcinogenic activity associated with halogenated acetones and acroleins in the mouse skin assay. *Cancer Lett.* **48**: 197–203.
132. Bignami, M. et al. (1980). Mutagenicity of halogenated aliphatic hydrocarbons in Salmonella typhimurium, Streptomyces coelicolor and Aspergillus nidulans. *Chem-Biol. Interact.* **30**: 9–23.
133. Douglas, G.R., Nestmann, E.R., McKague, A.B., San, R.H.C., Lee, E.G., Liu-Lee, V.W., and Kobel, D.J. (1985). Determination of potential hazards from pulp and paper mills: Mutagenicity and chemical analysis. In: *Carcinogens and Mutagens in the Environment—Volume 5: The Workplace*. Stich, H.F. (Ed.). CRC Press, Boca Raton, FL, pp. 151–166.
134. Gordon, W.P. et al. (1985). The genotoxicity of 2-bromoacrolein and 2,3-dibromopropanal. *Carcinogenesis* **6**: 705–709.
135. Meier, J.R. et al. (1985). Identification of mutagenic compounds formed during chlorination of humic acid. *Mutat. Res.* **157**: 111–122.
136. Meier, J.R., Bull, R.J., Stober, J.A., and Cimino, M.C. (1985). Evaluation of chemicals used for drinking water disinfection for production of chromosomal damage and sperm-head abnormalities in mice. *Environ. Mutagen.* **7**: 201–211.
137. Merrick, B.A. et al. (1987). Chemical reactivity, cytotoxicity, and mutagenicity of chloropropanones. *Toxicol. Appl. Pharmacol.* **91**: 46–54.
138. Rosen, J.D., Segall, Y., and Casida, J.E. (1980). Mutagenic potency of haloacroleins and related compounds. *Mutat. Res.* **78**: 113–119.
139. Segall, Y., Kimmel, E.C., Dohn, D.R., and Casida, J.E. (1985). 3-Substituted 2-halopropenals: mutagenicity, detoxification and formation from 3-substituted 2,3-dihalopropenal promutagens. *Mutat. Res.* **158**: 61–68.
140. Gilman, A.G., Rall, T.W., Neis, A.S., and Taylor, P. (1991). *Goodman and Gilman's Pharmacological Basis of Therapeutics*, 8th Edn. Pergamon Press, New York, pp. 364–365.
141. Farber, B. and Abramow, A. (1985). Acute laryngeal edema due to chloral hydrate. *Isr. J. Med. Sci.* **21**: 858–859.
142. Silver, W. and Stier, M. (1971). Cardiac arrhythmias from chloral hydrate. *Pediatrics* **48**(2): 332–333.
143. Hirsch, I.A. and Zauder, H.L. (1986). Chloral hydrate: A potential cause of arrhythmias. *Anesth. Analg.* **65**: 691–692.
144. Nordenberg, A., Delisle, G., and Izukawa, T. (1971). Cardiac arrhythmia in a child due to chloral hydrate ingestion. *Pediatrics* **47**: 134–135.
145. van Heijst, A.N., Zimmerman, A.N., and Pikaar, S.A. (1977). Chloral hydrate—the forgotten poison. *Ned. Tijdschr. Geneesk.* **121**(40): 1537–1539.
146. Lambert, G.H., Muraskas, J., Anderson, C.L., and Myers, T.F. (1990). Direct hyperbilirubinemia associated with chloral hydrate administration in the newborn. *Pediatrics* **86**: 277–281.
147. Daniel, F.B. et al. (1992). Ninety-day toxicity study of chloral hydrate in the Sprague-Dawley rat. *Drug. Chem. Toxicol.* **15**: 217–232.
148. Sanders, V.M. et al. (1982). Toxicology of chloral hydrate in the mouse. *Environ. Health Perspect.* **44**: 137–146.
149. Klinefelter, G.R., Suarez, J.D., and Roberts, N.L. (1995). Preliminary screening test for the potential of drinking water disinfectant by-products to alter male reproduction. *Reprod. Toxicol.* **9**: 571–578.
150. National Toxicology Program (NTP). (2000). Toxicology and Carcinogenesis Studies of Chloral Hydrate in B6C3F1 Mice (Gavage Studies). NTP TR 502, Silver Springs, MD.
151. IRIS. (2000). Chloral Hydrate. U. S. Environmental Protection Agency. Washington, DC. Available at http://www.epa.gov/iris/subst/0304.htm.
152. NTP. National Toxicology program. (1980). Chloral Hydrate. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/Resstatc/10609-C.html.
153. Meier, J.R., Blazek, W.F., and Knohl, R.B. (1987). Mutagenic and clastogenic properties of 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone: A potent bacterial mutagen in drinking water. *Environ. Mol. Mutagen.* **10**: 411–424.
154. Mullins, P.A. and Proudlock, R.J. (1990). *Assessment of Nuclear Anomalies in Mice After Administration of MX*. Water Research Centre, Medmenham, UK.
155. Meier, J.R. et al. (1996). Urine mutagenicity and biochemical effects of the drinking water mutagen, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) following repeated oral administration to mice and rats. *Toxicology* **110**: 59–70.

156. Vaittinen, S.L. et al. (1995). Subchronic toxicity of 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) in Wistar rats. *Food Chem. Toxicol.* **33**(12): 1027–1037.
157. Komulainen, H., Kosma, V.M., and Vaittinen, S. (1997). Carcinogenicity of the drinking water mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX). *J. Natl. Cancer Inst.* **89**: 848–856.
158. Hyttinen, J.M., Myohanen, S., and Jansson, K. (1996). Kinds of mutations induced by 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) in the hprt gene of Chinese hamster ovary cells. *Carcinogenesis* **17**: 1179–1181.
159. Clayton, G.D. and Clayton, F.E. (Eds.). (1981). *Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology*, 3rd Edn. John Wiley & Sons, New York.
160. *Merck Index.* (1983), 10th Edn. Merck Co., Rahway, NJ.
161. Condie, L.W., Daniel, F.B., Olson, G.R., and Robinson, M. (1994). Ten and ninety-day toxicity studies of chloropicrin in Sprague-Dawley rats. *Drug Chem. Toxicol.* **17**(2): 125–137.
162. York, R.G., Butala, J.H., Ulrich, C.E., and Schardein, J.L. (1994). Inhalation developmental toxicities of chloropicrin in rats and rabbits. *Teratology* **49**(5): 419.
163. NCI. (1978). Bioassay of Chloropicrin (CAS No. 76-06-2) for Possible Carcinogenicity. Carcinogenesis Program, National Institute of Health, Bethesda, MD, NCI-CG-TR-65.
164. NTP. National Toxicology program. (1980). Chloropicrin. Available at http://ntp-server.niehs.nih.gov/htdocs/Results_Status/ResstatC/10848-P.html.
165. Lubbers, J.R. and Bianchine, J.R. (1984). Effects of the acute rising dose administration of chlorine dioxide, chlorate and chlorite to normal healthy adult male volunteers. *J. Exp. Pathol. Toxicol. Oncol.* **5**: 215–228.
166. Abdel-Rahman, M.S., Couri, D., and Bull, R.J. (1980). Kinetics of ClO_2 and effects of ClO_2, ClO_2^-, and ClO_3^- in drinking water on blood glutathione and hemolysis in rat and chicken. *J. Environ. Pathol. Toxicol.* **3**: 431–449.
167. Bercz, J.P. et al. (1982). Subchronic toxicity of chlorine dioxide and related compounds in drinking water in the nonhuman primate. *Environ. Health Perspect.* **46**: 47–55.
168. Couri, D. and Abdel-Rahman, M.S. (1980). Effect of chlorine dioxide and metabolites on glutathione dependent system in rat, mouse and chicken blood. *J. Environ. Pathol. Toxicol.* **3**: 451–460.
169. Harrington, R.M., Romano, R.R., Gates, D., and Ridgway, P. (1995). Subchronic toxicity of sodium chlorite in the rat. *J. Am. Coll. Toxicol.* **14**: 21–33.
170. Heffernan, W.P., Guion, C., and Bull, R.J. (1979). Oxidative damage to the erythrocyte induced by sodium chlorite, *in vivo*. *J. Environ. Pathol. Toxicol.* **2**: 1487–1499.
171. Moore, G.S. and Calabrese, E.J. (1982). Toxicological effects of chlorite in the mouse. *Environ. Health Perspect.* **46**: 31–37.
172. Moore, G.S., Calabrese, E.J., and Leonard, D.A. (1980). Effects of chlorite exposure on conception rate and litters of A/J mice. *Bull. Environ. Contam. Toxicol.* **25**: 689–696.
173. Couri, D. et al. (1982). Assessment of maternal toxicity, embryotoxicity and teratogenic potential of sodium chlorite in Sprague-Dawley rats. *Environ. Health Perspect.* **46**: 25–29.
174. Couri, D., Abdel-Rahman, M.S., and Bull, R.J. (1982). Toxicological effects of chlorine dioxide, chlorite and chlorate. *Environ. Health Perspect.* **46**: 13–17.
175. Kurokawa, Y. et al. (1986). Long-term *in vivo* carcinogenicity tests of potassium bromate, sodium hypochlorite, and sodium chlorite conducted in Japan. *Environ. Health Perspect.* **69**: 221–235.
176. Kurokawa, Y. et al. (1986). Dose-response studies on the carcinogenicity of potassium bromate in F344 rats after long-term oral exposure. *J. Natl. Cancer Inst.* **77**: 977–982.
177. Yokose, Y. et al. (1987). Studies of carcinogenicity of sodium chlorite in B6C3F1 mice. *Environ. Health Perspect.* **76**: 205–210.
178. Ishidate, M. et al. (1984). Primary mutagenicity screening of food additives currently used in Japan. *Food Chem. Toxicol.* **22**: 623–636.
179. Bloxham, C.A., Wright, N., and Hoult, J.G. (1979). Self-poisoning by sodium chlorate: Some unusual features. *Clin. Toxicol.* **15**: 185–188.
180. Helliwell, M. and Nunn, J. (1979). Mortality in sodium chlorate poisoning. *Br. Med. J.* **6171**: 1119.
181. Steffen, C. and Seitz, R. (1981). Severe chlorate poisoning: Report of a case. *Arch. Toxicol.* **48**: 281–288.
182. Yoshida, Y. et al. (1977). A cytological study of Heinz body-hemolytic anemia. Report of a case of sodium chlorate poisoning complicated by methemoglobinemia and acute renal failure. *Acta. Haematol. Jpn.* **40**: 147–151.
183. Heywood, R., Sortwell, R.J., Kelly, P.J., and Street, A.E. (1972). Toxicity of sodium chlorate to the dog. *Vet. Rec.* **90**: 416–418.
184. Sheahan, B.J., Pugh, D.M., and Winstanley, E.W. (1971). Experimental sodium chlorate poisoning in dogs. *Res. Vet. Sci.* **12**: 387–389.
185. NTP. (1998). Developmental Toxicity Evaluation for Sodium Chlorate (CAS No. 7775-09-9) Administered by Gavage to New Zealand White Rabbits on Gestational Days 6 through 29. NTP Study: TER97005. NTIS# PB2003-101297.
186. Kurokawa, Y. et al. (1985). Dose-related enhancing effect of potassium bromate on renal tumorigenesis in rats initiated with N-ethyl- N-hydroxyethyl-nitrosamine. *Jpn. J. Cancer Res. (Gann).* **76**: 583–589.
187. Prieto, R. and Fernandez, E. (1993). Toxicity and mutagenesis by chlorate are independent of nitrate reductase in Chlamydomonas reinhardtii. *Mol. Gen. Genet.* **237**: 429–438.
188. Kuwahara, T. et al. (1984). Two cases of potassium bromate poisoning requiring long-term hemodialysis therapy for irreversible tubular damage. *Nephron.* **37**: 278–280.
189. Kurokawa, Y., Maekawa, A., Takahashi, M., and Hayashi, Y. (1990). Toxicity and carcinogenicity of potassium bromate - A new renal carcinogen. *Environ. Health Perspect.* **87**: 309–335.
190. Onodera, H. et al. (1986). Eosinophilic bodies in the proximal renal tubules of rats given potassium bromate. *Bull. Natl. Inst. Hyg. Sci.* **103**: 15–20.
191. NTP. (1996). Sodium Bromate (CAS No. 7789-38-0): Short Term Reproductive and Developmental Toxicity Study When Administered to Sprague-Dawley Rats in the Drinking Water. NTP Study Number: RDGT94007. NTIS# PB96-190640.
192. DeAngelo, A.B. et al. (1998). Carcinogenicity of potassium bromate administered in the drinking water to male B6C3F1 mice and F344/N rats. *Toxicol. Pathol.* **26**(5): 587–594.
193. IRIS. (2001). Bromate (CASRN 15541-45-4). U. S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/iris/subst/1002.htm.
194. U.S. EPA. (1996). Proposed guidelines for carcinogen risk assessment; notice. April 23, 1996. *Fed. Reg.* **61**(79): 17960–18011.
195. Venkatapathy, R., Moudgal, C.J., and Bruce, R.M. (2004). Assessment of the oral rat chronic lowest observed adverse

effect level model in TOPKAT, a QSAR software package for toxicity prediction. *JCICS* **44**(5): 1623–1629.

196. Moudgal, C.J., Lipscomb, J.C., and Bruce, R.M. (2000). Potential health effects of drinking water disinfection by-products using quantitative structure-toxicity relationship. *Toxicology* **147**: 109–131.
197. U.S. EPA. (1988). Health and Environmental Effects Document for Chloroacetic Acid. ECAO-CIN-G038. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH.

HEALTH EFFECTS OF MICROBIAL CONTAMINANTS AND BIOTOXINS IN DRINKING WATER

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Although drinking water quality has increased dramatically over the last century because of better treatment of raw water through processes such as disinfection, protection of source waters, and better sewage disposal practices, increasing pressure on available water sources through factors such as increased population, increased consumption, inadequate sewage treatment, runoffs, confined feedlot operations, and floods have resulted in a heavier load of contaminating micro-organisms into many water treatment plants. Established disinfection and filtration techniques may not always remove such microbial contaminants from drinking water. Although a majority of these contaminants are harmless, a few of them are pathogens and may cause diseases in populations exposed to the contaminated drinking water, especially in sensitive individuals and in the immunocompromised.

Drinking water pathogens that have been implicated in waterborne diseases include algae, bacteria, fungi, protozoa, and viruses. Waterborne diseases are usually acute in nature, are rarely fatal, and are often characterized by gastrointestinal symptoms (1). The severity and duration of illness is generally greater in weakened immune systems such as in children, the elderly, people on chemotherapeutic drugs, and those with AIDS (1).

ALGAE

Unlike other waterborne micro-organisms, such as bacteria, viruses, protozoa, and fungi, algae use photosynthesis as their primary mode of nutrition. Algae are not pathogenic to humans, but some species produce biotoxins that may be harmful to humans at high enough concentrations. In particular, algae produce toxins that affect the liver (hepatotoxins) and the nervous system (neurotoxins). The most environmentally relevant toxins are produced by cyanobacteria.

Cyanobacteria

Cyanobacteria, or blue-green algae, have characteristics of both algae and bacteria, and they generally occur in calm, nutrient-rich waters. People may be exposed to cyanobacterial toxins by drinking or bathing in contaminated water. Symptoms include skin irritation, stomach cramps, vomiting, diarrhea, fever, sore throat, headache, muscle and joint pain, blisters, and liver damage (2). Species that produce hepatotoxins include some strains of *Microcystis, Anabaena, Oscillatoria, Nodularia, Nostoc, Cylindrospermosis*, and *Umezakia*, whereas some strains of *Aphanizomenon* and *Oscillatoria* produce neurotoxins (2). Although physical methods of coagulation and filtration may remove cyanobacteria from water, ozonation and treatment with permanganate are necessary to destroy the toxins (2).

BACTERIA

Bacteria are cylindrical or spherical single-celled micro-organisms that possess no nucleus. Common types of pathogenic bacteria that are found in drinking water include *Salmonella, Shigella, Campylobacter, Legionella, Escherichia coli, Vibrio cholerae*, and *Pseudomonas*. The health effects of common bacterial pathogens are described below.

Aeromonas

Aeromonas is an opportunistic bacterium that is commonly found in ground and surface waters, sewage, biofilms, and filtration units, and it may occasionally cause enteritis, septicemia, colitis, and puncture wound infections, particularly in the immunocompromised (3–6). Several species of *Aeromonas* may exist in the source waters including *A. bestiarum, A. caviae, A. eucrenophilia, A. hydrophilia, A. media, A. popoffii, A. salmonicida, A. schubertii*, and *A. veronii* (7). *Aeromonas* in water may be controlled through filtration and disinfection with chlorine, whereas *Aeromonas* in biofilms are relatively resistant to chlorination (8).

Campylobacter

C. coli and *C. jejuni* are found in sewage, ground and surface waters, and biofilms and are behind one of the most common bacterial causes of enteritis (3,9,10). *Campylobacter* may be controlled through chlorination (11).

Escherichia Coli

Of the more than 140 known serotypes of *E. coli*, 11 serotypes are known to cause gastrointestinal and other diseases in humans, including enteritis, colitis, kidney disease, and hemolytic uremic syndrome (3,9,12). The serotype *E. coli* O157:H7 is known to cause bloody diarrhea in infants (13). *E. coli* is generally transmitted through sewage and ground and surface waters, and it may be effectively controlled through disinfection (14).

Legionella

Of the 25 identified species of *Legionella*, a few may cause a type of pneumonia called Legionnaire's disease (13). The majority (90%) of the cases of Legionnaire's disease in the United States are caused by *L. pneumophila*, which is transported through ground and surface waters and aerosolized water, such as in hot water cooling towers, and is known to cause legionellosis, nosocomical and respiratory infections, pneumonia, and Pontiac fever (3,9,15,16). Free-floating *Legionella* may be effectively controlled through treatment with ozone, chlorine dioxide, and UV light, but *Legionella* inside suspended particles or free-living amoeba may be immune to disinfection (17).

Mycobacterium

Various species of NTM or nontuberculosis causing *Mycobacterium*, including *M. avium complex* (MAC), *M. chelonei, M. fortuitum, M. gordonae, M. kansasii, M. marinum, M. paratuberculosis, M. phlei*, and *M. xenopi*, are disseminated through biofilms, sewage, ground and surface waters, air, biofilms, and aerosolized water and can cause nosocomial infections, septicemia, skin lesions, various pulmonary diseases, and lymphadenitis, particularly in the immunocompromised (3). In addition, MAC colonizes water distribution systems, thereby recontaminating treated drinking water and generally infects the immunocompromised (3). *Mycobacterium* is relatively resistant to disinfection and can survive in hot water (18).

Pseudomonas

P. aeruginosa and *P. pseudomallei* are commonly found in ground and surface waters, sewage, and biofilms, and they cause various gastrointestinal, nosocomial, and respiratory infections in the immunocompromised (3,9). *Pseudomonas* may be disinfected through chlorination or UV treatment (19).

Salmonella

A majority of the waterborne *Salmonella* species are commonly found in sewage and surface waters and are pathogenic to humans. *S. enteritidis, S. montevideo B*, and *S. typhimurium* cause gastroenteritis and salmonellosis, whereas *S. typhi* and *S. paratyphi* (A & B) cause typhoid and paratyphoid fevers, respectively (9,20). *Salmonella* may be controlled by disinfection (21,22).

Shigella

S. sonnei, S. flexneri, S. boydii, and *S. dysenteriae* are found in sewage and ground and surface waters and may cause dysentery in exposed individuals (9,23). *S. sonnei* causes the bulk of waterborne infections among the four *Shigella* species listed above. Common disinfection processes are effective against controlling *Shigella* in drinking water.

Vibrio

V. cholerae is the most well known of the *Vibrio* species. It causes cholera, an acute intestinal disease with diarrhea, vomiting, and dehydration, and it is found in sewage and ground and surface waters (9,20). Severe cases of cholera may be fatal if left untreated for a few hours. *V. fluvialis, V. mimicus, V. parahaemolyticus*, and *V. vulnificus* are transmitted though surface waters and marine life and may cause enteritis and gastroenteritis (9). *Vibrio* may effectively be disinfected through treatment with chlorine (24).

Yersinia Enterocolitica

Y. enterocolitica is found in sewage and surface water and is carried by animals and humans (9). It can cause gastrointestinal illness including enteritis (9). *Y. enterocolitica* can be controlled through the use of chlorine (25).

FUNGI

Species such as *Aspergillus, Penicillium, Alternaria, Candida, Trichophyton*, and *Cladosporium* have been isolated from chlorinated water and service mains (26,27). Inhalation of large numbers of fungal spores can cause respiratory diseases, including pneumonia, fever, and meningoencephalitis, especially in the immunocompromised (28,29). Fungal spores are relatively resistant to chlorine (30), but a combination of coagulation, slow sand filtration, and disinfection can reduce the number of spores to a limited extent (31).

PROTOZOA

Protozoa are single-celled nucleated organisms that are typically larger than bacteria and lack a cell wall. Protozoa that are waterborne and pathogenic to humans are often found as resistant forms that protect themselves from environmental stresses (13). Common protozoa found in drinking water include *Giardia, Entamoeba*, and *Cryptosporidium*. The health effects associated with exposure to protozoa are described below.

Acanthamoeba

Acanthamoeba is a group of amoebae found in sewage and drinking water that can cause meningoencephalitis and amebic keratitis (9,32,33) and have been associated with causing cutaneous lesions and sinusitis in the immunocompromised (33). *Acanthamoeba* are relatively resistant to disinfection and have to be removed through filtration (34).

Cryptosporidium

Cryptosporidium, especially *C. parvum*, is commonly found in ground and surface waters, sewage, and springs and causes cryptosporidiosis in humans (9,35,36). Cryptosporidiosis may be severe and chronic in the immunocompromised and may hasten death (37). *Cryptosporidium* is resistant to disinfection by chlorine and chloramines, although ozone, chlorine dioxide, and filtration are more effective (38,39).

Cyclospora

C. cayetanensis is found in sewage and surface waters and causes gastroenteritis including diarrhea, abdominal cramping, decreased appetite, and fever (40). The symptoms may be chronic and unremitting in the immunocompromised (41). *Cyclospora* may be resistant to chlorine and have to be removed through filtration (42).

Entamoeba

E. histolytica is found in drinking water contaminated by sewage and causes amoebic dysentery with symptoms ranging from acute bloody diarrhea and fever to mild gastroenteritis (9,13). The effects of disinfection on *Entamoeba* are unknown. However, *Entamoeba* cysts are less robust than those of some other types of protozoa.

Giardia

G. lamblia are found in ground and surface waters, sewage, and springs and cause giardiasis, a gastrointestinal disease manifested by diarrhea, fatigue, and cramps (9,43). *Giardia* cysts can remain infective in water for 1 to 3 months, depending on the temperature (13). *Giardia* cysts are resistant to chlorine disinfection but may be removed through filtration (44).

Microspora

Microsporidia, especially *Enterocytozoon bieneusi* and *Encephalitozoon intestinalis*, are fairly common in the environment and may cause microsporidiosis in humans, especially the immunocompromised (45,46). Symptoms include diarrhea and illnesses of the respiratory tract, urogenital tract, eyes, kidneys, liver, or muscles (45–47). *Microsporidia* spores are more susceptible to disinfection using chlorine than *Cryptosporidia* (48).

Naegleria

N. fowleri is an opportunistic amoeba that is primarily found in ambient waters, drinking water, and recreational facilities that contain warm water, such as swimming pools, and causes primary amoebic meningoencephalitis (PAM), a fatal disease that leads to death within 72 hours after the appearance of symptoms (9,49). However, no reported occurrences of *Naegleria* outbreaks through drinking water in the United States exist, although there have been several fatalities from *N. fowleri* contacted through recreational water (49). Data suggest that disinfection through chlorination may not be effective in removing *Naegleria* at the doses typically used in treatment plants (50). However, exposure to *Naegleria* may be reduced by avoiding contact with warm waters.

Toxoplasma

T. gondii is found in surface waters and may cause toxoplasmosis in fetuses and the immunocompromised (51). Although *Toxoplasma* oocysts originate from cat feces, transmission may also come from tissue or meat of other infected animals (51). Symptoms include fever, swelling of the lymph glands, blindness, mental retardation, and encephalitis (52). Although chlorination is not effective against *Toxoplasma*, filtration may be used in removing the organism (53).

VIRUS

Viruses are a large group of infectious agents that consist of a protein coat and a nucleic acid core. Most pathogenic waterborne viruses cause gastrointestinal diseases, whereas others may cause serious sequelae such as diabetes. Pathogenic viruses found in drinking water include adenoviruses, caliciviruses, Norwalk virus, coxsackieviruses, echovirus, hepatitis viruses, poliovirus, and rotavirus. The health effects of common viruses are described below.

Adenovirus

Adenoviruses are transported through ground and surface waters, sewage, and mucus and cause gastroenteritis, pharyngitis, conjunctivitis, and the common cold, especially in children (9). Adenoviruses are relatively resistant to disinfectants (13).

Astrovirus

Astroviruses are small, star-like viruses that are transported through ground and surface waters and sewage and cause gastroenteritis, especially in very young children and in the immunocompromised (9,54). Astroviruses are resistant to disinfection, but infection may be prevented through frequent handwashing (55).

Calicivirus

The calicivirus, including the Norwalk virus, is a common cause of gastroenteritis and is transported through ground and surface waters and sewage (9). Illness is generally mild, although gastroenteritis-induced dehydration may cause death in infants and young children (9). Ozone disinfection is effective against the caliciviruses (56).

Enterovirus

The most common enteroviruses (viruses that are found in the intestine) include the coxsackieviruses, echoviruses, and the polioviruses. Enteroviruses are generally found in ground and surface waters and sewage (9). Coxsackieviruses and echoviruses produce a variety of illnesses, including meningitis, enteritis, cold, fever, and heart disease (9). The polioviruses cause poliomyelitis, a paralytic disease (9). Enteroviruses may be resistant to chlorination (57).

Hepatitis Virus

Hepatitis A and E viruses cause infectious hepatitis, an illness characterized by inflammation of liver, fever, abdominal pain, weakness, and a lack of appetite (3,9). Hepatitis E infections are mild except for pregnant women, who may have a fatality rate of about 39% (13). Hepatitis A virus may be more resistant to disinfection than other enteric viruses (58).

Rotavirus

Rotaviruses are found in sewage and ground and surface waters and cause acute gastroenteritis, especially in children (3,9). Rotaviruses may be removed through filtration or inactivated by chlorine, chlorine dioxide, and ozone (59–61).

BIBLIOGRAPHY

1. CDC. (2000). *Safe Water Systems for the Developing World: A Handbook for Implementing Household-Based Water*

Treatment and Safe Storage Projects. Department of Health and Human Services, Centers for Disease Control and Prevention, Atlanta, GA.

2. World Health Organization. (1999). *Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring and Management*. J. Bartram and I. Chorus (Eds.). WHO, Geneva, Switzerland.
3. Reasoner, D.J. (1991). Pathogens in drinking water—are there any new ones? *Proc. AWWA Water Quality Technol. Conf.* Denver, CO.
4. Moyer, N.P. (1989). *Aeromonas* gastroenteritis: another waterborne disease? *Proc. AWWA Water Quality Tech. Conf.* Denver, CO.
5. van der Kooij, D. (1991). Nutritional requirements of Aeromonads and their multiplication in drinking water. *Experientia.* 47, Birkauser Verlag, Basel, Switzerland.
6. Havelaar, A.H., Versteegh, J.F.M., and During, M. (1990). The presence of *Aeromonas* in drinking water supplies in the Netherlands. *Zbl. Hyg.* **190**: 236–256.
7. Szczuka, E. and Kaznowski, A. (2004). Typing of clinical and environmental *Aeromonas* sp. strains by random amplified polymorphic DNA PCR, repetitive extragenic palindromic PCR, and enterobacterial repetitive intergenic consensus sequence PCR. *J. Clin. Microbiol.* **42**(1): 220–228.
8. Meheus, J. and Peeters, P. (1989). Preventive and corrective actions to cope with *Aeromonas* growth in water treatment. *Water Supply* **7**: 10-1–10-4.
9. Hazen, T.C. and Toranzos, G.A. (1990). Tropical source waters. In: *Drinking Water Microbiology*, G.A. McFeters (Ed.). Springer-Verlag, New York, pp. 32–53.
10. Fung, D.Y.C. (1992). Foodborne illness. In: *Encyclopedia of Microbiology*, Vol. 2, J. Lederberg (Ed.). Academic Press, San Diego, CA, pp. 209–218.
11. Blaser, M.J., Smith, P.F., Wang, W-L.L., and Hoff, J.C. (1986). Inactivation of *Campylobacter jejuni* by chlorine and monochloramine. *Appl. Environ. Microbiol.* **51**: 307–311.
12. Principie, M.A., Faber, W.W., Freud, S., and Wang, X.P. (1995). *Escherichia coli* occurrences in the New York City distribution system. *Proc. 1995 AWWA Annu. Conf.* Denver, CO.
13. Cohn, P.D., Cox, M., and Berger, P.S. (1995). Health and aesthetic aspects of water quality. In: *Water Quality and Treatment*, 5th Edn. R.D. Letterman (Ed.). McGraw-Hill, New York.
14. Mitchell, R. (1972). *Water Pollution Microbiology*. John Wiley & Sons, New York.
15. States, S.J., Conley, L.F., Knezevich, C.R., Keleti, G., Sykora, J.L., Wadowsky, R.M., and Yee, R.B. (1989). Free-living amoebae in public water supplies: Implications for *Legionella, Giardia*, and *Cryptosporidia*. *Proc. Annu. AWWA Water Quality Technol. Conf.* Denver, CO.
16. Harf, C. and Monteil, H. (1988). Interactions between free-living Amoebae and *Legionella* in the environment. *WST* **20**(11–12): 235–239.
17. States, S.J., Wadowsky, R.M., Kuchta, J.M., Wolford, R.S., Conley, L.F., and Yee, R.B. (1990). *Legionella* in drinking water. In: *Drinking Water Microbiology*, G.A. McFeters (Ed.). Springer-Verlag, New York.
18. Pelletier, P.A., du Moulin, G.C., and Stottmeier, K.D. (1988). Mycobacteria in public water supplies: Comparative resistance to chlorine. *Microbiol. Sci.* **5**: 147–148.
19. Homberger, F.R., Pataki, Z., and Thomann, P.E. (1993). Control of *Pseudomonas aeruginosa* infection in mice by chlorine treatment of drinking water. *Lab Anim. Sci.* **43**(6): 635–637.
20. Brock, T.D. (1979). *Biology of Microorganisms*, 3rd Edn. Prentice-Hall, Englewood Cliffs, NJ.
21. Engelbrecht, R.S., Severin, B.F., Masarik, M.T., Farooq, S., and Lee, S.H. (1975). New Microbial indicators of disinfection efficiency. U.S. National Technical Information Service, AD Report, AD-A03057.
22. Butterfield, C.T., Wattie, E., Megregian, S., and Chambers, C.W. (1943). Influence of pH and temperature on the survival of coliforms and enteric pathogens when exposed to free chlorine. *Public Health Rep.* **58**: 1837–1866.
23. Metcalf and Eddy, Inc. (1979). *Wastewater Engineering: Treatment, Disposal, Reuse*. McGraw-Hill, New York.
24. Rice, E.W. et al. (1993). *Vibrio cholerae* 01 can assume a ‘rugose’ survival form that resists killing by chlorine, yet retains virulence. *Int. J. Environ. Health Res.* **3**: 89–98.
25. Lund, V. (1996). Evaluation of *E. coli* as an indicator for the presence of *Campylobacter jejuni* and *Yersinia enterocolitica* in chlorinated and untreated oligotrophic lake water. *Water Res.* **30**: 1528–1534.
26. Rosenzweig, W.D., Minnigh, H.A., and Pipes, W.O. (1986). Fungi in potable water distribution systems. *J. AWWA.* **78**: 53–55.
27. Frankova, E. and Horecka, M. (1995). Filamentous soil fungi and unidentified bacteria in drinking water from wells and water mains near Brastislava. *Microbial. Res.* **150**: 311–313.
28. Bennett, J.E. (1994). Fungal Infections. In: *Harrison's Principles of Internal Medicine*, 13th Edn., K.J. Isselbacher, E. Braunwald, J.D. Wilson, J.B. Martin, A.S. Fauci, and D.L. Kasper (Eds.). McGraw-Hill, New York, pp. 854–865.
29. Geldreich, E.E. (1990). Microbial quality control in distribution systems. In: *Water Quality and Treatment*, F.W. Pontius (Ed.). American Water Works Association, McGraw-Hill, New York.
30. Rosenzweig, W.D., Minnigh, H.A., and Pipes, W.O. (1983). Chlorine demand and inactivation of fungal propagules. *Appl. Environ. Microbiol.* **45**: 182–186.
31. Niemi, R.M., Knuth, S., and Lundstrom, K. (1982). Actinomycetes and fungi in surface waters and in potable water. *Appl. Environ. Microbiol.* **43**: 378–388.
32. Sawyer, T.K. (1989). Free-living pathogenic and nonpathogenic Amoebae in Maryland soils. *Appl. Environ. Microbiol.* **55**: 1074–1077.
33. Marciano-Cabral, F. and Cabral, G. (2003). *Acanthamoeba* spp. as agents of disease in humans. *Clin. Microbiol. Rev.* **16**(2): 273–307.
34. de Jonchkheere, J. and van de Voorde, H. (1976). Differences in destruction of cysts of pathogenic and nonpathogenic *Naegleria* and *Acanthamoeba* by chlorine. *Appl. Environ. Microbiol.* **31**: 294–297.
35. Pontius, F.W. (1993). Protecting the public against *Cryptosporidium*. *J. AWWA.* **85**(8): 18, 22, 122–123.
36. Craun, G.F. et al. (1998). Waterborne outbreaks of Cryptosporidiosis. *J. AWWA.* **90**(9): 81–91.
37. Janoff, E.N. and Reller, L.B. (1987). *Cryptosporidium* species, a protean Protozoan. *J. Clin. Microbiol.* **25**: 967–975.
38. Korich, D.G. et al. (1990). Effects of ozone, chlorine dioxide, chlorine, and monochloramine on *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* **56**: 1423–1428.
39. Peeters, J.E. et al. Effect of disinfection of drinking water with ozone or chlorine dioxide on survival of *Cryptosporidium parvum* oocysts. *Appl. Environ. Microbiol.* **55**: 1519–1522.

40. Huang, P. et al. (1995). The first reported outbreak of diarrheal illness associated with *Cyclospora* in the United States. *Ann. Intern. Med.* **123**(6): 409–414.
41. Soave, R. and Johnson, W.D. (1995). *Cyclospora*: Conquest of an emerging pathogen. *Lancet* **345**: 667–678.
42. Rabold, J.G. et al. (1994). *Cyclospora* outbreak associated with chlorinated drinking water. *Lancet* **244**: 1360–1361.
43. Crockett, C.S. and Haas, C.N. (1997). Understanding Protozoa in your watershed. *J. AWWA.* **89**(9): 62–73.
44. Logsdon, G.S., Dewalle, F.B., and Hendricks, D.W. (1984). Filtration as a barrier to passage of cysts in drinking water. In: *Giardia and Giardiasis*, S.L. Erlandsen and E.A. Meyer (Eds.). Plenum Press, New York.
45. Goodgame, R.W. (1996). Understanding intestinal spore-forming Protozoa: *Cryptosporidia, Microsporidia, Isospora*, and *Cyclospora*. *Ann. Intern. Med.* **1214**: 429–441.
46. Bryan, R.T. (1995). Microsporidiosis as an AIDS-related opportunistic infection. *Clin. Infect. Dis.* **21**(Suppl. 1): 62–65.
47. Cali, A. (1991). General *Microsporidium* features and recent findings on AIDS isolates. *J. Protozool.* **38**: 625–630.
48. Rice, E.W., Johnson, C.H., Naumovitz, D.W., Marshall, M.M., Plummer, C.B., and Sterling, C.R. (1999). Chlorine disinfection studies of *Encephalitozoon* (*Septata*) *Intestinalis*. Abstracts, 99th General Meeting, American Society for Microbiology, Q-130.
49. CDC. (1992). Primary Amoebic Meningoencephalitis—North Carolina, 1991. *Morbidity and Mortality Weekly Report 41*, 437–440.
50. Chang, S-L. (1978). Resistance of pathogenic *Naegleria* to some common physical and chemical agents. *Appl. Environ. Microbiol.* **35**: 368–375.
51. Sinclair, M. (1997). Health Stream. Cooperative Research Centre for Water Quality and Treatment. **8**: 1.
52. Fishback, J.L. (1992). Toxoplasmosis. In: *Encyclopedia of Microbiology*. Vol. 4. J. Lederberg (Ed.). Academic Press, San Diego, CA, pp. 255–264.
53. Girdwood, R.W.A. (1995). Some clinical perspectives on waterborne parasitic Protozoa. In: *Proceedings, Protozoan Parasites and Water*. Symposium held at York, England, September 1994. W.B. Betts, D. Casemore, C. Fricker, H. Smith, and J. Watkins (Eds.). Royal Society of Chemistry, London.
54. Kurtz, J.B. and Lee, T.W. (1987). Astroviruses: Human and animal. In: *Novel Diarrhea Viruses*. John Wiley & Sons, New York.
55. White and Fenner. (1994). *Med. Virol*. 415–416.
56. Shin, G-A. and Sobsey, M.D. (2003). Reduction of Norwalk Virus, Poliovirus 1, and Bacteriophage MS2 by ozone disinfection of water. *Appl. Environ. Microbiol.* **69**(7): 3975–3978.
57. Abad, F.X., Pinto, R.M., and Bosch, A. (1997). Disinfection of human enteric viruses on fomites. *FEMS Microbiol Lett.* **156**(1): 107–111.
58. Peterson, D.A., Hurley, T.R., Hoff, J.C., and Wolfe, L.G. (1983). Effect of chlorine treatment on infectivity of Hepatitis A virus. *Appl. Environ. Microbiol.* **45**: 223–227.
59. Rao, V.C. et al. (1988). Removal of Hepatitis A virus and Rotavirus by drinking water treatment. *J. AWWA.* **80**: 59–67.
60. Berman, D. and Hoff, J.C. (1984). Inactivation of simian rotavirus SA11 by chlorine, chlorine dioxide, and monochloramine. *Appl. Environ. Microbiol.* **48** 317–323.
61. Chen, Y-S. and Vaughn, J.M. (1990). Inactivation of human and simian rotaviruses by chlorine dioxide. *Appl. Environ. Microbiol.* **56**: 1363–1366.

DRINKING WATER AND PUBLIC HEALTH PROTECTION

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INTRODUCTION

The provision of drinking water for communities is an urban utility, but a utility with a difference. As with other urban utilities, such as electricity and gas, water for household use is a necessity that cannot readily be obtained by urban householders for themselves. The difference is that, while water may satisfy many household needs, including drinking, it has the potential of spreading disease, often without the knowledge of the consumer. As a result, water supplies have become subject to regulations for assuring adequate quality, regulations that are not faced by other municipal public utilities.

Beginning with the water supply for Rome some 2000 years ago, the responsibility for water supply and its quality rested with the community. During the nineteenth century, with the beginning of the industrial era and the rapid growth of cities, public water supplies began to be provided by private entrepreneurs who sought profit in providing an essential service, frequently in competition with others. In the interest of getting a larger share of the market, they might provide a water of better quality than a competitor. The experiences with the provision of water for London from the Thames in the 1850s illustrate that the selection of the source of a water supply is important. Then Dr. John Snow took advantage of the competition between two water suppliers to prove that water was responsible for the transmission of cholera.

As cities grew, the need for large capital investments to provide adequate water supplies of high quality resulted in most cities abandoning private utilities when it became clear that they did not have the financial resources for the construction of the reservoirs, the long transmission lines, and the treatment plants. Decisions for selection of sources and treatment, which were introduced in the late nineteenth—early twentieth century, became the responsibility of the community, and not a regulatory body.

Treatment in the form of filtration and then chlorination was widely introduced, although not primarily through regulation. City officials recognized that they had an obligation to their constituencies to provide water that would not spread typhoid and cholera. Some cities were slow to assume this responsibility, and, in the United States, some newly organized state health agencies began to institute regulations. The choice of sources between a costly high-quality upland supply and a polluted source and the treatment to be provided was local.

The first nationwide water quality regulations in the United States were introduced by the federal government in 1909 to assure the safety of water to which the public was exposed in interstate and international traffic. Many states adopted these regulations even for smaller cities that did not have train or bus service. These federal regulations were upgraded over the years, and the bulk of this chapter is devoted to the nature of these regulations at the federal level until the passage of the Safe Drinking Water Act (SDWA) in 1974, after the U.S. Environmental Protection Agency (USEPA) became responsible for ensuring the safety of all public water supplies.

This article recounts the high points in the history of the role that urban water supplies play in the health of those who are obliged to drink from public supplies, beginning with concerns with the water supply for Rome, followed by the story of the cholera outbreaks in London that led to the recognition that water was responsible for the spread of infectious disease, the introduction of successful public health measures to control infectious disease, and the explosion of the chemical revolution that became responsible for the spread of chronic disease through ingestion of public water supplies (1).

WATER SUPPLY FOR THE CITY OF ROME

Among the major ancient cities of the world, none was better provided with water for its citizens than Rome. Initially, the city obtained its water from the Tiber River, which ran through the city. When it was apparent that the water had become heavily polluted, Appius Claudius built an aqueduct, the Aqua Appia, in 312 B.C. from the Tiber, about 11 miles upstream. Some 40 years later, the need was so great that a second aqueduct, 40 miles long, the Anio Novis, was built. Sextus Julius Frontinus, the water commissioner of Rome, wrote two books describing the water works of the city and their management (2). By A.D. 305, 14 aqueducts were serving the city.

The aqueducts fed the city by gravity with relatively short sections passing over valleys on stone arches, some three tiers high. Many of them carried water into the twentieth century. Such aqueducts remain throughout Europe and the Middle East as monuments to the early Romans.

The water from the aqueducts passed through large cisterns and from these was distributed through lead pipes to other cisterns, to public buildings, baths, and fountains, and to a relatively small number of private residences. Incidentally, they also built stone sewers to carry off wastewater from bathtubs and toilets in the larger buildings.

Frontinus questioned the wisdom of Augustus, whom he considered a most cautious ruler, in building one of the aqueducts, the Alsietinian, because the quality of its water was very poor and not suitable for the people. He speculated that Augustus built the aqueduct to serve nonpotable purposes and thereby "to avoid drawing on better sources of supply." The most important nonpotable use was for a *naumachia*, an artificial lake that was used for exhibitions of sham naval battles (Fig. 1). This is also current practice in American cities that erect stadia for baseball, football, and basketball on behalf of the team owners. The surplus nonpotable water was used for landscape irrigation and fountains. Words from an inscription state: "I gave the people the spectacle of a naval combat.... Besides the rowers, three thousand men fought in these fleets."

Thus, Rome can claim to be the first city to employ a dual distribution system and to base the use of its water supply on its quality. The water quality from the aqueducts was variable, and the Marcia aqueduct carried the best water. Frontinus points out that it was "determined to separate (the aqueducts) and then to arrange that the Marcia should serve wholly for drinking purposes, and that the others should be used for purposes adapted to their special qualities."

It is interesting to note that, in 1958, some 2000 years later, the United Nations Economic and Social Council enunciated a policy (3): "No higher quality water, unless there is a surplus of it, should be used for a purpose that can tolerate a lower grade."

THE MIDDLE AGES AND THE INDUSTRIAL REVOLUTION

Beginning in the sixth century, the Roman Empire began to disintegrate and, up to the fourteenth century, infectious diseases rode rampant throughout Europe. Leprosy, bubonic plague, smallpox, diphtheria, measles, influenza, and countless other afflictions were epidemic, particularly

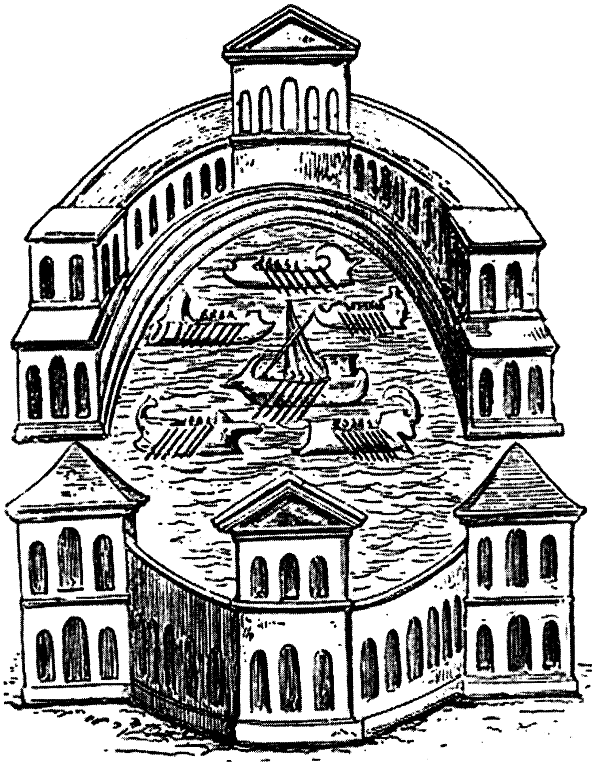

Figure 1. Naumachia (from a coin of Domitian) (2).

in the cities. Water was only one of the many vectors for the spread of disease. Knowledge of the specific vectors was limited, and food received the most attention. Quarantine was the principal approach to control of the spread of disease. The lack of proper sanitation and the dense urban populations were largely responsible for the epidemics and there was little focus on water quality and its availability.

The major accomplishment toward the end of the Middle Ages was the establishment of hospitals, often for specific diseases, by local governments and workers' guilds. Little of importance with regard to the water environment and the public health emerged during that period.

THE GREAT SANITARY AWAKENING

In the middle of the nineteenth Century, the causes of the many common diseases of the day that afflicted the growing urban populations that accompanied the Industrial Revolution were still unknown. Water was beginning to be piped to houses of the well-to-do while the poor either carried their water from wells or bought water from purveyors who obtained the water at the most convenient sources. When the water was contaminated, which was its general condition in urban areas, the spread of disease was inevitable.

A more significant and serious situation resulted from the growing installation rate of piping and then water closets in homes and commercial establishments. In addition to the impact of a poor quality water for drinking was the necessity for disposing of the discharges of these new flush toilets. London had found it necessary to construct storm sewers to drain the streets to permit the conduct of commerce. The obvious solution was to discharge the household wastes from the toilets to the storm sewers, which, in turn, discharged directly into the Thames River, which ran through London and served as a source of water for several private companies that distributed the water to households.

London was exemplary of the unsavory and squalid conditions in all cities in the early years of the century. The medical fraternity believed that the diseases were spread by poisons in the miasmatic air emanating from the "bowels of the earth." The Thames at London at that time was a tidal river and the heavily polluted waters would flow very slowly to sea. In warm periods, Londoners avoided crossing London Bridge because the air was so foul. A headline of the period read "India is in Revolt and the Thames Stinks." The drapery in the Houses of Parliament, located on bank of the Thames, needed to be soaked in chloride of lime to make the meeting room tolerable, and stirred the Parliament to establish the first of many committees to see to alleviating the situation.

Two cholera outbreaks in the summer of 1854 were the greatest in London's history. The first developed in Soho, a densely populated section in the heart of the city. Dr. John Snow, then physician to Queen Victoria Hospital, and reasonably the first epidemiologist, undertook to mark the deaths in the summer of 1953. In 2 days, 197 people died, and after 10 days more than 500 people died in an area only 250 yards across (4). Plotting the deaths on a map of the area (Fig. 2), the result resembled a target, with the greatest concentration of hits at the center. A church-owned well on Broad Street was identified at the site as being the source of the water ingested by the victims. The water had appeared to be of excellent quality. A woman living about a mile away regularly sent a cart to carry water to her home; she and a guest from outside London died of cholera in that epidemic.

Dr. Snow examined the well site and concluded that a tannery on property owned by the church had a cesspool for discharge of its wastewaters. He ordered the church to remove the handle on the pump, ending the epidemic, but, by that time, the epidemic might well have been spent. At any rate, this demonstration was the first to suggest that drinking water was the source of the cholera. This was generations before the germ theory of disease had been elucidated, and Snow's other studies in London were even more convincing. The John Snow Pub is on the site of the Broad Street pump, and these data decorate its walls.

Annual death rates from cholera among households using Thames River water ranged from 10 to 110 per 10,000 households in 1832, increasing to 200 per 10,000 among those taking water from the downstream reaches of the river. While this justified the inference that water was responsible, Dr. Snow found a more definitive proof during the 1854 epidemic. Two private water companies, the Southwark and Vauxhall Company and the Lambeth Company were in direct competition, serving piped water to the same area near the center of London but on the south side of the river. These water companies were characterized as "by far the worst of all those that take their water from the Thames, with 120 to 180 deaths per 10,000 households in 1849 for each of the two companies" (6). In 1852, however, the Lambeth Company, to attract more customers, improved the aesthetic quality of the Thames River water by moving its intake upstream above the heaviest pollution from London.

Snow's data showed that, in the 1854 epidemic, the death rate among those using Lambeth water was 37 deaths per 10,000 households as compared with 315 per 10,000 households for those using the intake downstream. During that period, the death rate in all of London was 59 per 10,000 households (256,423 deaths) among those taking water from all sources in London.

In addition to establishing that the cholera outbreaks were caused by drinking water, Snow demonstrated the importance of source selection. As is pointed out below, almost a century later, some cities still chose to take water from run-of-river sources when better sources were available primarily because it was less costly. Professor Fair, in presenting his philosophy about water supply, characterized the issue by declaring that he "preferred the virginal to the repentant," a paraphrase of the philosophy of Allen Hazen, possibly the most important engineer in the early history of water supply in the United States, who put it: "Innocence is better than repentance." (7).

THE EMERGENCE OF WATER AS A PUBLIC HEALTH ISSUE

The Industrial Revolution, beginning in the late eighteenth century in Britain and extending to Europe and the United States, was responsible for an explosive increase in

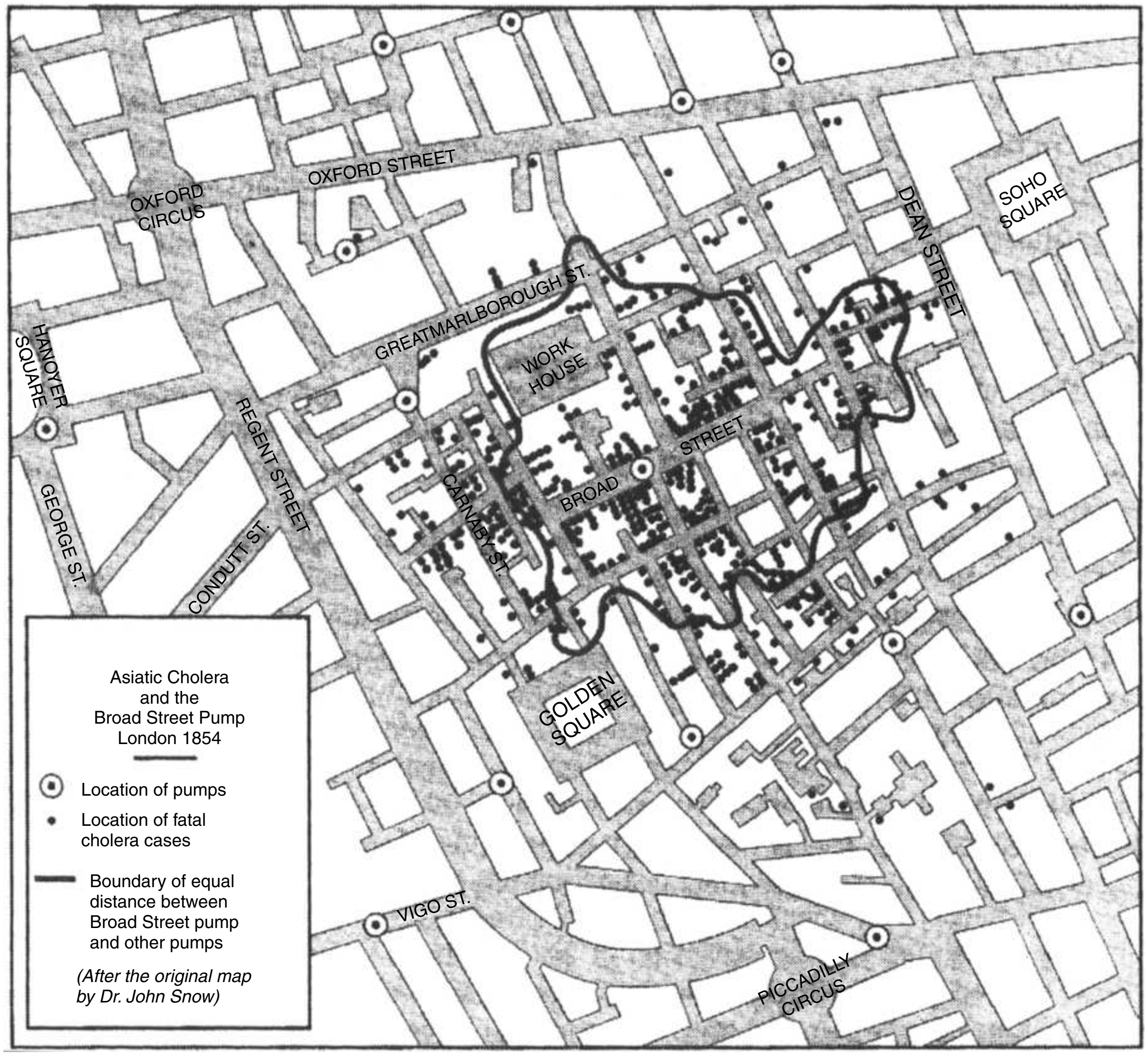

Figure 2. Map of Soho showing the location of those who died from cholera within the vicinity of the Broad Street pump in London 1854 (5).

urbanization with the development of the slums so "celebrated" by Dickens. It did eventually result in the English government and the northeastern states in the United States establishing agencies for addressing the terrible health conditions that emerged. Massachusetts, Pennsylvania, and New York established health boards to improve housing conditions; this resulted in the establishment of regulations for water supply and disposal of household wastes (Fig. 3).

These efforts at regulating activities that might damage the environment led to the establishment of the public health movement. Two figures of lasting fame: Sir Edwin Chadwick, a lawyer, in England (8), and Lemuel Shattuck, a physician (9) in Massachusetts, who was inspired by Chadwick, were responsible for the creation of regulatory agencies and laws protecting the public from the wide range of microbial and chemical contaminants that inevitably found their way to the nearby streams and rivers that were drawn upon for water supply. Shattuck's plan for the board of health for Massachusetts called for its membership to be composed of two physicians, one counselor-at-law, one chemist or natural philosopher, one civil engineer, and two persons of other professions or occupations. This comprehensive view of the needs for an agency for the protection of the public health was the springboard for the establishment of a sanitary engineering specialty within civil engineering. Shattuck had pointed out that competence in "planning and constructing public works" was essential to the provision of water supply and the disposal of household wastes.

In 1886, the Massachusetts legislature passed "An Act to Protect the Purity of Inland Waters" and, to implement the Act, it called for the establishment of an engineering department in the State Board of Health. Among its activities was the establishment of the Lawrence Experiment Station, the first of its kind, which was instrumental in attracting engineers, chemists, and biologists from the Massachusetts Institute of Technology, many of whom were responsible not only for spreading the study of water-related diseases and their control but also

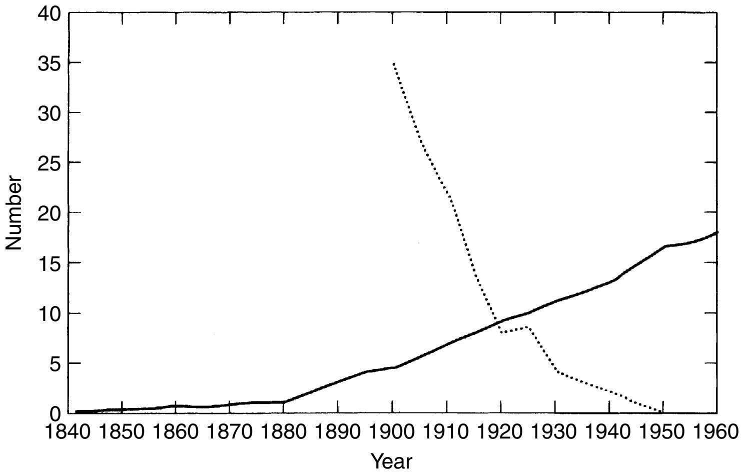

Figure 3. Simultaneous decline in typhoid fever death rate and rise in number of community water supplies in the United States (——deaths per 100,000 population; water supplies: 1000s) (*Source*: F. W. Pontius).

in the introduction of community water supply systems. From a total of only 17 water supply systems in the state in 1869, the number grew to 138 in 1890 while the annual death rate from typhoid fever in the state dropped from 89 per 100,000 in 1873 to 37 in 1890, and by 1940 to 0.2 (Fair 1945).

Despite the appearance of regulatory agencies, many years passed before they played a significant role in the monitoring of municipal water supply and wastewater collection, treatment, and disposal systems. Actually, there was, is, and should be far less need for regulation of drinking water quality than for regulation of wastewater discharges.

In the early days of public water supplies, most were privately owned and needed to meet the requirements of the communities they served. When they were inadequate to the task, sometimes because they failed to satisfy the communities they served, but more generally because the rapid growth of the cities called for capital investments beyond the capacity of the private purveyors to meet, the community government became responsible for the water supply. When the community government itself was providing the water, there seemed to be little need for regulating the performance of their own utility as its objectives would naturally be to protect its citizenry from public health risks.

A good example of this was the early history of the water supply for London, as mentioned above, where the private companies were generally loathe to invest in improvements. At the end of the nineteenth century, a Metropolitan Water Board (MWB) was created to take over responsibility for the water supply of London from eight private companies. In some other cities in England, private water companies continued to serve satisfactorily and continue to this day. The MWB established new technology and were seen to be at the leading edge of water supply technology and they set their own standards which were emulated by other communities.

In the case of New York City, its early private purveyors also were inadequate to their responsibilities. The driving forces were the need to have water to prevent epidemics of yellow fever (which were not related to water) and to fight fires. One of the last private efforts was that inspired by Aaron Burr, who promised a water supply as a condition of establishing the Bank of the Manhattan Company, the predecessor of the Chase Manhattan Bank. He had little interest in providing water and "this brilliant and unprincipled man suffered a series of political disasters that plunged him ... to ruin and exile." (10). Burr's plans were doomed.

The city finally decided to develop its own supply and, after extensive study had to choose between two possible sources: the Bronx River very near the city and the Croton River some 40 miles distant. The former was considerably lower in cost but the latter promised a much better quality of water and a greater quantity for the future. The City Board of Water Commissioners Committee on Fire and Water, addressing this question in 1835 opted for the Croton and for public ownership in this language (10):

> The question remains, ought the Corporation of the City of New York Committee to embark on this great work? The Committee are firmly of the opinion, that it ought to be done by no other body, corporate or personal. ... The control of the water of the City should be in the hands of this Corporation, or in other words, in the hands of the *people*.

The City celebrated the delivery of high-quality water from the Croton Aqueduct to New York City by gravity at high pressure in ample quantity in 1842, then one of the largest water supplies in the world. It still provides about 15% of the water that the City uses. This costly choice was made by the city officials not to meet a regulation but to serve their constituency well. Another example is the city of Cincinnati, Ohio, which installed granular activated carbon (GAC) filtration in the 1980s though it is not required by regulations. Many cities do more than the existing regulations require because the regulations tend to be years behind our knowledge. Water officials desiring to serve their community best may find it wise to anticipate quality problems that will not be addressed by regulations for years. Unfortunately, the reception given new regulations is not always one of appreciation by many water officials but of concern for the costs that may be involved. Industry groups such as the American Water Works Association (AWWA) often challenge regulations that are in the process of being promulgated to reduce public health risks because it would increase costs and water rates.

On the other hand, regulations for the quality and quantity of discharges of wastewaters to receiving waters are necessary, because the cost burden falls on the community while those who benefit are generally residents of other communities and not liable for the costs. This is also one of the reasons why the Clean Water Act (CWA) and similar earlier programs have been obliged to meet a significant share of the costs.

THE BEGINNING OF WATER TREATMENT

The relationship between source, water quality, and disease was demonstrated in the United States but much later than cholera in England and with much lower typhoid fever rates. Kober (11) made a study of typhoid rates in American cities from 1902 through 1908, summarized in Table 1. New York City, with its upland supply, had the lowest rate of the 61 cities with 15 typhoid deaths per 100,000 while Pittsburgh, with its run-of-river supply, suffered the highest death rate, 120 per 100,000.

Filtration of water was introduced well before the turn of the nineteenth century in Europe, where run-of-river supplies were more common. An eightfold increase of filtration in the United States reduced the typhoid death rate from water supply from 1900 to 1913 by 55% (12).

The availability of filtration mistakenly seemed to make the need for selecting better sources unnecessary. Philadelphia, which had been taking water from run-of-river sources and had been one of the last of the large U.S. cities to adopt filtration, was suffering a typhoid death rate of 75 per 100,000 into the twentieth century. The city officials had contended that filtration was not as effective as boiling the water. In 1900, a reform mayor was determined to address the issue. A panel of distinguished engineers prepared "a report that was characterized as not having any surprises." (13). It recommended filtration and continued use of water from the lower Delaware and Schuylkill Rivers. The report stated that "Water from upcountry sources might be preferable but the great cost of building aqueducts and reservoirs made that option very expensive and really unnecessary since filtration would provide safe water."

Table 1. Typhoid Rates in American Cities, 1902 Through 1908

Source	Number of Cities	Death Rate per 100,000
Groundwater	4	18.1
Impoundments and protected watersheds	18	18.5
Small lakes	8	19.3
Great lakes	7	33.1
Mixed surface and groundwater	5	45.7
Run-of-river supplies	19	61.6

Source: (12).

In 1911, before the filters were operational, a typhoid outbreak in Philadelphia resulted in 1063 deaths. After filtration, the death rate dropped to 13 per 100,000, still a relatively high figure.

Philadelphia still takes most of its water from the "mouth" (more properly, the "anus") of the Delaware River and has had to adopt Herculean methods to deliver water of good quality ever since. A multimedia study of environmental health risks in Philadelphia in the 1980s determined that the water supply posed the highest risk of all sources of pollution in the city. Since then improved treatment processes along with stricter USEPA standards have been introduced.

Many cities have no alternatives and are obliged to draw from run-of-river sources. Slow sand filtration became the treatment of choice in Massachusetts in the 1870s. In the 1890s, the Louisville Water Company, which took water from the Ohio River, introduced sedimentation of the water prior to filtration. For better removal of turbidity, they introduced chemical coagulation and rapid sand filtration.

The introduction of chlorination for disinfection of water for municipal water supply took place in Boonton, New Jersey, in 1908 following decades of study of the use of chlorine in Europe and the United States (14). It clearly was the greatest step in the reduction of the transmission of infectious diseases via water supply.

An example of the role of chlorine was the effect it had in a city drawing water from a clear lake. Chlorine reduced the annual typhoid death rate from about 20 to 2 per 100,000 population, which was then reduced to virtually zero with the addition of filtration (Fair et al. 1968). Together with pasteurization of milk and better handling of human wastes, typhoid virtually disappeared in the United States by the middle of the twentieth century.

THE CHEMICAL REVOLUTION

While infectious disease was brought under control, although other diseases emerged later, two other problems arose. The first was that water treatment tools were believed to be so effective, engineers became sanguine about the need to seek waters of high quality; treatment would make it safe. The conventional treatment of the midtwentieth century, which remains the conventional treatment now, at the beginning of the twenty-first century—chemical coagulation, rapid sand filtration, and chlorination—does little to remove the trace synthetic organic chemicals in ambient water resulting from the post World War II surge in industrial development what has been labeled the "chemical revolution" (1).

The second problem is truly ironic—the life-saving treatment, chlorination, increases the risk from synthetic organic chemicals created by the chlorine itself. Other disinfection byproducts have surfaced and added to the problem of the trace synthetic organic chemicals discharged from industry and households using a wide range of such chemicals for house and garden.

The first published material about disinfection byproducts (DBPs) emanated from Rook's work at the Rotterdam water treatment plant, which drew water from the mouth of the Rhine River (15). While it had been picked up quickly by USEPA, the potential had been recognized 5 years earlier. Dr. Joshua Lederberg, a Nobel Prize geneticist, who had been somewhat active in drinking water issues, wrote a 1969 syndicated column in the Washington Post. One column was headlined "We're so accustomed to using chlorine that we tend to overlook its toxicity" (16):

> What little we do know of the chemistry of chlorine reactions is portentous. It should sometimes react . . . to form substances that may eventually reach and react with genetic material, DNA, of body cells . . . That chlorine is also intended to inactivate viruses should provoke questions about the production of mutagens in view of the close similarity between viruses and genes.

USEPA was created in 1970, but Lederberg failed in attempts to attract funds to follow this up with his research team. The discovery of trihalomethanes and other disinfection byproducts and concerns regarding the potential cancer risks associated with chloroform would be a major driving force behind passage of the 1974 SDWA.

THE INTRODUCTION OF REGULATIONS

In the absence of regulations, many cities adopted practices that were believed to be the most appropriate for their own conditions on the recommendations of professional engineers and water scientists. As noted above, the spread of disease had been controlled in large measure by the quarantine of the sick. It was not unreasonable, therefore, for federal authority over the control of the spread of disease via water to be initially addressed by the U.S. Congress in the Interstate Quarantine Act of 1893 (17).

Under the Act, the surgeon general of the U.S. Public Health Service (USPHS) was empowered "to make and enforce such regulations as are necessary to prevent the introduction, transmission, or spread of communicable disease from foreign countries into the states or possessions, or from one state or possession into any other state or possession."

Interstate regulations were first promulgated in 1894 with the first water-related regulation adopted in 1912, which prohibited the use of the common cup on carriers in interstate commerce (18).

The first federal drinking water standards were adopted in 1914. The USPHS was then part of the U.S. Treasury Department and was charged with responsibility for the health care of the sailors of the Merchant Marine. The surgeon general of the USPHS recommended and the Treasury Department adopted standards for drinking water to be supplied to the public on interstate carriers, then called "Treasury Standards." Because the group that was charged with developing the standards could not agree on physical and chemical parameters, only a bacterial standard of 100 microorganisms per milliliter was adopted. The organism adopted was *Bacteria coli*, now known as *Escherichia coli*. It was further stipulated that not more than one of five 10-mL portions (2 *Bacteria coli* per 100 mL) would be permitted (19). These coliform organisms were not themselves pathogenic but, originating in large numbers in the human colon and found in feces, they served as a surrogate for enteric pathogens because they were more resistant to removal and were present in large numbers and, if they were not present, it could be inferred that the enteric pathogens likely would not be present. Many local and state officials adopted the standard and monitored the water systems that served interstate carriers for themselves and on behalf of the Treasury Department. A federal commitment was made in 1915 to review the regulations on a regular basis.

By 1925, most large cities drawing water from run-of-river sources were already using filtration and chlorination and having little difficulty in meeting the 1914 coliform standard of 2 100 mL^{-1} (2 coliforms per milliliter). Following a principle of attainability, the standard was tightened to 1 100 mL^{-1}. In addition, standards were established for physical and some chemical constituents, including lead, copper, zinc, and dissolved solids (20).

The 1925 standards introduced the concept of relative risk. The preamble stated in part:

> The first step toward the establishment of standards which will ensure safety of water supplies conforming to them is to agree upon some criterion of safety. This is necessary because "safety" in water supplies, as they are actually produced, is relative and quantitative, not absolute. Thus, to state that a water supply is "safe" does not necessarily signify that no risk is ever incurred in drinking it. What is usually meant, and all that can be asserted from any evidence at hand is that the danger, if any, is so small that it cannot be discovered by available means of observation.

In 1941, an advisory committee for revision of the 1925 standards was assembled by the USPHS, composed of representatives of federal and state agencies, scientific associations, and members at large, which produced the 1942 standards (21). One new initiative was the introduction of requirements for monitoring microbial water quality in the distribution system, with specifications for the minimum number of samples to be collected each month according to the size of the community. Specifications for the laboratories and procedures involved were provided.

Maximum permissible concentrations were established for lead, fluoride, arsenic, and selenium as well as for salts of barium, hexavalent chromium, heavy metals, and other substances having deleterious physiological effects. Maximum concentrations where other alternative sources were not available were set for copper, the total of iron and manganese, zinc, chlorides, sulfates, phenolic compounds, total solids, and alkalinity.

Only minor changes were introduced in 1946 (22). Publication in the *Federal Register* was introduced, assuring more rapid dissemination of changes that might be made, one of which was the authorization in March 1957 of the use of the membrane filter procedure for the bacteriological examination of water samples.

World War II (for the United States, 1942–1946) was the first war where deaths of American troops by infectious disease did not exceed deaths in combat. Steps had been introduced to reduce exposure to mosquitoes that were responsible for malaria and other related diseases in the tropics and facilities were provided to assure chlorination of the drinking water. In the postwar period, and driven by the need to make up for years during which the construction of state-side water-related civilian infrastructure had been dormant, attention was turned to making heavy investments for urban water supply.

The need for standards was apparent. Dr. Abel Wolman (23) addressed this issue thus:

> From its beginning, society by one means or another, has surrounded itself with restraints. These have had, for the most part, empiric origins—moral, ethical, economic, or spiritual. All the restraints have had the common basis of an assumed benefit to the particular society establishing them. As societies became more complex and more sophisticated, efforts towards both standardization and restraint became more frequent, more necessary, and presumably more empiric, although examples of the last are not as numerous as one might expect.

He then went on to characterize the types of standards that are necessary:

- Regularization of techniques of measurement;
- Establishment of limits of concentration or density of biologic life and physical and chemical constituents;
- Regularization of administrative practice;
- Regularization of legislative fiat; and
- Specification of materials.

The increasing complexity of the issues is exemplified in all that follows, including not only in the specific regulations required but also in the methodologies of reaching consensus among the many stakeholders involved. The beginning of the "chemical revolution" and regulating the thousands of synthetic organic compounds (SOCs) that are being invented annually and that find their way into the environment and into waters drawn on for drinking began with the 1962 update of the federal Drinking Water Standards.

The establishment of the 1962 USPHS standards involved examining many new issues, including two important problems not previously addressed: radioactivity and SOCs. A new 18-member Advisory Committee was established representing 13 professional and scientific organizations that included consulting engineers, state officials, industry, academics, and water utility executives as well as personnel from the Food and Drug Administration and the U.S. Geological Survey. In addition, 10 officers of the USPHS formed a Technical Subcommittee that, with a six-member Task Force on Toxicology, were advisory to the main Committee (24).

The 1962 USPHS standards were by far the most comprehensive to that date. They included three physical characteristics, odor, color, and turbidity; the last was the most controversial. The turbidity was established at 5 units over the objections of many on the committee from communities that were filtering their waters and who recommended 1 unit, which they could easily meet. Representatives from the northeast, where impounded surface sources were used without filtration, would have had to provide filtration, a measure they believed unnecessary. The bacteriological quality requirement was modified, essentially allowing no more than a monthly average of one coliform per milliliter when the membrane filter technique is used.

The chemical standards were the most difficult to address. Fourteen parameters were listed, but the SOC problem was resolved with the introduction of a Carbon Chloroform Extract (CCE) standard of $0.2\,\mathrm{mg\,L^{-1}}$. A manual was prepared describing the procedure to be used; adsorption of organics by passing a sample of the water through a granular activated carbon (GAC) filter and then desorbing the filter with chloroform (25). The standard was meaningless as a measure of public health risk, because SOCs could not be distinguished from natural organics that are generally of little health consequence, except when they are precursors for chlorination and the creation of trihalomethanes (THMs). But the CCE standard was an attempt to address the SOC problem. The treatment to be provided to remove SOCs was the installation of GAC filters in the treatment train. Forty years later, only a handful of GAC filter plants are being used for treating the most vulnerable public water supplies, those drawing from run-of-river sources. It can be assumed that, at this writing, few supplies that draw from large rivers are removing SOCs that may be present.

The 1962 Standards did introduce two principles that had not been incorporated in previous standards. The first was that "The water supply should be taken from the most desirable source which is feasible, and effort should be made to prevent or control pollution of the source." The second issue was the absence of regulations related to availability of service. A community might be found to be violating the standards if one of the standards is not met but no violation is involved if water service is curtailed because of drought or mechanical failure. The 1962 Standards state "Approval of water supplies shall be dependent in part on: ... adequate capacity to meet peak demands without development of low pressures or other health hazards."

The 1962 Standards were accepted by all the states, with minor modifications either as regulations or guidelines, but were binding only on about two percent of the communities, those that served interstate carriers (26).

PRELUDE TO THE 1974 SAFE DRINKING WATER ACT

On June 3, 1968, the keynote speaker at the Annual Conference of the AWWA quoted from a report of the Secretary of the U.S. Department of Health Education and Welfare (27): "Fifty million Americans drink water that does not meet Public Health Service drinking water standards. Another 45 million Americans drink water that has not been tested by the Public Health Service."

The AWWA officials were reluctant to publish the paper because it appeared to be too critical of the water supply industry. They acceded only when the author happily agreed to allow rebuttals (28). The task force that prepared the report was not satisfied that the USPHS drinking water standards adequately reflect the health need of the people of the United States. Several issues troubled them.

Little information is available on the health implications of trace substances that may produce disease after exposure over long periods of time. Health experts have repeatedly pointed out that grave, delayed physical manifestations can result from repeated exposure to concentrations of environmental pollutants so small that victims do not report symptoms to a physician.

Furthermore, an individually acceptable amount of water pollution, added to a bearable amount of air pollution, plus nuisances from noise and congestion, can produce a totally unacceptable health environment. It is entirely possible that the biological effects of these environmental hazards, some of which reach individuals slowly and silently over decades or generations, will first begin to reveal themselves after their impact has become irreversible.

In a prescient paper on cancer hazards, Hueper (29) stated:

> It is obvious that with the rapidly increasing urbanization and industrialization of the country and the greatly increased demand on the present resources of water from lakes, rivers, and underground reservoirs, the danger of cancer hazards will grow considerably within the foreseeable future.

Hueper (29) went on to report that studies in Holland revealed that cities drawing water from polluted rivers had higher cancer death rates than those taking water from higher-quality underground sources. At about the same time, the Genetic Study Section of the National Institutes of Health (30) reported that a number of widely used chemicals are known to induce genetic damage in some organisms and that chemicals mutagenic to one species are likely to be mutagenic to others. They believed that when large populations are exposed to highly mutagenic compounds, and they are not demonstrably mutagenic to individuals, the total number of deleterious mutations in the whole population over an extended period of time could be significant.

In 1969, at the beginning of a review of the 1962 standards, the USPHS Bureau of Water Hygiene undertook a comprehensive survey of water supplies in the United States, known as the Community Water Supply Study (CWSS) (31). A total of 969 public water systems, representing about five percent of the total number of systems in the United States serving 18 million people, about 12% of the population being served, were tested (32). About 41% of the systems served did not meet the guidelines in the 1962 Standards. Deficiencies were found in source protection, disinfection, clarification, pressure in the distribution systems, and combinations of these. The small systems, mainly those serving fewer than 500 people, had the greatest difficulty in maintaining water quality. The study revealed that several million people were being supplied with water of inadequate quality and about 360,000 people were being supplied with potentially dangerous drinking water.

The results of the CWSS generated interest in federal legislation that would bring all community water systems under the purview of federal regulations. In 1972, a report of an investigation of the quality of Mississippi River water, as withdrawn from the Carrolton filtration plant in New Orleans, extracted by GAC filtration and a solvent, revealed 36 organic chemicals in the finished water (33). Later, the U.S. General Accounting Office, an agency of the Congress, released a report of the results of an investigation of 446 community water supply systems in six states around the country and found that only 60 of them fully complied with the bacterial and sampling requirements of the 1962 Standards (34). Bacteriological and chemical monitoring were inadequate in five of the states.

In addition to government concern, public organizations and the press had begun to give attention to water supply issues. A three-part series in *Consumer Reports* drew attention to the organic contaminants in New Orleans drinking water (35) Several points were made at the outset of the series that are appropriate today:

> New Orleans, like many other American cities gets its drinking water from a heavily polluted source.... Many industries discharge their wastes into the river and many upriver cities discharge their sewage into it ... runoff from farmland carries a wide variety of pesticides, herbicides, fertilizers, and other agricultural chemicals that swell the Mississippi's pollution burden.
>
> Few New Orleans residents are alarmed. They have been repeatedly assured by city officials that their water, processed according to established water-treatment principles, meets the drinking water standards of the US Public Health Sevice and is "safe." And so it probably is, if one takes "safe" to mean that the water won't cause typhoid, cholera, or other bacterial diseases—the diseases that the standard water treatment is designed to prevent.
>
> In 1969, the Federal Water Pollution Control Administration sampled New Orleans drinking water.... Thirty six (organic compounds) were identified; others were found but could not be identified.
>
> Three of the organic chemicals (chloroform, benzene, and bis-chloroethyl ether) were carcinogens, shown to cause cancer in animal experiments. Three others were toxic, producing liver damage in animals when consumed even in small quantities for long periods. The long-term effects ... are unknown.

The Environmental Defense Fund (EDF) conducted an epidemiologic study in the New Orleans area that compared cancer death rates from communities using lower Mississippi River water as a source with those from nearby communities that were using groundwater sources. The report indicating higher cancer rates among those using the Mississippi River Water was released to the press on November 7, 1974 (36–38). Further publicity followed on December 5, when Dan Rather on CBS aired nationally a program titled "Caution, drinking water may be dangerous to your health." It is interesting to note that upon learning of this situation and the passage of the SDWA, the City of Vicksburg, which had been drawing its water from the Mississippi River, shifted its source to groundwater.

These events, together with the revelation at the time that the chlorine used to make water microbiologically safe would create a family of compounds, trihalomethanes, that were themselves believed to be carcinogenic, led to the passage of the 1974 SDWA.

DRINKING WATER IN DEVELOPING COUNTRIES

The safety of drinking water cannot be examined without considering the problems of drinking water supply and safety in the countries of Asia, Africa, and Latin America. In the industrialized world, attempts are being made to eliminate the use of chlorine for disinfection. Several cities in the Netherlands have abandoned chlorine and other disinfectants entirely because of their concern for DBPs. On the other hand, the situation in the developing world is so serious that the availability of chlorine for every water supply would reduce infant mortality by about 90%.

In 1991, cholera broke out in the Pacific coast of Peru, most probably introduced by maritime traffic from Asia by the discharge of ballast water into the coastal zone from which fish are taken for food, often eaten uncooked. Within two weeks, most of the Peruvian coast, where half of the 22 million Peruvians reside, was host to the disease. Of the some 322,000 cases reported for the year, 55% occurred in the first 12 weeks of the epidemic. The case fatality rate was 0.9% signifying about 30,000 deaths in 1991. By the end of the year, 15 other countries in the Americas, including the United States and Canada, had reported outbreaks caused by the same strain of cholera (39).

Because of its explosive and urban character, contaminated water was identified as the medium for the rapid spread and the intensity of the disease in the cities. Most of the cities had conventional water treatment plants with filtration for water drawn from surface sources. Investigation revealed that chlorination was curtailed and often entirely absent when well water was used. Some Peruvian officials blamed the USEPA for the failure to use chlorine because it had been trumpeting the cancer risks associated with chlorine in water supplies (40).

A serious cholera outbreak occurred in early 2001 in KwaZulu-Natal in the Republic of South Africa, with more than 30,000 cases and some 100 deaths (41). At the height of the outbreak, more than 1000 cases were being reported daily. The reason stated was that the people do not have access to tapwater and are obliged to rely on water from very polluted streams. Even where “bleach” is available, it is not used because it is believed to interfere with fertility. Boiling is not feasible, as firewood is scarce.

In 1980, only 44% of the total population of the developing countries was being served with water by any means, including carrying water of questionable quality long distances from standposts. In urban areas, 69% of the population was being served and very little of that can be considered safe because few cities maintained 24-hour service. When water pressure in distribution pipes is absent, which is most of the day, treated drinking water inevitably becomes contaminated from infiltration of groundwater that is highly contaminated because sewerage systems are absent or in poor condition.

International agencies such as the World Health Organization, the World Bank, the regional development banks, and the developed countries along with the developing countries designated the 1980s the “international drinking water supply and sanitation decade,” during which special efforts were to be made to bring water to the people of the developing world. Ten years later, the population in the developing countries with water supplies had increased to 69%, but the number of people unserved in urban areas had increased by 31 million (42). The rate of urbanization in Asia Africa and Latin America is so great that, even with intensified financial support in grants and loans, the number of urban residents without water service is growing. More important is that those who are counted as having water service do not have safe water by any standard. All that is required to reduce the infant death rate is the type of treatment facilities and their operation and maintenance that was conventional in the industrial world almost a hundred years ago.

Given the nature of world travel today, it is clearly in the self-interest of the industrialized countries to help the developing countries provide water that at least meets 1925 U.S. standards. This would reduce infectious disease that is the major health risk to people and visitors in these countries.

THE FUTURE OF PUBLIC WATER SUPPLY

The history of the monitoring and control of drinking water quality from its earliest days through the present has lessons for those charged with protecting the public health, particularly for those responsible for providing the drinking water to their constituents. This volume demonstrates, if nothing else, that setting standards is a difficult and lengthy procedure. It may be many years, even decades between the time a new risk surfaces and regulations for its control are established and many years more before they are published. Also, years must be allowed for constructing the necessary facilities for eliminating the risks. It behooves the professionals in water utility leadership to educate themselves concerning new risks and prepare to address them before the standards appear in the *Federal Register*. The object is to minimize health risks to the public. Failure, or the perception of failure, drives the public to bottled water with its own risks and costs that are a hardship for a sizable fraction of the population.

A not unrelated issue that is growing in importance as our population ages is the significant percent of the population that is more vulnerable to contaminants by virtue of compromised immune systems. Standards for this population may need to be promulgated.

A similar solution is now being proposed in addressing the quality of water suitable for the potable reuse of wastewaters. Wastewaters contain a large number and a great variety of SOCs. The California Department of Health Services is proposing for the regulation of water quality for groundwater recharge with reclaimed wastewater to potable water aquifers drawn on for drinking water that total organic carbon (TOC) limits be set (43). Again, the carbon compounds may be innocuous or toxic, but in any case a maximum contaminant level (MCL) for TOC of wastewaters is hardly appropriate to assure drinking water safety.

This principle carried over to the 1976 USEPA National Interim Primary Drinking Water Regulations, referred to by this language in Appendix A as "background used in developing the national interim primary drinking water regulations":

> Protection of water that poses no threat to the consumer's health depends on continuous protection. Because of human frailties associated with protection, priority should be given to selection of the purest source. Polluted sources should not be used unless other sources are economically unavailable, and then only when personnel, equipment, and operating procedures can be depended upon to purify and otherwise continually protect the drinking water supply.

This principle is being ignored today, in part because of our faith in treatment technology. Reclaimed wastewater is being proposed as a source for drinking water supplies. Wastewater is hardly likely to be the purest source, and its use for potable reuse is resisted by consumers. Use of reclaimed wastewater for nonpotable purposes is currently being practiced in many hundreds of communities in the United States (44,45), and will be increasingly considered for relieving the pressure on limited high-quality resources.

BIBLIOGRAPHY

1. Okun, D.A. (1996). From cholera to cancer to cryptosporidiosis. *J. Environ. Eng.* **122**: 453–458.
2. Frontinus, S.J. (A.D. 97). *The Two Books on the Water Supply of the City of Rome.*, transl. Clemens Herschel, 1899. Boston: Dana Estes and Company.
3. United Nations. (1958). *Water for Industrial Use*. UN Report E/3058ST/ECA/50. Economic and Social Council, New York.
4. Longmate, N. (1966). *King Cholera: The Biography of a Disease*. Hamish Hamilton, London.
5. Cosgrove, J.J. (1909). *History of Sanitation*. Standard Sanitary Manufacturing Co, Pittsburgh, PA.
6. Snow, J. (1936). *Snow on Cholera*. Oxford Univ. Press, England.
7. Okun, D.A. (1991). Clean water and how to get it. *J. New Engl. Water Works Assoc.* **105**(1): 110.
8. Ives, K.J. (1990). The Chadwick Centenary. *The Life and Times of Sir Edwin Chadwick: 1800–1890*. University College, London.
9. Fair, G.M. (1945). Engineers and engineering in the Massachusetts State Board of Health. *New Engl. J. Med.* **232**: 443–446.
10. Blake, N.M. (1956). *Water for the Cities*. Syracuse University Press, Syracuse, NY.
11. Kober, G.M. (1908). *Conservation of life and health by improved water supply*. *Engineering Record* 57.
12. Ellms, J.W. (1928). *Water Purification*. McGraw-Hill, New York.
13. McCarthy, M.P. (1987). *Typhoid and the Politics of Public Health in 19th-Century Philadelphia*. American Philosophical Society, Philadelphia.
14. Baker, M.N. (1948). *The Quest for Pure Water*. American Water Works Association, Denver.
15. Bellar, T.A., Lichtenberg, J.J., and Kroner, R.C. (1974). The occurrence of organohalides in chlorinated drinking water. *J. Am. Water Works Assoc.* **66**: 703.
16. Lederberg, J. (1969). *We're so accustomed to using chlorine that we tend to overlook its toxicity*. *The Washington Post* May 3, p. A15.
17. United States Statutes. (1893). Interstate Quarantine Act of 1893. *U.S. Statutes at Large*. Chap. 114, Vol. 27, p. 449, Feb. 15.
18. McDermott, J.H. (1973). Federal drinking water standards—past, present, and future. *J. Environ. Eng. Div. Am. Soc. Civil Eng.* **EE4**(99): 469.
19. Borchardt, J.A. and Walton, G. (1971). *Water Quality and Treatment*, 3rd Edn. McGraw-Hill, New York.
20. USPHS. (1925). Report of the Advisory Committee on Official Water Standards. *Public Health Reports* **40**: 693.
21. USPHS. (1943). Public Health Service Drinking Water Standards and Manual of Recommended Water Sanitation Practice. *Public Health Reports* **56**: 69.
22. USPHS. (1946). Public Health Service Drinking Water Standards. *Public Health Reports* **61**: 371.
23. Wolman, A. (1960). Concepts of policy in the formulation of so-called standards of health and safety. *J. Am. Water Works Assoc.* **52**: 11.
24. USPHS. (1962). *Public Health Service Drinking Water Standards*. HEW, Washington, DC.
25. Middleton, F.M., Rosen, A.A., and Burttschell. (1962). Manual for recovery and identification of organic chemicals in water. *J. Am. Water Works Assoc.* **54**: 223–227.
26. Train, R.S. (1974). Facing the real cost of clean water. *J. Am. Water Works Assoc.* **66**: 562.
27. USDHEW (U.S. Department of Health, Education and Welfare). (1967). *A Strategy for a Livable Environment*. HEW, Washington, DC.
28. Okun, D.A. (1969). Alternatives in water supply. *J. Am. Water Works Assoc.* **61**(5): 215–224.
29. Hueper, W.C. (1960). Cancer hazards from natural and artificial water pollutants. *Proc. Conf. Physiol. Aspects Water Quality*. USPHS (U.S. Public Health Service), Washington, DC.
30. National Institutes of Health. Undated. *Report of Chemical Mutagens as a Possible Health Hazard*. Bethesda, MD: NIH Genetics Study Section.
31. USPHS. (1970). *Community Water Supply Study: Analysis of National Survey Findings*. PB214982. National Technical Information Service, Springfield, VA.
32. USPHS. (1970). *Community Water Supply Study: Significance of National Findings*. PB215198/BE. National Technical Information Service, Springfield, VA.
33. USEPA. (1972). *Industrial Pollution of the Lower Mississippi River in Louisiana*. USEPA Region VI, Dallas.
34. Symons, G.E. (1974). That GAO Report. *J. Am. Water Works Assoc.* **66**: 275.
35. Harris, R.H. and Brecher, E.M. (1974). *Is the water safe to drink? Part I. The problem. Part II. How to make it safe.*

Part III. What you can do. *Consumer Reports* 436 (June), 538 (July), 623 (August).

36. *The States-Item*. (1974). Cancer victims could be reduced—deaths tied to New Orleans water **98**(129)1 (Nov. 7).
37. Page, T., Talbot, E., and Harris, R.H. (1974). *The Implication of Cancer-Causing Substances in Mississippi River Water*. Environmental Defense Fund, Washington, DC.
38. Page, T., Harris, R.H., and Epstein, S.S. (1976). Drinking water and cancer mortality in Louisiana. *Science* **193**: 55.
39. Salazar-Lindo, E. and Alegre, M. (1993). The Peruvian cholera epidemic and the role of chlorination in its control and prevention. In: *Safety of Water Disinfection; Balancing Chemical and Microbial Risks*. G. Craun (Ed.). International Life Sciences Institute, Washington, DC.
40. Anderson, C. (1991). Cholera epidemic traced to risk miscalculation. *Nature* **354**: 255.
41. *Yahoo! Asia—News*. (2001). Cholera infections sky-rocket in South Africa (Feb. 1).
42. Okun, D.A. (1991). A water and sanitation strategy for the developing world. *Environment* **33**(8): 16. Washington, DC: Heldref Publications.
43. California Code of Regulations. (2001). *Title 22. Draft Recycling Criteria*. Sacramento: State Department of Health Services.
44. Okun, D.A. (1997). Distributing reclaimed water through dual systems. *J. Am. Water Works Assoc.* **89**(11): 52–64.
45. Okun, D.A. (2000). Water reclamation and unrestricted nonpotable reuse: A new tool in urban water management. *Annual Rev. Public Health* **21**: 223–245.

1962 U.S. PUBLIC HEALTH SERVICE STANDARDS

From *Drinking Water Regulation and Health*, Wiley 2003

Adoption of the 1962 U.S. Public Health Service standards was completed by publication in the Federal Register, March 6, 1962 (pp. 2152–2155). The full text of these standards is provided below.

PREFACE BY THE ADVISORY COMMITTEE

Domestic water supplies should protect the health and promote the well-being of individuals and the community. In this report on the revision of the 1946 edition of the USPHS drinking water standards, the objective of the committee is to recommend minimum requirements for reaching these goals. The USPHS drinking water standards were first adopted in 1914 to protect the health of the traveling public. The general and widespread use of these standards since that time has led to a series of revisions that have been applicable to water supplies generally. The development of atomic energy and other technological advances require that these standards again be revised. To carry out this revision, the chief sanitary engineer of USPHS appointed the undersigned advisory committee. A technical subcommittee of USPHS officers and a toxicological task force were established to collect information and prepare suggestions for the consideration of the advisory committee.

In preparing this report on the revision of the standards, the committee established the following guidelines:

1. The proposed standards should be discussed widely, and due cognizance should be given to international and other standards of water quality before a final report is submitted.
2. A new section on radioactivity should be added.
3. Greater attention should be given to the chemical substances being encountered increasingly, in both variety and quantity, in water sources.
4. In establishing limits for toxic substances, intake from food and air should be considered.
5. The rationale employed in determining the various limits should be included in an appendix.
6. The proposed format, with the exceptions noted above, should not differ greatly from the present standards.
7. The standards should be generally acceptable and should be applicable to all public water supplies in the United States, as well as to those supplies used by carriers subject to USPHS regulations.
8. The following two types of limits used in previous editions should be continued:
   a. Limits that, if exceeded, shall be grounds for rejection of the supply. Substances in this category may have adverse effects on health when present in concentrations above the limit.
   b. Limits that should not be exceeded whenever more suitable supplies are, or can be made, available at reasonable cost. Substances in this category, when present in concentrations above the limit are either objectionable to an appreciable number of people or exceed the levels required by good water quality control practices.
9. These limits should apply to the water at the free-flowing outlet of the ultimate consumer.

This revision of the drinking water standards includes, for the first time, limiting concentrations of radioactivity in water. The effects on large population groups of chronic exposure to low levels of radioactivity are not yet well defined. The limits presented herein are an effort to derive conservative values from the best information now available and may be adjusted upward or downward as new and better data become available.

The committee has taken cognizance of the growing problem of potentially harmful chemicals in sources of drinking water. Limits for several new chemicals have been added, including a gross limit for the concentration of some types of synthetic chemicals. It was not feasible, however, to include limits for all the many chemicals that have varying degrees of toxic potential. Consideration was given to the more common chlorinated hydrocarbon and organophosphate insecticides, but the information available was not sufficient to establish specific limits for these chemicals. Moreover, the concentrations of these chemicals, where tested, have been below those that would constitute a known health hazard. The committee believes that pollution of water supplies with such contaminants can become significant and urges that the problem be kept under closer surveillance. Further, the committee recommends that regulatory actions be taken to minimize concentrations of such chemicals in drinking water.

In view of the accelerating pace of new developments affecting water quality, the committee recommends that a mechanism be established for continual appraisal and appropriate revision of the standards. It also recommends that USPHS intensify its continuing studies toward the development of basic information on the relationship of the biological, chemical, physical, and radiological aspects of water quality to health.

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U.S. Geological Survey: S. K. Love
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Drinking Water Standards

Definition of Terms. The terms used in these standards are as follows:

Adequate protection by natural means involves one or more of the following processes of nature that produce water consistently meeting the requirements of these standards: dilution, storage, sedimentation, sunlight, aeration, and the associated physical and biological processes that tend to accomplish natural purification in surface waters and, in the case of groundwaters, the natural purification of water by infiltration through soil and percolation through underlying material and storage below the ground water table.

Adequate protection by treatment is anyone or any combination of the controlled processes of coagulation, sedimentation, sorption, filtration, disinfection, or other processes that produce a water consistently meeting the requirements of these standards. This protection also includes processes that are appropriate to the source of supply; works that are located, designed, and constructed to eliminate or prevent pollution; and conscientious operation by well-trained and competent personnel whose qualifications are commensurate with the responsibilities of the position and acceptable to the reporting agency and the certifying authority.

Certifying authority is the surgeon general of USPHS or his duly authorized representatives. (Reference to the certifying authority is applicable only for those water supplies to be certified for use on carriers subject to the USPHS regulations—42 CFR Part 72.)

The coliform group includes all organisms considered in the coliform group as set forth in *Standard Methods for the Examination of Water and Wastewater*, current edition [11th ed., 1960], prepared and published jointly by the American Public Health Association, American Water Works Association, and Water Pollution Control Federation.

Health hazards are conditions, devices, or practices in the water supply system and its operation that create, or may create, a danger to the health and well-being of the water consumer. An example of a health hazard is a structural defect on the water supply system, whether of location, design, or construction, that may regularly or occasionally prevent satisfactory purification of the water supply or cause it to be polluted from extraneous sources.

Pollution, as used in these standards, is defined as the presence of any foreign substance (organic, inorganic, radiological, or biological) in water which tends to degrade its quality so as to constitute a hazard or impair the usefulness of the water.

Reporting agencies are the respective official state health agencies or their designated representatives.

The standard sample for the bacteriological test shall consist of

1. For the bacteriological fermentation tube test, five standard portions of either: (a) 10 mL or (b) 100 mL
2. For the membrane filter technique, not less than 50 mL

Water supply system includes the works and auxiliaries for collection, treatment, storage, and distribution of the water from the sources of supply to the free-flowing outlet of the ultimate consumer.

Source and Protection

The water supply should be obtained from the most desirable source feasible, and effort should be made to prevent or control pollution of the source. If the source is not adequately protected by natural means, the supply shall be adequately protected by treatment.

Frequent sanitary surveys shall be made of the water supply system to locate and identify health hazards that might exist in the system. The manner and frequency of making these surveys, and the rate at which discovered health hazards are to be removed, shall be in accordance with a program approved by the reporting agency and the certifying authority.

Approval of water supplies shall be dependent in part on

a. Enforcement of rules and regulations to prevent development of health hazards
b. Adequate protection of the water quality throughout all parts of the system, as demonstrated by frequent surveys
c. Proper operation of the water supply system under the responsible charge of personnel whose qualifications are acceptable to the reporting agency and the certifying authority
d. Adequate capacity to meet peak demands without development of low pressures or other health hazards
e. Record of laboratory examinations showing consistent compliance with the water quality requirements of these standards

For the purpose of application of these standards, responsibility for the conditions in the water supply system shall be considered to be held by

a. The water purveyor, from the source of supply to the connection to the customer's service piping.
b. The owner of the property served and the municipal, county, or other authority having legal jurisdiction, from the point of connection to the customer's service piping to the free-flowing outlet of the ultimate consumer.

Bacteriological Quality

Sampling. Compliance with the bacteriological requirements of these standards shall be based on examinations of samples collected at representative points throughout the distribution system. The frequency of sampling and the location of sampling points shall be established jointly by the reporting agency and the certifying authority after investigation by either agency, or both, of the source, method of treatment, and protection of the water concerned.

The minimum number of samples to be collected from the distribution system and examined each month should be in accordance with the number in (Fig. 1) for the population served by the system. For the purpose of uniformity and simplicity in application, the number determined from (Fig. 1) should be in accordance with the following: for a population of 25,000 or less, to the nearest 1; 25,001–100,000, to the nearest 5: and more than 100,000 to the nearest 10.

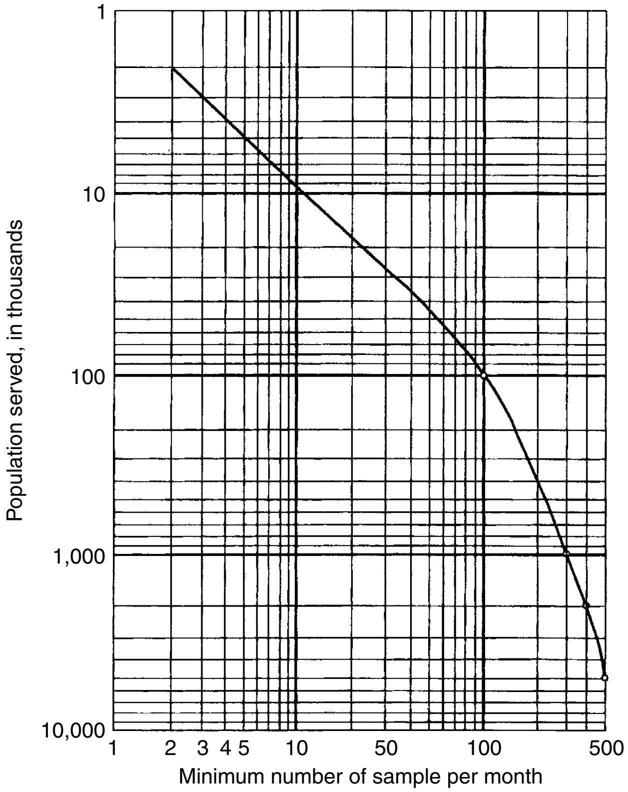

Figure 1. Relation between minimum number of samples to be collected per month and population served.

In determining the number of samples examined monthly, the following samples may be included, provided all results are assembled and available for inspection, and the laboratory methods and technical competence of the laboratory personnel are approved by the reporting agency and the certifying authority:

a. Samples examined by the reporting agency
b. Samples examined by local government laboratories
c. Samples examined by the water works authority
d. Samples examined by commercial laboratories

The laboratories in which these examinations are made and the methods used in making them shall be subject to inspection at any time by the designated representatives of the certifying authority and the reporting agency. Compliance with the specified procedures and the results obtained shall be used as a basis for certification of the supply.

Daily samples collected following a bacteriologically unsatisfactory sample as provided in Secs. 3.21, 3.22, and 3.23 shall be considered as special samples and shall not be included in the total number of samples examined. Neither shall such special samples be used as a basis for prohibiting the supply, provided that

1. When waters of unknown quality are being examined, simultaneous tests are made on multiple portions of a geometric series to determine a definitive coliform content.
2. Immediate and active efforts are made to locate the cause of pollution.
3. Immediate action is taken to eliminate the cause.
4. Samples taken following such remedial action are satisfactory.

Limits. The presence of organisms of the coliform group as indicated by samples examined shall not exceed the following limits:

When 10-mL standard portions are examined, not more than 10% in any month shall show the presence of the coliform group. The presence of the coliform group in three or more 10-mL portions of a standard sample shall not be allowable if this occurs

a. In two consecutive samples.
b. In more than one sample per month when less than twenty are examined per month.
c. In more than 5 per cent of the samples when twenty or more are examined per month.

When organisms of the coliform group occur in three or more of the 10-mL portions of a single standard sample, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

When 100-mL standard portions are examined, not more than 60% in any month shall show the presence of the coliform group. The presence of the coliform group in all five of the 100-mL portions of a standard sample shall not be allowable if this occurs:

a. In two consecutive samples.
b. In more than one sample per month when less than five are examined per month.
c. In more than 20 percent of the samples when five or more are examined per month.

When organisms of the coliform group occur in all five of the 100-mL portions of a single standard sample, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

When the membrane filter technique is used, the arithmetic mean coliform density of 0 standard samples examined per month shall not exceed 1 per 100 mL. Coliform colonies per standard sample shall not exceed 3 per 50 ml, 4 per 100 mL, 7 per 200 mL, or 13 per 500 mL in

a. Two consecutive samples.
b. More than one standard sample when less than 20 are examined per month.
c. More than 5% of the standard samples when 20 or more are examined per month.

When coliform colonies in a single standard sample exceed the above values, daily samples from the same sampling point shall be collected promptly and examined until the results obtained from at least two consecutive samples show the water to be of satisfactory quality.

Physical Characteristics

Sampling. The frequency and manner of sampling shall be determined by the reporting agency and the certifying authority. Under normal circumstances, samples should be collected one or more times per week from representative points in the distribution system and examined for turbidity, color, threshold odor, and taste.

Limits. Drinking water should contain no impurity that would cause offense to the sense of sight, taste, or smell. Under general use, the following limits should not be exceeded: turbidity, 5 units; color, 15 units; and threshold odor number, 3 units.

Chemical Characteristics

Sampling. The frequency and manner of sampling shall be determined by the reporting agency and the certifying authority. Under normal circumstances, analyses for substances listed below need be made only semiannually. If, however, there is some presumption of unfitness because of the presence of undesirable elements, compounds, or materials, periodic determinations for the suspected toxicant or material should be made more frequently, and an exhaustive sanitary survey should be made to determine the source of the pollution. Where the concentration of a substance is not expected to increase in processing and distribution, available and acceptable source water analyses performed in accordance with standard methods may be used as evidence of compliance with these standards.

Where experience, examination, and available evidence indicate that particular substances are consistently absent from a water supply or below levels of concern, semiannual examinations for those substances may be omitted when approved by the reporting agency and the certifying authority.

The burden of analysis may be reduced in many cases by using data from acceptable sources. Judgment concerning the quality of water supply and the need for performing specific local analyses may depend in part on information produced by such agencies as (1) USGS, which determines chemical quality of surface water and groundwater of the United States and publishes these data in *Water Supply Papers* and other reports, and (2) USPHS, which determines water quality related to pollution (or the absence of pollution) in the principal rivers of the United States and publishes these data annually in *National Water Quality Network*. Data on pollution of waters as measured by carbon chloroform extracts (CCES) may be found in the latter publication.

Limits. Drinking water shall not contain impurities in concentrations that may be hazardous to the health of the consumers. It should not be excessively corrosive to the water supply system. Substances used in its treatment shall not remain in the water in concentrations greater than required by good practice. Substances that may have deleterious physiological effect, or substances for which physiological effects are not known, shall not be introduced into the system in a manner that would permit them to reach the consumer.

The chemical substances shown in Table 1 should not be present in a water supply in excess of the listed concentrations where, in the judgment of the reporting agency and the certifying authority, other more suitable supplies are or can be made available.

The presence of substances in excess of the concentrations listed in Table 2 shall constitute grounds for rejection of the supply.

Fluoride. When fluoride is naturally present in drinking water, the concentration should not average more than the appropriate upper limit shown in Table 3. Presence of fluoride in average concentrations greater than two times the optimum values in Table 3 shall constitute grounds for rejection of the supply. Where fluoridation (supplementation of fluoride in drinking water) is practiced, the average fluoride concentration shall be kept within the upper and lower control limits shown in Table 3. In addition to the sampling required by Sec. 5.1, fluoridated and defluoridated supplies shall be sampled with sufficient frequency to determine that the desired fluoride concentration is maintained.

Table 1. A Water Supply with Concentrations Exceeding These Limits Should Be Avoided If Possible[a]

Substance	Concentration (mg/L)
Alkyl benzene sulfonate (ABS)	0.5
Arsenic (As)	0.01
Chloride (Cl)	250.0
Copper (Cu)	1.0
Carbon Chloroform extract (CCE)	0.2
Cyanide (CN)	0.01
Fluoride (F)	—[b]
Iron (Fe)	0.3
Manganese (Mn)	0.05
Nitrate (NO_3)[c]	45.0
Phenols	0.001
Sulfate (SO_4)	250.0
Zinc (Zn)	5.0

[a] Refer to Section 5.2.1 (in this Appendix).
[b] See Section 5.2.3.
[c] In areas in which the nitrate content of water is known to be in excess of the listed concentration, the public should be warned of the potential dangers of using the water for infant feeding.

Table 2. A Water Supply with Concentrations Exceeding These Limits Should Be Rejected[a]

Substance	Concentration (mg/L)
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.01
Chromium (Cr^{6+})	0.05
Cyanide (CN)	0.2
Fluoride (F)	—[b]
Lead (Pb)	0.05
Selenium (Se)	0.01
Silver (Ag)	0.05

[a] Refer to Section 5.2.2.
[b] See Section 5.2.3.

Radioactivity

Sampling. The frequency of sampling and analysis for radioactivity shall be determined by the reporting agency and the certifying authority after consideration of the likelihood of significant amounts being present. Where concentrations of ^{226}Ra or ^{90}Sr may vary considerably, quarterly samples composited over a period of 3 months are recommended. Samples for determination of gross activity should be taken and analyzed more frequently. As indicated in Sec. 5.1, data from acceptable sources may be used to indicate compliance with these requirements.

Limits. The effects of human radiation exposure are viewed as harmful and any unnecessary exposure to ionizing radiation should be avoided. Approval of water supplies containing radioactive materials shall be based on the judgment that the radioactivity intake from such water supplies when added to that from all other sources will not result in an intake greater than the radiation protection guidance recommended by the Federal Radiation Council and approved by the President. Water supplies shall be approved without further consideration of other sources of radioactivity intake of ^{226}Ra and ^{90}Sr when the water contains these substances in amounts not exceeding 3 and 10 $\mu\mu$Ci/L, respectively. When these concentrations are exceeded, a water supply shall be approved by the certifying authority if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action.

The Federal Radiation Council, in its Memorandum for the President, Sept. 13, 1961, recommended that "routine control of useful applications of radiation and atomic energy should be such that expected average exposures of suitable samples of an exposed population group will not exceed the upper value of Range II (20 $\mu\mu$Ci/day of ^{226}Ra and 200 $\mu\mu$Ci/day of ^{90}Sr).

Table 3. Recommended Fluoride Control Limits[a]

Annual Average of Maximum Daily Air Temperature[b], °F	Recommended Control Limits for Fluoride Concentration, mg/L		
	Lower	Optimum	Upper
50.0–53.7	0.9	1.2	1.7
53.8–58.3	0.8	1.1	1.5
58.4–63.8	0.8	1.0	1.3
63.9–70.6	0.7	0.9	1.2
70.7–79.2	0.7	0.8	1.0
79.3–90.5	0.6	0.7	0.8

[a] Refer to Section 5.2.3.
[b] Based on temperature data obtained for a minimum of 5 years.

In the known absence[1] of ^{90}Sr and alpha emitters, the water supply is acceptable when the gross beta concentrations do not exceed 1000 $\mu\mu$Ci/L. Gross beta concentrations in excess of 1000 $\mu\mu$Ci/L shall be grounds for rejection of supply except when more complete analyses indicate that concentrations of nuclides are not likely to cause exposures greater than the Radiation Protection Guides as approved by the President on recommendation of the Federal Radiation Council.

Recommended Analytical Methods

Analytical methods to determine compliance with the requirements of these standards shall be those specified in *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, and WPCF, New York, current edition [11th ed., 1960], and those specified as follows:

Barium. Rainwater, F. H., and L. L. Thatcher: *Methods for the Collection and Analysis of Water Samples*, USGS, Water Supply Papers, 1454, Govt. Printing Office, Washington, DC.

Carbon Chloroform Extract (CCE). *Method for Determining the Carbon Chloroform Extract (CCE) in Drinking Water*, R. A. Taft San. Eng. Center, USPHS, Cincinnati (1961).

Radioactivity. *Laboratory Manual of Methodology; Radionuclide Analysis of Environmental Samples*, Tech. Rept. R59-6, R. A. Taft San. Eng. Center, USPHS, Cincinnati; and Methods of Radiochemical Analysis, Tech. Rept. 173, Joint WHO-FAO Committee, World Health Organization (1959).

Selenium. Magin, C. B., et al.: Suggested Modified Method for Colorimetric Determination of Selenium in Natural Water, J. Am. Water Workd Assoc. 52:119 (Sept. 1960).

Organisms of the Coliform Group. All of the details of techniques in the determination of bacteria of this group, including the selection and preparation of apparatus and media, the collection and handling of samples, and the intervals and conditions of storage allowable between collection and examination of the water sample, shall be in accordance with *Standard Methods for the Examination of Water and Wastewater*, current edition, and the procedures shall be those specified therein for

1. Membrane Filter Technique, standard test, or
2. Completed Test, or
3. Confirmed Test, procedure with brilliant green lactose bile broth.
4. Confirmed Test, procedure with Endo or eosin methylene blue agar plates.[2]

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[1] Absence is taken here to mean a negligibly small fraction of the above specific limits where the limit for the unidentified alpha emitters is taken as the listed limit for ^{226}Ra.

[2] The Confirmed Test is allowed, provided the value of this test to determine the sanitary quality of the specific water supply being examined is established beyond reasonable doubt by comparisons with Completed Tests performed on the same water supply.

ION EXCHANGE AND DEMINERALIZATION

National Drinking Water
Clearinghouse

Ion exchange and membrane processes are becoming used extensively in water and wastewater treatment. Ion exchange is primarily used for the removal of hardness ions, such as magnesium and calcium, and for water demineralization. Reverse osmosis (RO) and electrodialysis, both membrane processes, remove dissolved solids from water using membranes.

ION EXCHANGE AND DEMINERALIZATION ARE BECOMING WIDELY USED

Ion exchange units can be used to remove any charged (ionic) substance from water, but are usually used to remove hardness and nitrate from groundwater.

Water is pretreated to reduce the suspended solids and total dissolved solids (TDS) load to the ion-exchange unit. Methods of pretreatment include:

- filtration,
- coagulation and filtration,
- cold lime with or without soda ash,
- hot lime with or without soda ash,
- evaporation or distillation,
- electrodialysis,
- RO,
- continuous deionization,
- ultrafiltration,
- degasification, or
- combinations of the above.

(Source: Owens, 1995)

RO systems are compact, simple to operate, and require minimal labor, making them suitable for small systems. They are also suitable for systems where there is a high degree of seasonal fluctuation in water demand.

Electrodialysis is a process that also uses membranes. However, in electrodialysis, direct electrical current is used to attract ions to one side of the treatment chamber. Electrodialysis systems include a source of pressurized water, a direct current power supply, and a pair of selective membranes.

ION EXCHANGE

Ion exchange effectively removes more than 90 percent of barium, cadmium, chromium (III), silver, radium, nitrites, selenium, arsenic (V), chromium (VI), and nitrate. Ion exchange is usually the best choice for small systems that need to remove radionuclides.

Advantages

- Ion exchange process, like reverse osmosis, can be used with fluctuating flow rates.

- Effluent contamination is virtually impossible.
- Large variety of specific resins are available from suppliers. Each resin is effective in removing specific contaminants.

Limitations

- Ion exchange waste is highly concentrated and requires careful disposal.
- Potential for unacceptable levels (peaks) of contamination in effluent.
- Usually not feasible with high levels of TDS.
- Pretreatment required for most surface waters.
- Ion exchange units also are sensitive to the presence of competing ions. For example, influent with high levels of hardness will compete with other cations (positive ions) for space on the exchange medium, and the exchange medium must be regenerated more frequently.

Process

Inorganics removal is accomplished through adsorption of contaminant ions onto a resin exchange medium. As the name implies, one ion is substituted for another on the charged surface of the medium, which is usually a synthetic plastic resin. This resin surface is designed as either cationic or anionic (negatively charged). The exchange medium is saturated with the exchangeable ion before treatment operations.

During ion exchange, the contaminant ions replace the regenerant ions because they are preferred by the exchange medium. When there are no ions left to replace the contaminant ions, the medium is regenerated with a suitable solution, which resaturates the medium with the appropriate ions. Because of the required "down time," the shortest economical regeneration cycles are once per day.

The resin exchange capacity is expressed in terms of weight per unit volume of the resin. The calculation of the breakthrough time for an ion exchange unit requires knowledge of the resin exchange capacity, the influent contaminant concentration, and the desired effluent quality.

Equipment

Typical ion exchange units consist of prefiltration, ion exchange, disinfection, storage, and distribution elements (see Fig. 1).

Chemicals

Sodium chloride is often used to regenerate the exchange medium in ion exchangers because of the low cost of the chemical. However, this can result in a high sodium residual in the finished water, which may be unacceptable for individuals with salt restricted diets. This problem can be avoided by using other regenerant materials, such as potassium chloride.

REVERSE OSMOSIS (RO)

RO can effectively remove nearly all inorganic contaminants from water. It removes more than 70 percent of arsenic (III), arsenic (IV), barium, cadmium, chromium (III), chromium (VI), fluoride, lead, mercury, nitrite, selenium (IV), selenium (VI), and silver. Properly operated units will attain 96 percent removal rates. RO can also effectively remove radium, natural organic substances, pesticides, and microbiological contaminants. RO is particularly effective when used in series. Water passing through multiple units can achieve near zero effluent contaminant concentrations.

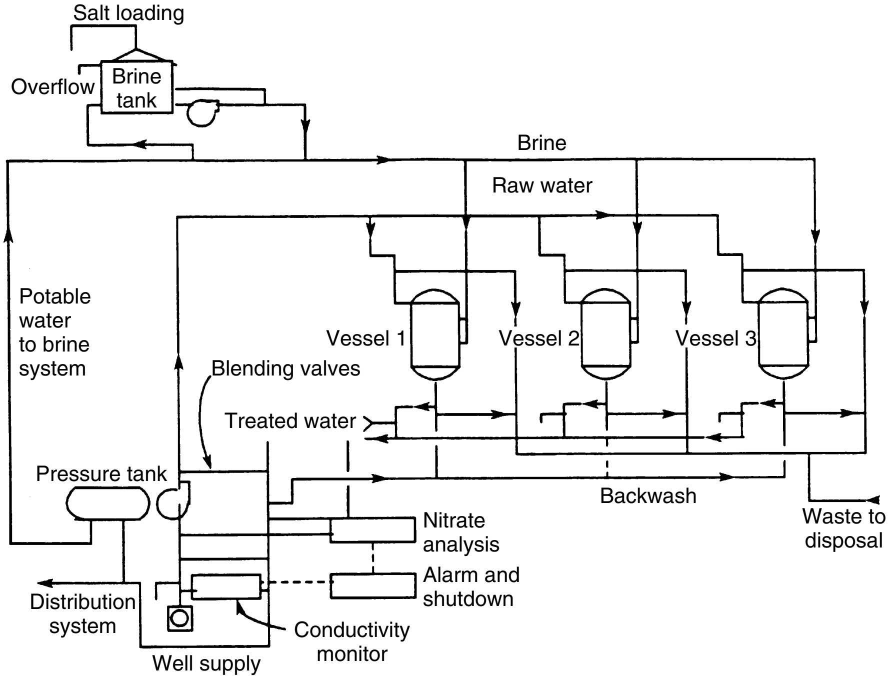


Figure 1. Ion exchange treatment system. *Source*: U.S. Environmental Protection Agency, 1989.

Advantages

- Removes nearly all contaminant ions and most dissolved non-ions.
- Relatively insensitive to flow and TDS level, and thus suitable for small systems with a high degree of seasonal fluctuation in water demand.
- RO operates immediately, without any minimum break-in period.
- Low effluent concentration possible.
- Bacteria and particles are also removed.
- Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications.

Limitations

- High capital and operating costs.
- Managing the wastewater (brine solution) is a potential problem.
- High level of pretreatment is required in some cases.
- Membranes are prone to fouling.

Process

RO removes contaminants from water using a semipermeable membrane that permits only water, and not dissolved ions (such as sodium and chloride), to pass through its pores. Contaminated water is subject to a high pressure that forces pure water through the membrane, leaving contaminants behind in a brine solution. Membranes are available with a variety of pore sizes and characteristics.

Equipment

Typical RO units include raw water pumps, pretreatment, membranes, disinfection, storage, and distribution elements (see Fig. 2). These units are able to process virtually any desired quantity or quality of water by configuring units sequentially to reprocess waste brine from the earlier stages of the process. The principal design considerations for reverse osmosis units are:

- operating pressure,
- membrane type and pore size,
- pretreatment requirements, and

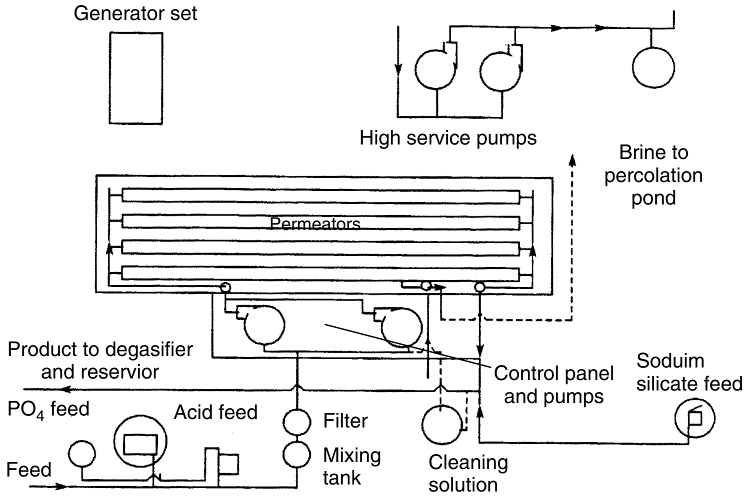


Figure 2. Schematic of a reverse osmosis system. *Source: U.S. Environmental Protection Agency, 1989.*

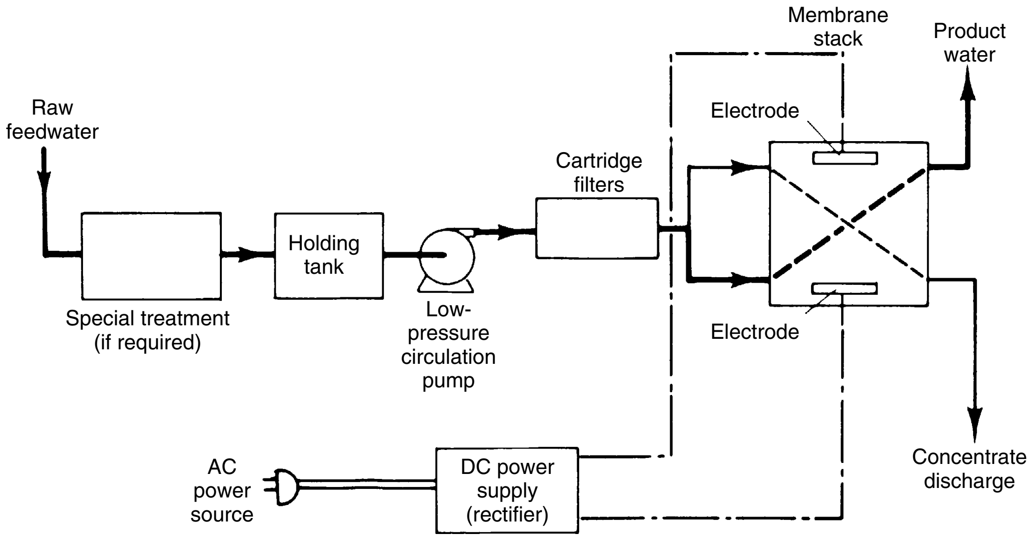


Figure 3. Basic components of an electrodialysis unit. *Source: U.S. Agency for International Development, 1980.*

- product conversion rate (the ratio of the influent recovered as waste brine water to the finished water).

Electrodialysis

Electodialysis is very effective in removing fluoride and nitrate, and can also remove barium, cadmium, and selenium (see Fig. 3).

Advantages

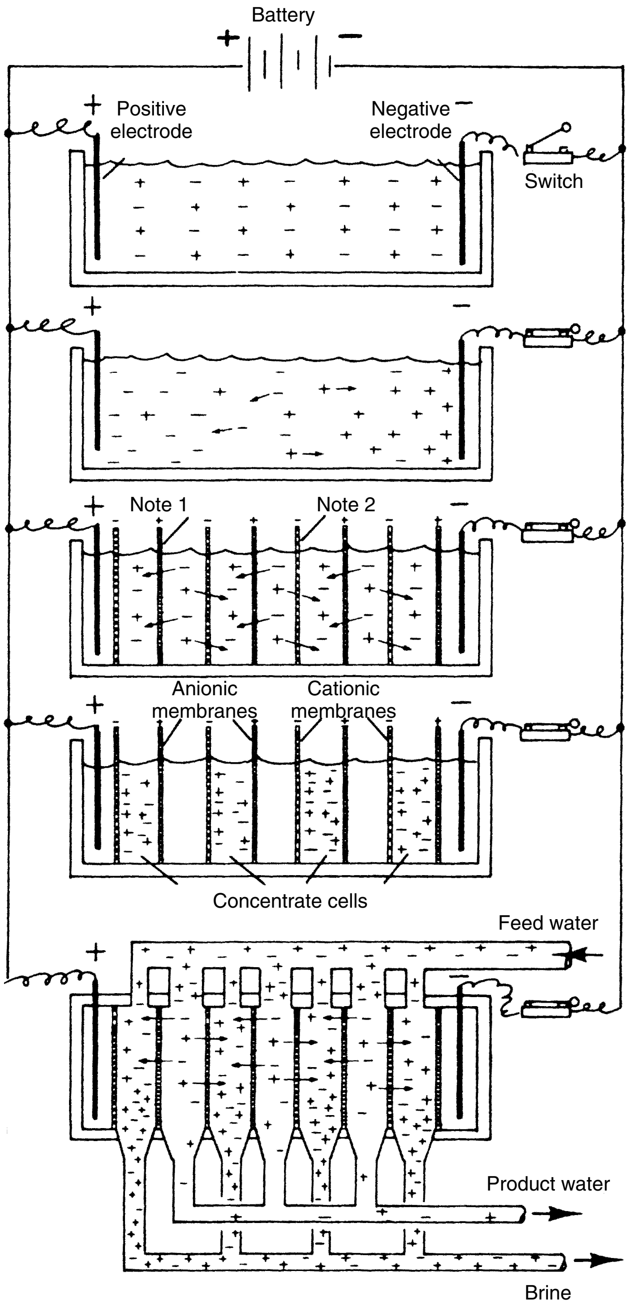
- All contaminant ions and most dissolved non-ions are removed.
- Relatively insensitive to flow and TDS level.
- Low effluent concentration possible.

Limitations

- High capital and operating costs.
- High level of pretreatment required.
- Reject stream is 20–90 percent of feed flow.
- Electrodes require replacement.

Process

The membranes adjacent to the influent stream are charged either positively or negatively, and this charge attracts counter-ions toward the membrane. The membranes are designed to allow either positively or negatively charged ions to pass through the membrane, thus ions



Many of the substances which make up the total dissolved solids (TDS) in brackish water are strong electrolytes. When dissolved in water they ionize; that is, the compounds dissociate into ions which carry an electric charge. Typical of the ions in brackish water are Cl^{-1}, Na^{+1}, HCO_3^{-1}, Mg^{+2},$SO4^{-2}$, and Ca^{+2}. These ions tend to attract the dipolar water molecules and to be diffused in times, fairly evenly throughout a solution.

If two electrodes are placed in a solution of ions and energized by a battery orother direct current source, the current is carried through the solution by the charged particles and the ions tend to migrate to the electrode of the opposite charge.

If alternately fixed charged membranes (which are selectively permeable to ions of the opposite charge) are placed in the path of the migrating ions, the ions will be trapped between the alternate cells formed.

Note 1: A positively fixed charge (anionic) membrane will allow negative ions to pass, but will repel positive ions.

Note 2: A negatively fixed charge (cationic) membrane will allow positive ions to pass, but will repel negative ions.

If this continued, almost all the ions wiould become trapped in the alternate cells (concentrate cells). The other cells, which lack ions, would have a lower level of dissolved constituents and would have a high resistance to current flows.

The phenomenon illustrated above is used in electrodialysis to remove ions from incoming saline water on a continuous basis. Feedwater enters both the concentrate and product cells. Up to about half of the ions in the product cells migrate and are trapped in the concentrate cells. Two streams emerge form the device: One of concentrated brine and the other with a much lower concentration of TDS (product water).

Figure 4. Movement of ions in the electrodialysis process. *Source: U.S. Agency for International Development, 1980.*

move from the product water stream through a membrane to the two reject water streams (see Fig. 4).

Equipment

The three essential elements of the system are (1) a source of pressurized water, (2) a direct current power supply, and (3) a pair of selective membranes. The average ion removal varies from 25 to 60 percent per stage. Multistage units can increase the efficiency of removal. Many membrane pairs are "stacked" in the treatment vessel.

Chemicals

Fouling of membranes may limit the amount of water treated. Fouling is caused when membrane pores are clogged by salt precipitation or by physical obstruction of suspended particulates. Particulates, suspended in water, can be removed in pretreatment but salts that exceed their solubility product at the membrane surface must be controlled chemically by pH reduction (to reduce carbonate concentration) or chelation of metal ions (by use of phosphate, for example). A reversal of the charge on the membranes, a process called electrodialysis reversal (EDR), helps to flush the attached ions from the membrane surface, thus extending the time between cleanings.

Where Can I Find More Information?

Information on ion exchange/demineralization was primarily obtained from two sources: Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities, *EPA/625/5-90/025; and* Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities, *EPA/625/4-89/023. Both may be ordered free from the U.S. Environmental Protection Agency Office of Research and Development at (513) 569-7562.*

These publications also may be ordered from the National Drinking Water Clearinghouse (NDWC); however, copying costs apply. The first book, item #DWBKGN09, an 82-page publication, costs $11.82; and the second, item #DWBKDM04, a 209-page book, costs $30.05. Shipping and handling charges also apply.

For further information or to order copies of "Tech Brief: Ion Exchange and Demineralization," item #DWBLPE56, "Tech Brief: Filtration," item #DWBLPE50, "Tech Brief: Disinfection," item #DWBLPE47, or "Tech Brief: Corrosion Control," item #DWBLPE52 call the NDWC at (800) 624-8301 or (304) 293-4191. These fact sheets are available at no cost, except for shipping and handling charges.

THE STATE OF THE WATER INDUSTRY—2004

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The water and wastewater treatment industry continues to be an evolving and often unpredictable business, and the year 2003 did not disappoint. The ongoing corporate consolidation in the industry produced surprises and new directions, whereas the headlong rush toward privatization seemed to falter, or at least slow a bit. Water resource issues and water management controversies continued to climb onto the front pages of the popular media; water quality scares, water rights battles, and water security issues gained significant public exposure. Wide-ranging debate over how to best fund the vast future capital needs of the water business began to take center stage. The extensive regional droughts of 2002 are still fresh in the minds of many people. And, although water stocks outperformed the general stock market this year, there still seem to be no big winners emerging. Below, we highlight the key industry developments of the past year, review the current characteristics of the market, and discuss the evolving drivers behind this business.

OVERVIEW

Studies and reports announcing the certainty and severity of future water challenges continue to be issued from the federal government, the various water-related trade associations, and environmental think tanks around the country. Earlier in the year, and to much fanfare, the American Council of Engineering Companies (ACEC) gave the water infrastructure system of the country a general grade of "D," and—supplementing numerous prior studies—the Congressional Budget Office predicted that we will need to spend more than $800 billion over the next 20 years to fix this problem. The increasing focus of concern among water industry and municipal officials is how to reconcile the difference between *current* spending rates and projected *future* needs—how to finance the "gap" that is becoming increasingly clear. As one observer put it, sometimes it seems that the fluid of most concern in this industry is not water, but red ink.

Although the trend to greater consolidation continued, 2003 may be remembered as the year in which the much-ballyhooed "foreign invasion" of recent years began to reverse directions. After practically tripping over each other in the rush to acquire assets during the late 1990s, many major European water companies began to shed major U.S. water businesses during the year. Although perhaps not totally unexpected, these divestitures constituted a major shift in the competitive dynamics and transactional trends in the business. In sum, several major players that have long been viewed as the prominent buyers in the industry, suddenly appeared to turn (at least partially) into sellers.

The reasons behind this shift are varied and complex (see discussion below), but it seems clear that a large-scale game of "musical chairs" is starting to happen in this industry. A considerable rearrangement of key assets

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is already starting to happen—in general, away from foreign companies and back toward domestic ownership. And, unfortunately for these foreign companies who were buying several years ago, average valuations in the industry are now lower (see Table 1), and the dollar has slid significantly against the Euro during the past couple of years.

Another longer term trend in the market—greater municipal outsourcing and private contract operation—also seemed to begin to shift direction or become less clear this year. The pace of privatization has been rapid during the past decade or so, and many analysts believe it was the perceived privatization opportunity that effectively drove much of the acquisition frenzy of the late 1990s. The last few years, however, have seen a gradual slowdown in this trend and an increasingly widespread reconsideration of the benefits of privatization of public water treatment operations. Starting with the much-publicized cancellation of Atlanta's water privatization plan and the postponement of programs in cities such as New Orleans and Stockton, the whole concept of water privatization has taken a major hit in public opinion circles during the past couple of years. For the first time in several years, the volume of outsourcing contracts in the country was actually down, and fairly sharply down, in 2003.

Nonetheless, the business of private contract operation is still projected to be one of the fastest growing market niches in the whole water industry. The forces behind privatization remain strong primarily because of the difficult position of municipalities. Public works managers are between a rock and a hard place—costs, technical requirements, and regulatory complexities continue to increase, but the general public remains resistant to increasing taxes and user's fees. As the contract operations firms point out, often the best solution to this dilemma

Table 1. 40 Publicly Traded Companies with Interests in the Water Industry

Company	Symbol	Revenues $ mils.	Income $ mils.	Market Cap. $ mils.
American States	awr	213	17.2	388.36
Ameron	amn	576	27.7	316.224
Aqua America	wtr	367	71	1940.4
Artesian Resources	arina	36	4.2	110.175
Badger Meter	bmi	184	7.6	123.222
Calgon Carbon	ccc	278	4.5	272.22
California Water	cwt	277	19.3	473.2
Clarcor	clc	741	55	1068.925
Clorox	clx	4140	486	10478.26
Cuno	cuno	288	26.8	688.708
Danaher	dhr	5290	537	14579.18
Dionex	dnex	232	34.6	1158.792
FlowServe	fls	2370	49.2	1103.448
Fluor	flr	8810	179	3348.06
Franklin Electric	fele	360	34.5	652.365
Glacier Water	hoo	71.2	−1.5	42.21
Great Lakes Chemical	glk	1470	−33	1277.144
Insituform Tech.	insu	491	23.5	424
Ionics	ion	349	−19.6	507.656
Isco	isko	62.5	1.46	48.8196
ITT Industries	itt	5630	391	7088.6
Layne Christenson	layn	278	2	164.3
Lindsay Mfg.	Inn	166	12.8	292.994
Metpro	mpr	74	6.4	141.681
Middlesex Water	msex	63.8	7.2	216.452
Millipore	mil	800	101	2434.144
Pall	pll	1660	151	3311.28
Pentair	pnr	2720	144	2637.96
Robbins & Myers	rbn	568	14.5	286.375
SJW Corporation	sjw	150	18.7	292.89
Southwest Water	swwc	164	6.1	205.506
Suez SA	sze	55850	−3360	21906.9
Tetra Tech	ttek	922	54	1188.096
Thermo Electron	trno	2100	173	4619.42
URS	urs	3190	58	978.51
Valmont Industries	vmi	826	26	522.41
Vermont Pure Hldgs.	vps	76	1.35	72.846
Veolia Environne.	ve	36740	−2490	11736.9
Waterpik	pik	305	11	156.86
Watts Water Tech.	wts	676	34	623.76

may be to turn to private companies to finance, build, and operate their water or wastewater systems.

From the perspective of Wall Street, the water industry was relatively stronger this year, and most water funds and indices outperformed in generally stronger markets. But even though performance was stronger, we still have not seen any really "big winners" in the industry—stocks that have returned investors many times their original investment. However, the professional stock-pickers assure us that there *will* be such companies emerging in the near future (Table 1).

An emerging issue in the water industry—one that is likely to loom considerably larger in the future—is the appropriate balance of the federal government and local authorities in the financing and management of water resources in this country. Groups like AMSA (the Association of Metropolitan Sewerage Agencies) claim that the federal government is sidestepping the whole issue of clean water. In an aggressive public information campaign that the group began to mount in 2003, they pointed out that in 1980, over half of the total capital investment in clean water came from federal funds, whereas today that figure is less than 10%.

Certainly, watershed management and water quality are interstate issues—water quality and management issues rarely follow state boundaries. Another lobbying group, the Water Infrastructure Network—a coalition of various elected officials, water utilities, and water resource groups—points out that clean water supports $50 billion per year in water-based recreation, $300 billion per year of coastal tourism, $45 billion in commercial fishing, and of course, hundreds of billions in basic manufacturing and industry. Despite the obvious criticality of water to the overall economy, so far there are few indications that the federal government plans to address the complex funding issues facing the business.

And other new challenges continue to arise and bedevil the U.S. water industry. Following the events of 9/11 and the discovery of potential terrorist interest in public drinking water supplies, security quickly moved to the forefront of immediate challenges facing the industry. Although there has been a lot of discussion about security threats, most of the work remains to be done, and most of the dollars still need to be spent—one more increment to the total cost of providing the public with acceptable drinking water.

A related problem also received new visibility this year—the issue of backup electrical power in the water system. During the massive northeastern blackout of August 14, several major cities that rely primarily on pumping for water distribution (as opposed to cities like New York with largely gravity-fed systems) were without sufficient water for several hours. An outbreak of fire during that particular day, for example, in downtown Cleveland or Detroit, could have been catastrophic. Installation of sufficient backup power for pumping and distribution has quickly become a high priority at many water systems across the country.

Technology development and implementation continues to be an active area, attracting many new players, and holding out hope for future solutions. The full-scale commercialization of membrane filtration is a good example—more and more water and wastewater utilities are now examining this technology, as its costs have come down dramatically in recent years. Although the much-discussed Tampa desalination plant suffered extensive operating problems this year, including the bankruptcy filing of its operator, the market for this particular technology—particularly in desalination and water reuse applications—remains strong. Other areas include *in situ* repair and relining of aging distribution pipelines; "smart" monitoring, metering, and system control software; and a wide range of other new treatment, distribution, and conservation technologies.

In response to these changing social, political, and economic drivers, the water industry continues to undergo gradual evolution and coalescence. With such dramatic changes occurring in technology, asset ownership, regulation, and public concern, the water industry seems certain to remain in a constant state of change for the foreseeable future.

Another way to gauge the impact of these changes on the commercial industry is to look back at our list of public companies in *The Environmental Benchmarker and Strategist* from just 5 short years ago, in late 1998. The experiences of these companies—most of which have now disappeared from the ranks of the public companies—illustrates some general trends in the industry since that time:

- Air and Water Technologies—sold by Vivendi in 2000
- American Water Works—purchased by Thames Water/RWE in 2001
- Aquarion—purchased in 1999 by Yorkshire Water (now Kelda)
- Azurix—Enron's heralded entry into the water industry; dead three years later
- BetzDearborn—purchased by Hercules, later sold to General Electric in 2002
- Cadiz—company virtually disappeared after major water storage program was nixed by the state of California in 2002
- Culligan—acquired by U.S. Filter in 1998, and now for sale again
- E-One—sold to Precision Castparts in the late 1990s
- Hach—acquired by Danaher Corporation in 1998
- Nalco—bought by Suez in 1999 and sold to private investors in 2003
- Osmonics—acquired by General Electric in 2003
- Recovery Engineering—acquired by Procter and Gamble in 1998
- Stone and Webster—filed for bankruptcy, assets acquired by Shaw Group
- Thermo Instrument Systems—collapsed back into parent Thermo Electron
- US Filter—acquired by Vivendi, spun into Veolia subsidiary, most of its noncontract services businesses now for sale again

- U.S. Liquids—suffered through extreme financial difficulties, selling off assets, and now trading at a few cents per share
- United Water—remaining traded stock acquired by Suez in 2001
- Western Water—like Cadiz, has shrunk down considerably, perhaps a company before its time in water rights trading
- Zurn—company was sold to U.S. Industries in 1998

MARKET SIZE AND GROWTH CHARACTERISTICS

According to recent Department of Commerce statistics, the water and environmental business in this country comprises more than $200 billion of revenues per year, encompasses some 115,000 companies and organizations, and employs more than 1.4 million workers. More specifically, the water and wastewater industry is generally estimated at around $90 to $100 billion per year; the comparable world market is about five times as large, or around $500 billion.

Estimates of the true size of this business vary, largely due to one key reason—it is a tough business to define and "encircle"—definitions differ, and even where they do not differ, market estimates still vary widely. Perhaps the most thoroughly researched and widely cited numbers on the overall domestic water industry are those published annually by Environmental Business International, as shown in Table 2.

Because it is such a broad and varied business, it is not meaningful to try to capture the overall industry's growth rate in a single figure either; different sectors of the business are growing at considerably different rates. For example, the more mature chemicals sector and infrastructural supply businesses (pumps, pipes, tanking, and so on) are probably growing in the 2% to 3% range. The water and wastewater utility sectors, which comprise the largest individual source of revenues in the industry, largely reflect population and GNP growth and show growth in the 3% to 4% range. Other businesses, tied to the upgrading and replacement of our vast water infrastructure, such as consulting engineering and instrumentation/monitoring, show slightly higher growth in the 6% to 8% range.

On the other hand, other sectors of the business boast growth well above these rates. The contract operations and outsourcing sector of the business has demonstrated growth in the 15% to 20% range for several years and even given the recent slowdown is still likely to average something in the 8% to 10% range. And although the overall treatment technology sector shows average growth of around 5%, there are certain niches—such as the membrane treatment and advanced oxidation technologies—which are currently enjoying growth more in the 10% to 15% range.

Table 2. Size of the Water Industry (Revenues in Millions)

Business Segment	2003 Revenue	'04–'06 Growth
Water treatment equipment	$8,860	4–6%
Delivery equipment	$8,880	2–3%
Chemicals	$3,660	0–1%
Contract operations	$2,290	6–10%
Consulting/engineering	$6,090	5–6%
Maintenance services	$1,640	3–5%
Instruments/monitoring	$800	5–7%
Analytical testing	$480	2–4%
Wastewater utilities	$30,780	3–4%
Drinking water utilities	$32,650	3–4%
Total U.S. water industry	$96,130	

Source: *Environmental Business Journal*, 2003

KEY MARKET DRIVERS

As we have discussed, a handful of key factors—economic and social demands and political realities—are driving the overall development of the water industry. These drivers, in turn, are giving rise to various trends and effects that will likely dominate the water industry for years to come. Some of the key factors are listed below.

Water Scarcity and Water Quality Problems Are Growing

This is clearly the critical core issue behind this entire industry and the ultimate driver behind the challenges and growth projected for the water business over the coming decades. The gradual development of this situation has resulted from decades (indeed, centuries) of unfettered industrial expansion, continuing population growth, and a careless and uninformed belief that the environment would take care of itself. We do not need to recite the statistics again here, as they are well known—the millions of children who die each year because of unsanitary water conditions, the major cities of the world that still discharge their untreated wastes directly into the natural waterways, the number of people even in the United States who still drink water that is out of compliance with the Safe Drinking Water Act, and so on. Hundreds of studies have pinpointed the lack of sufficient clean water as one of the most serious threats facing humankind.

Public Awareness and Concerns Are Growing

As these water scarcity and quality problems have become more serious and more apparent, the public has become better informed and more concerned about the water problems that their children and grandchildren may inherit. One needs only to look at the pages of the popular press to see how broad and widespread this recognition is becoming. Stories about water scarcity or pollution problems are common headlines and have even become the stuff of popular Hollywood entertainment. As the general public becomes more aware and concerned about water, peoples' demands and perceptions will become a more important driver in determining the shape of the business. (One need only look at the explosive growth of the bottled water industry over the past few years to see how significantly customer perceptions—rightly or wrongly—can create and drive new markets.)

Regulatory Controls and Enforcement Are Growing

In turn, as public awareness and concern have grown, it has translated inexorably into greater government review, legislation, and regulatory control. Although environmental regulation and enforcement have waxed and waned during the past three decades, when it comes to drinking water, the public is insistent on ever-stronger regulatory protection of our water resources. For example, there were just nine new bodies of regulations, or rules, implemented between 1974 and 1996. Since the 1996 reauthorization of the Safe Drinking Water Act (SDWA), there have been more than 10 new rules implemented.

Under the SDWA, some key ongoing areas of regulatory development include the disinfection byproduct rule, the interim enhanced surface water treatment rule, the arsenic rule, and the groundwater rule. On the *waste*water side of the business, the primary governing legislation is the Clean Water Act, where key trends have included a more intense focus on *nonpoint* source runoff, continuing implementation of the total maximum daily load (TMDL) regulations, and programs geared toward combined and sanitary sewer overflow regulations to control wet weather runoff in metropolitan areas. Overlying these strictly regulated areas is the growing concern about potentially "introduced" compounds—terrorism—and all of the security concerns regarding primary drinking water supplies that have arisen as a result of 9/11. And finally, although the pace and intensity vary, regulatory controls are also becoming stronger in most other regions of the globe.

Meeting These Needs Is Going to Require Huge Expenditures

Finally, for municipalities and industry to comply with these regulations and to maintain and expand water infrastructure, huge capital expenditures will be required over the coming decades. As we have mentioned, numerous studies have predicted how large this expenditure must be; the estimates vary, but it is definitely in the hundreds and hundreds of billions of dollars. These dollars represent a huge challenge to this country, but they also constitute a huge opportunity for firms that serve the water and wastewater treatment industry.

KEY INDUSTRY TRENDS

These drivers, in turn, are leading to various trends and developments, both in terms of how the economy uses water and in terms of supply and demand within the commercial water technologies and services industry.

Continuing Consolidation and Ownership Changes

The water industry has been experiencing a dramatic rearrangement of ownership and increasing consolidation, as firms strategically position to address these opportunities. The dizzying pace of transactions the last few years—particularly those involving the larger domestic players and major foreign acquirers—has dramatically altered the face of this industry.

On the other hand, it would be easy to get the impression—particularly in the last few months—that events may actually be headed in the other direction. Quite abruptly, several key buyers (who have pumped hundreds and hundreds of millions of dollars into U.S. water acquisitions in recent years) seem to be reversing direction and deciding to spin off key businesses. In September, Suez announced that it had sold its Nalco water treatment unit to a group of private equity investors for $4.2 billion—roughly the same price for which it had acquired the business 4 years earlier. In its announcement, the company cited a narrowing strategic focus and the need of the parent organization to reduce its debt.

But the real surprise came in late September, when Veolia's U.S. Filter unit announced plans to sell off many businesses it had acquired through the 1990s. U.S. Filter has been the "king" of the emerging water industry for more than a decade, having conducted dozens of consolidating acquisitions during the 1990s, before being acquired by Veolia (Vivendi) in 1999. Although many had expected the company to spin off a few units here and there as it continued to focus its business, few expected a divestiture of this magnitude. Veolia cited considerations similar to those of Suez—the need to reduce high debt at the parent company level and further strategic concentration on its historical core business in contract operations and outsourcing services.

As of early February 2004, the sale of U.S. Filter's businesses is still ongoing. Everpure, the firm's water filtration products business, recently sold to Pentair Corporation at a very high price–$215 million for a business doing $60 million in revenue per year and producing some $20 million of EBITDA per year. The well-known Culligan subsidiary has attracted interest, but to date, it has not been sold. The remaining bulk of U.S. Filter's equipment business, which represents $1.2 billion in revenues, also remains on the block. U.S. Filter's preference that the business be sold as one piece, and the likelihood that it will trade at a multiple of greater than one times revenues, has obviously restricted the pool of capable and interested buyers. There simply are not many buyers financially capable of undertaking that large a purchase.

Some of the major British water companies also have begun to divest various units, again, primarily equipment and product businesses. In other recent transaction news:

- Ionics, one of the larger remaining independent players in the water industry, acquired Ecolochem, a private water treatment company, at a value of more than three times revenues. This was a large deal for Ionics, which has been struggling financially during the last 2 years.
- ITT Industries maintained its rapid pace of expansion in the industry, buying several more small players, but also commencing a bid for the major German ultraviolet treatment technology firm Wedeco. Wedeco had approximately $150 million of revenue in its latest fiscal year. ITT remains one of the most active buyers in the U.S. water market.

- Pentair acquired WICOR, a unit of Wisconsin Energy that produces water systems, filtration products, and swimming pool products and services. The deal was priced at $850 million in cash for a company generating approximately $750 million in revenues. At the same time, Pentair announced the divestiture of some of its other nonwater-related businesses, culminating a dramatic strategic repositioning of the firm into almost a water industry "pure play."
- Philadelphia Suburban Water company, now the largest independent investor-owned utility in the country, continues to make additional acquisitions. Most recently, it acquired several businesses from Allete Water in North Carolina. Philadelphia Suburban also changed its name to Aqua America to reflect its new and broader strategy.
- Finally, as always, there are also numerous smaller deals occurring, including the acquisition of Flowmatic, a reverse osmosis component manufacturer, by Watts Water, and the sale of Waterlink's remaining Barneby Sutcliffe operation to Calgon Carbon Corporation.

So many major assets are up for sale at the same time that the competitive situation in the water treatment equipment industry has been turned upside down. It will be interesting to watch where these various assets end up and to see which companies step forward to be major players in the next generation of this industry. Most observers are betting on the various diversified U.S. companies mentioned above—ITT Industries, GE Water, Pentair, and perhaps several others who have not yet made their first move. But the big questions remain—how can companies that were committed buyers turn into sellers in just a few short years? Was something wrong with their business strategies? Will the new owners of these assets be more logical owners than the previous ones? And most importantly, what will be the ultimate impact of this massive ownership rearrangement on employees, shareholders, and finally, the customer?

The Pace of Privatization and Outsourcing Begins to Slow

As mentioned before, one of the most controversial aspects of the water industry today involves the transfer of water management, treatment, and distribution operations from public to private control. Although private operation of water and wastewater utilities has been common in parts of Europe for decades, increasing privatization in North America and other parts of the world seems to be generating increasingly bitter political debate. During the past couple of years, it has become considerably less clear how far privatization will actually proceed in this country. The highly publicized misfortunes of several large projects like Atlanta, combined with an active and organized opposition movement, has forced a wholesale reevaluation of water and wastewater privatization. A number of large projects have been shelved or put on hold, and the whole nature of private contract operations is undergoing a major shift.

As a result, although the industry had been growing at rates of as high as 25% per year, considerably lower growth is now expected. As an example of how tough the last year was, one industry publication recently indicated that the U.S. contract operations business had seen the number of contracts drop off by 20%, whereas the *value* of the contracts declined by almost 73% during the year. OMI and Thames stand to lose as much as $300 million if their project in Stockton, California, is unwound. United Water was a big loser with the Atlanta job and with PRASA in Puerto Rico, which would have been one of the world's largest privatization projects.

The contract operations business also seems to be experiencing somewhat of a shift from a major "big-city" project orientation to smaller and shorter term contracts for smaller municipalities. The firms that have focused on this latter type of business seem to be doing reasonably well, whereas the firms that have focused on the huge projects seem to be having a more difficult time. Nonetheless, many firms continue to believe that contract operators have a very important and growing role to play in the industry. Veolia/U.S. Filter is obviously still very optimistic about the potential to manage the larger privatization jobs successfully and profitably, as indicated by its current effort to strategically reposition the firm primarily as a contract services provider.

And, in the bigger scheme of things, it is important to note that the simple threat of privatization has already forced widespread efficiencies by itself—a sort of "de facto" privatization. In summary, despite the concerns of labor organizations and various public interest groups, the urgency of infrastructural needs and the political barriers against major tax increases make it seem likely that privatization will continue to grow. At the same time, it is clear that private operators are going to be judged by a very demanding and critical public. A few other key trends are also important to note in any broad review of this industry.

Increased Focus on Water Recycling and Reuse. There are continuing and inexorable pressures toward greater water reuse and recycling systems—an obvious but as yet largely untapped means of addressing water shortages. With technologies readily available today, wastewater can easily be cleaned to levels where it can be recycled back into primary usage and at steadily declining costs. Examples of new wastewater reuse projects are coming out regularly now—typically for irrigation projects, or for more innovative applications, such as one recent project where treated wastewater was injected into the ground to act as a barrier against seawater intrusion to protect underground freshwater aquifers in Southern California.

Direct reuse of wastewater, particularly for drinking, is still a bit of a stretch for most Americans (and indeed is only commercially practiced in a small handful of locations around the world). However, this resistance is primarily due to poor understanding of the hydrologic cycle and our nation's current water usage patterns. For example, on some major river systems in the United States, water is used and reused up to 20 times as it travels to the sea. The discharge water from one wastewater treatment plant contributes to the raw water intake for a primary drinking water plant a few miles downstream. As a result of 30 years of steady progress under the Clean Water Act, the discharged waters from wastewater treatment plants are often cleaner than the rivers and streams they flow into. This type of *indirect* reuse of wastewater for drinking (after it has flowed in and out of a river, or into and out of an underground aquifer, and then through a treatment process) is clearly widespread and is obviously "acceptable" to most Americans.

An interesting statistic to remember when evaluating the long-term impact of wastewater reuse to extend our primary water resources is that only a tiny percentage of our primary water supply is actually used for drinking. Compared with the roughly 1200 gallons of water per capita per day that it currently takes to power the U.S. economy, an individual typically drinks less than a gallon a day. This leaves 1199 gallons per person per day that could be recovered without anyone ever having to drink "recycled" wastewater. Hence, even if only small incremental gains could be made in nonpotable water reuse, overall water availability could be substantially impacted. Over the longer term, we will move beyond our "linear" thinking of today and develop a more "circular" philosophy of water usage.

Conservation and Efficient Water Use

Closely related to improving our water reuse habits as a nation is the whole area of conservation of water and more efficient usage of water. During the droughts of 2002, many of us were forced to see how efficient we could become—and most of us found that it was not that difficult to save quite a bit of water. Indeed, water conservation ideas are only beginning to take advantage of the "low-hanging fruit." As water prices rise, there will be increasing incentives for people to use water more carefully and for industrial companies to retool their manufacturing systems to use less water.

OUTLOOK FOR THE FUTURE

As we have said many times, the challenges and requirements of the water industry are likely to be one of the most pressing problems facing humankind over the next century. The primary and overriding conclusion that falls out of the foregoing discussion is the inevitability of continuously rising water prices over the longer term future; as water becomes more scarce, there seems to be no alternative. Water is still very inexpensive—ridiculously cheap in many ways. And, at least in the United States, we are still on the highly inelastic portion of the demand curve for water, where increases in price have relatively little impact on usage. This inescapable conclusion and the vast scale of the world's water problems were highlighted in a special report in the July 2003 issue of the respected British newsweekly *The Economist*, which concisely concluded that water is "ill-governed and colossally under-priced." Discouragingly, the study also reported that the United States is the most wasteful nation on the earth in water usage.

As prices continue to increase, decisions about water usage will necessarily begin to take on greater economic significance. This will force us to focus on more efficient water usage and demand management techniques, technologies such as membrane desalination, and practices such as improved water conservation and recycling. All of these are already happening, but in the future, water expenditures will make up a larger and larger share of the GNP.

Water will increasingly be recognized as an economic good. However, exactly what that means is subject to varying interpretation. Some argue that water should be treated as a fully tradeable market commodity, subject to the general forces of supply and demand in an unregulated market—that water's value is essentially the same as its free market price. On the other hand, there is the antimarket argument—that water should be exempt from market forces because it is an essential prerequisite to life. Adherents to this philosophy argue that water is a basic human right and that forces greater than the free market are required to ensure that everyone has enough clean water to live.

Over the long term, some sort of intermediate position is likely to prevail—water should be treated as a scarce resource, which means that we have to balance economic and social objectives and carefully allocate water to its myriad uses. Market incentives can be a powerful means of properly managing and allocating a scare resource, but in the case of water, we must ensure that such markets are sufficiently regulated to protect social equity as well.

In closing, consider the following "big questions"—many more of which will continue to emerge in the future:

- Water is being transferred from American agriculture to American cities at an alarming rate. Farmers in the southwest are increasingly finding that current economics suggest that they stop farming and sell their underlying water rights to neighboring cities. What are the long-term implications of allowing our farmlands to dry up to slake the thirst of our ever-expanding cities?
- Why do we as a society treat such vast amounts of water to drinking quality standards when less than 1% is actually used for drinking? Should we really be incurring the capital costs of providing drinking quality water for fire fighting, mixing cement, washing cars, or watering yards?
- As sedimentary deposits fill the massive reservoirs that we have constructed during the last 60 to 80 years, how will we continue to provide controlled water supplies to the arid southwestern part of the country? We have become experts at building dams. What do we do with them when they no longer function?

So . . . the water industry is full of challenges, but it is also full of opportunities. Water is an essential prerequisite of life, and we are not going to find any substitutes for it. The amount of freshwater on this earth is relatively fixed, and we need to become much smarter and more efficient in our usage of that scarce resource. For creative, innovative, and well-managed firms, the water industry offers unrivaled opportunities.

THE GLOBAL DESALINATION MARKET: TRENDS AND OUTLOOK FOR THE FUTURE

Lisa Henthorne and Eric Jankel

The desalination market has reached an all-time high in terms of growth in capacity, primarily due to the fact that the cost to desalinate water continues to decrease and now stands at less than $2.00 per thousand gallons of produced clean drinking water. Remarkably, in 2001, over 845 million gallons per day (gpd) of new capacity was contracted for installation worldwide, making it the highest recorded year in contracts for new installations. The final numbers for 2002 are expected to be even higher. Prior to 1996, an average of about 265 million gpd of new capacity was contracted per year, which rose to about 500 million gpd average per year in the years between 1996 and 2000. As a result, this is a very exciting time to be involved in the desalination market. Presently, approximately 8.5 billion gpd of desalination capacity has been installed or contracted through the conclusion of calendar year 2001 in 9500 plants worldwide.

The desalination market is in a state of rapid change. Membrane plants using seawater as a source and reverse osmosis (RO) as a process are being designed and constructed with capacities that were unheard of as recently as 1-5 years ago. Examples include the Ashkelon, Israel, and Fujuirah, U.A.E., plants of 87 million gpd and 45 million gpd, respectively. Unit capacities for multiple stage flash (MSF) distillation units are approaching 20 million gpd each. The Middle East has traditionally been the focus of desalination, predominantly using thermal technology such as MSF, but today large-scale desalination plants are being built throughout the world; plants outside the Middle East prefer RO technology. As a result, there is a broad-based shift occurring, from thermal technologies to membrane technologies for desalination applications. In 1990, 60% of the world's existing desalination capacity used thermal technologies, whereas at the end of 2001, this had dropped to 47%; the remaining capacity uses membrane technology.

Worldwide, desalination installed capacity has grown at an average rate of 10.6% per year over the last 30 years. In more recent few years, the growth rate has begun to increase. The key drivers behind the tremendous growth in the desalination market can be summarized as follows:

1. Significant reductions in the cost of desalting water due to
   - improved productivity and reduced cost of membrane elements in reverse osmosis;
   - increased efficiencies and economies of scale improvements in thermal processes;
   - the global trend toward privatization of water/power projects; and
   - improved energy recovery devices, which reduce the net energy requirement for reverse osmosis.
2. Changing demographics, specifically, population growth in arid, semiarid areas, and water-deficient areas.
3. Continuing increased standards of living in water-deficient areas.
4. Environmental concerns and increasing regulatory requirements that are forcing water suppliers to examine and use alternative sources of raw water.
5. Concerns and reaction to sustained drought conditions; seawater desalination is a drought-proof source of raw water.
6. Increased demand for high-grade water for industrial and commercial applications.

There are several recent desalination activities of particular note going on around the world. Due to increasing revenues as the price of crude oil has risen, construction of new desalination capacity and refurbishment of installed desalination capacity in the Gulf States is taking place at a rapid pace, especially in the U.A.E. The first large-scale (90 million gpd) privatized wastewater reuse RO plant is under construction in Kuwait using ultrafiltration (UF) as a pretreatment.

For the first time, a large-scale seawater RO plant (25 million gpd) has begun operating in North America, in Tampa Bay, Florida. At least 10 more large-scale seawater RO plants are in the planning stages in California, Texas, and Florida. Large-scale (40 million gpd) nanofiltration (NF) plants are also pending startup of operations in the United States.

The growth of both thermal and membrane technologies is shown graphically in (Fig. 1).

The primary factor behind the increasing growth of membrane desalination is the rapidly declining cost of membranes. A U.S. government-funded research and development program in the early 1960s developed and commercialized the first membrane-based RO process. The membranes that resulted from this effort became commercially available in the 1970s. Continued development and improvements in membrane productivity and reduction in pricing of the membranes due to competition among key manufacturers has continued through today. Now, over 200 hundred RO and nanofiltration products are available. Today, membrane-based reverse osmosis has become an extremely competitive and cost-effective means of producing large volumes of very high quality water.

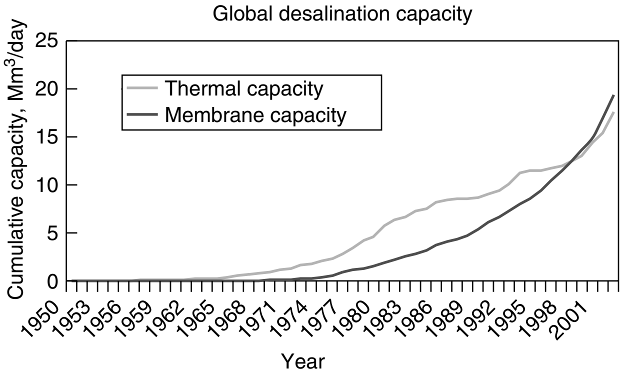


Figure 1. Cumulative capacity of all desalting technologies installed worldwide between 1950 and 2001 with projected plants in 2002.

Another way to evaluate the impact of the improvement in RO membrane properties on the cost of membrane technology is to consider the amount of water produced per unit capital cost. Figure 2 illustrates the increase in water produced using seawater desalination for the same capital investment, compared over time since 1980. These data indicate that for the same capital investment, approximately 27 times more water can be produced today using RO membranes than was possible in 1980.

Capital costs for membrane technology vary considerably based on the feedwater source and technology used. Table 3 provides a range of typical capital costs based on facilities contracted over the last few years and over a range of throughput capacities.

The privatized total water cost for seawater desalination using RO technology in large-scale facilities is generally in the $2.00 per thousand gpd price range.

A key recent project, which may portend future market trends and innovative approaches to membrane desalination in the United States, is the Tampa Bay Water program. This regional water utility, which supplies 225 million gallons per day of water to a five-county area, was required by regulators to reduce the pumping of groundwater at the same time that it faced a sustained period of drought. The utility responded by asking the industry to propose new alternatives for operating on a privatized basis. Through a long and arduous process, four bidders submitted tenders to supply a 25-million gpd desalination system. There are unique site-specific factors that contribute to the $2 per 1000 gpd price, including salinity fluctuations below average seawater levels (from 16,000 to 32,000 mg/L) and colocation; the adjacent power plant provides warmed cooling water and shared intake/outfall. The facility was developed by a privatized developer, Poseidon Resources, but ownership was transferred to Tampa Bay Water prior to the plant commissioning in May 2003.

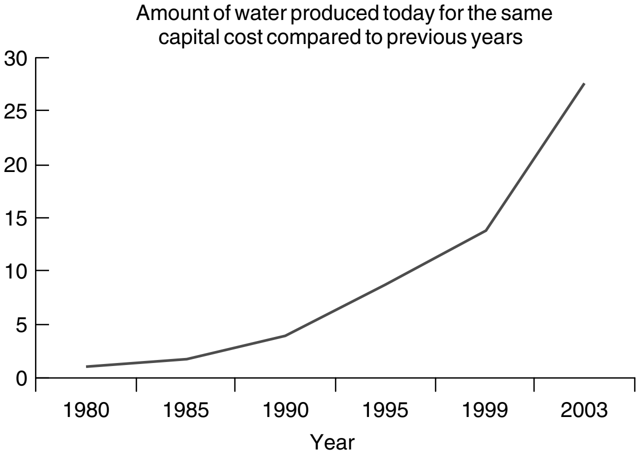


Figure 2. Change in water produced using seawater RO technology for the same capital investment over time.

Table 3. Range of Capital Costs for Membrane Desalination Plants (2001–2003)

Technology	Feedwater Source	Cost, $/gpd
NF	Wells with hardness and salinity	$1.13–$1.51
RO	Brackish wells	$1.13–$1.89
RO	Brackish surface	$1.51–$2.65
RO	Seawater	$2.84–$4.54
RO	Municipal wastewater	$2.27–$4.16

Covanta Water constructed the plant and would have operated the facility under a 25-year agreement with Tampa Bay Water. However, under a settlement agreement recently executed, Covanta has been expelled as the operator due to problems with the performance testing. Hydranautics, the RO membrane supplier used some unique design features for the facility, including a partial second pass to optimize product water quality. There are over 10,000 RO membranes installed at the facility, and their total energy demand is about 14 MW. Presently, the plant is experiencing difficulty in achieving successful pretreatment using the Covanta proprietary dual-sand filtration process.

The desalination market has a very bright future and should offer vast opportunities for private companies. The Middle East is still the largest market for desalination systems, maintaining approximately 49% of the worldwide contracted capacity. Figure 3 shows the percentage that each of the key regions of the world comprise, based on their desalination capacity contracted or installed through 2001.

Prospects for the continuing growth of the use of desalination technology are very optimistic. In the big picture, the availability of freshwater in the earth's hydrologic cycle is fixed; at the same time, the global population is growing, especially in arid and semiarid areas; standards of living are generally rising; existing sources of fossil groundwater are being depleted; surface supplies are being more stringently regulated; and the economic, political, and environmental costs of developing new sources of surface supply are increasing.

Reverse osmosis applications are anticipated to continue growing at roughly 11% to 12% in the future, and nanofiltration capacity is expected to grow at about 16%

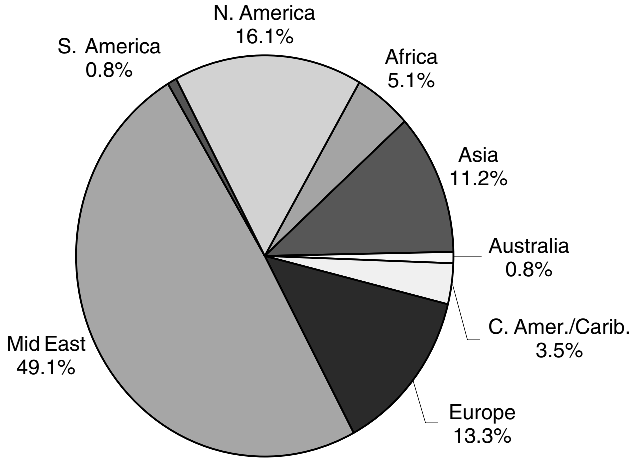
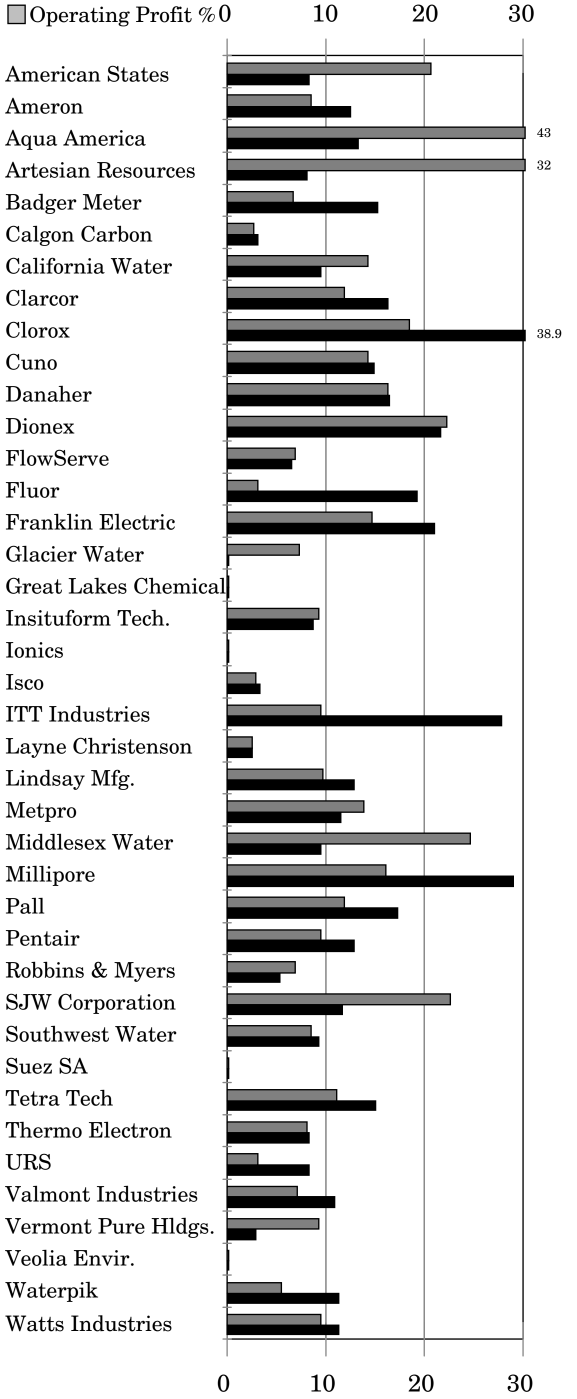


Figure 3. Distribution of desalination capacity by region based on installed capacity.

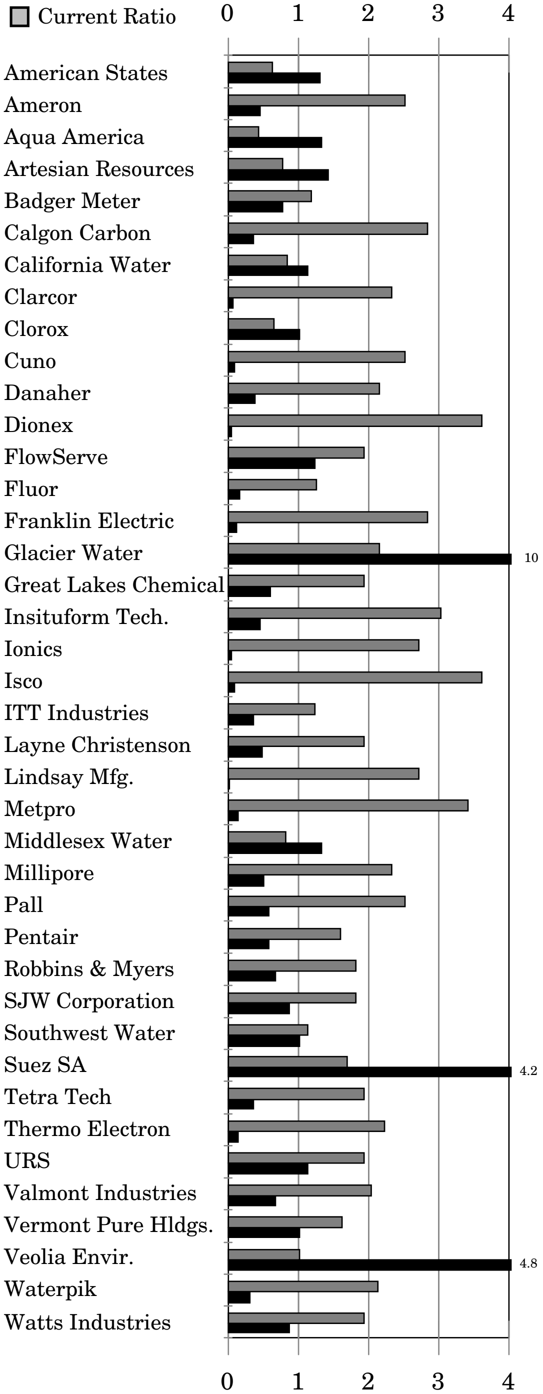
Table 4. Profitability and Performance[a,b]



[a] ■ Return on equity, %.

[b] Where there is no bar, the number is zero or has a negative value.

Table 5. Balance Sheet Information[a]



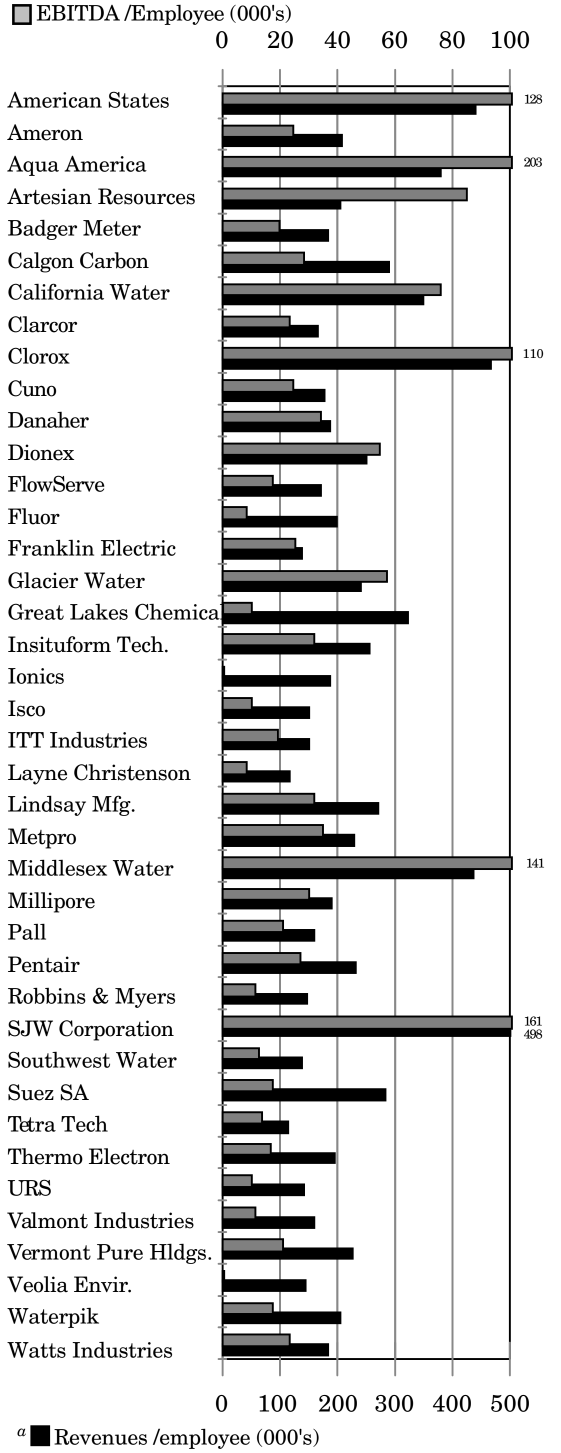
[a] ■ Debt/equity ratio.

per year. Thermal technologies and electrodialysis are anticipated to grow at lesser rates in the future. Over the period from 2004 to 2009, there will be over six billion gpd of new desalination capacity contracted at a capital investment of between $15 and $25 billion, as determined by our current evaluation and projections for the overall world desalination market.

FINANCIAL PERFORMANCE OF WATER COMPANIES

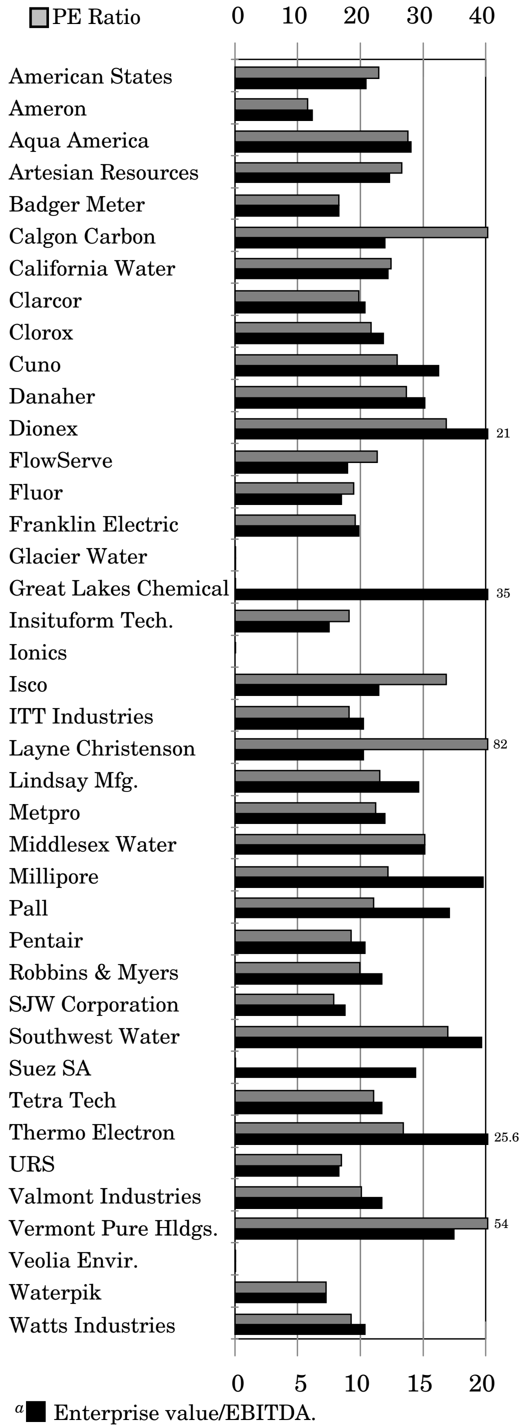
(*Note*: The data used to construct the charts and analysis in Tables 4–8 are from early February 2004.)

Table 6. Productivity Measures[a,b]



[b]Where there is no bar, the number is zero or has a negative value.

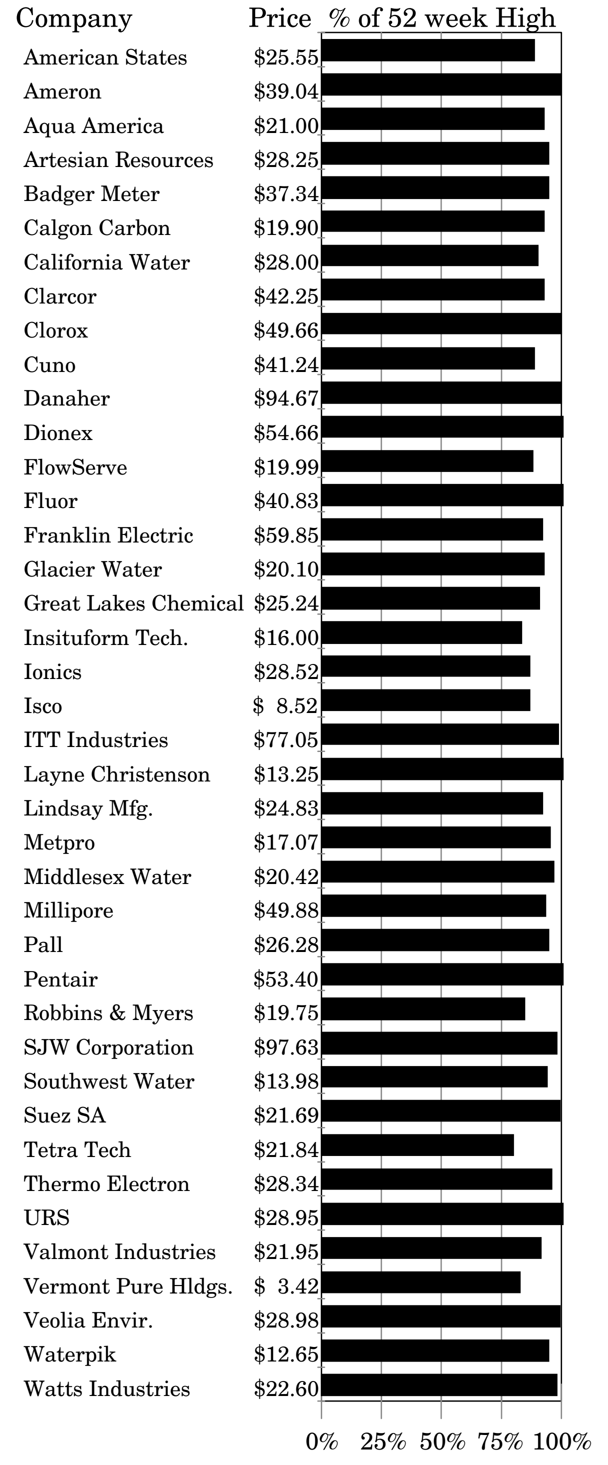
Table 7. Equity Valuations[a,b]



[b]Where there is no bar, the number is zero or has a negative value.

Table 8 demonstrates the recent strength in the broader stock market; most of the water firms traded at or near their 52-week highs, as was the overall market in early February. Table 7 is also a reflection of the price of the individual company's stock; most water firms show a P/E ratio between 15 and 20. The exceptions are a handful of firms, like Glacier Water and Great Lakes Chemicals, who have negative earnings for the trailing 12-month period used in these calculations, and for whom this is hence not a relevant measure.

Table 8. Stock Price Performance



Company	Price
American States	$25.55
Ameron	$39.04
Aqua America	$21.00
Artesian Resources	$28.25
Badger Meter	$37.34
Calgon Carbon	$19.90
California Water	$28.00
Clarcor	$42.25
Clorox	$49.66
Cuno	$41.24
Danaher	$94.67
Dionex	$54.66
FlowServe	$19.99
Fluor	$40.83
Franklin Electric	$59.85
Glacier Water	$20.10
Great Lakes Chemical	$25.24
Insituform Tech.	$16.00
Ionics	$28.52
Isco	$ 8.52
ITT Industries	$77.05
Layne Christenson	$13.25
Lindsay Mfg.	$24.83
Metpro	$17.07
Middlesex Water	$20.42
Millipore	$49.88
Pall	$26.28
Pentair	$53.40
Robbins & Myers	$19.75
SJW Corporation	$97.63
Southwest Water	$13.98
Suez SA	$21.69
Tetra Tech	$21.84
Thermo Electron	$28.34
URS	$28.95
Valmont Industries	$21.95
Vermont Pure Hldgs.	$ 3.42
Veolia Envir.	$28.98
Waterpik	$12.65
Watts Industries	$22.60

There is one important note about the Equity valuations in Table 7—the sometimes overlooked effect of simple arithmetic in ratio calculations. One of the inherent difficulties in interpreting either P/E ratios (or EBITDA multiples) is the effect of a very small value in the denominator. Generally speaking, companies with higher P/Es are perceived to be more valuable; however, this applies only within given ranges of "reasonableness." For example, the very high estimated P/E ratios for Layne Christenson or Vermont Pure are more the result of tiny earnings than intense interest in and demand for the stock. Detailed understanding of the company's individual economic circumstances and some judgment are needed to interpret what an individual P/E ratio really means.

Two different measures of profitability are shown in Table 4, operating profit as a percentage of revenue and return on equity. As can be seen, many companies in the water industry generate operating profits between 10% and 15%, which is higher than most other environmental companies. It is also clear that the water utility companies, as regulated local monopolies, have uniformly higher operating profits; see Artesian Resources, Aqua America, American States, and SJW. Return on equity measures not only general profitability, but also the relative balance of debt and equity in financing the company. Table 5 shows two key figures from a company's balance sheet, the current ratio, or ratio of currents assets to current liabilities, and the longer term debt to equity ratio. A higher current ratio usually implies a stronger short-term financial situation. As detailed in the cover story, note the relatively much higher debt levels of both key French companies. Veolia and Suez.

Table 6 illustrates two rough productivity measures—the amount of earnings (actually EBITDA is used here) and revenue that a company manages to generate per employee. Interestingly, when compared in this manner, water companies show a wide range of variation. Consulting and engineering firms, for example, typically show revenues per employee in the $100,000 to $150,000 range, whereas equipment manufacturers may show considerably higher figures. Note again the relatively high earnings per employee that the drinking water utilities are able to produce.

IRON AND MANGANESE REMOVAL

National Drinking Water
Clearinghouse

Iron and manganese are common in groundwater supplies used by many small water systems. Exceeding the suggested maximum contaminant levels (MCL) usually results in discolored water, laundry, and plumbing fixtures. This, in turn, results in consumer complaints and a general dissatisfaction with the water utility.

There are secondary standards set for iron and manganese, but these are not health related and are not enforceable. The secondary (aesthetic) MCLs for iron and manganese are 0.3 milligrams per liter (mg/L) and 0.05 mg/L, respectively.

Small water plants may choose to either sequestrate or remove iron and manganese. Sequestration only works for combined iron and manganese concentrations up to 1.0 mg/L and only in cases where the treatment is not permanent. Removal is usually achieved through ion exchange or oxidation/filtration. There are a number of chemical oxidants and filtration media available that can be used in various combinations

WHAT PROBLEMS ARE CAUSED BY IRON AND MANGANESE?

Small amounts of iron are often found in water because of the large amount of iron present in the soil and because corrosive water will pick up iron from pipes. Clothing washed in water containing excessive iron may become stained a brownish color. The taste of beverages, such as tea and coffee, may also be affected by iron. Manganese produces a brownish color in laundered clothing, leaves black particles on fixtures, and—as with iron—affects the taste of beverages, including coffee and tea.

Well water from the faucet or tap is usually clear and colorless. However, when water containing colorless, dissolved iron is allowed to stand in a cooking container or comes in contact with a sink or bathtub, the iron combines with oxygen from the air to form reddish-brown particles (commonly called rust). Manganese forms brownish-black particles. These impurities can give a metallic taste to water or to food.

The rusty or brown stains on plumbing fixtures, fabrics, dishes, and utensils cannot be removed by soaps or detergents. Bleaches and alkaline builders (often sodium phosphate) can make the stains worse. Over time, iron deposits can build up in pressure tanks, water heaters, and pipelines, reducing the quantity and pressure of the water supply.

Iron and/or manganese in water creates problems common to many water supply systems. When both are present beyond recommended levels, special attention should be paid to the problem. How iron and manganese are removed depends on the type and concentration and this helps determine the best procedure and (possible) equipment to use.

WHAT IS THE CHEMISTRY OF IRON AND MANGANESE IN WATER SYSTEMS?

Iron (Fe) and manganese (Mn) can be present in water in one of three basic forms:

1. Dissolved: ferrous (Fe^{2+}) and manganous (Mn^{2+})
2. Particulate: ferric (Fe^{3+}) and manganic (Mn^{4+}) states
3. Colloidal: very small particles (difficult to settle and filter).

The predominance of one form over another is dependent on the pH, Eh (redox potential), and temperature of the water. Knowledge of the forms or states of iron and manganese can help finetune a given treatment practice for these metals.

WHAT ARE THE MOST COMMON TREATMENT PROCESSES?

The majority of iron and manganese treatment systems employ the processes of oxidation/filtration. The oxidant chemically oxidizes the iron or manganese (forming a particle), and kills iron bacteria and any other disease-causing bacteria that may be present. The filter then removes the iron or manganese particles (Fig. 1).

Oxidation followed by filtration is a relatively simple process. The source water must be monitored to determine proper oxidant dosage, and the treated water should be monitored to determine if the oxidation process was successful.

Oxidation

Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron, manganese, or other chemicals being treated to the oxidizing agent. Ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $Fe(OH)_3$. Reduced manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble (MnO_2).

The most common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, and ozone. Oxidation using chlorine or potassium permanganate is frequently applied in small groundwater systems. The dosing is relatively easy, requires simple equipment, and is fairly inexpensive.

Chlorination is widely used for oxidation of divalent iron and manganese. However, the formation of trihalomethanes (THMs) in highly colored waters may be a problem. Chlorine feed rates and contact time requirements can be determined by simple jar tests.

As an oxidant, potassium permanganate ($KMnO_4$) is normally more expensive than chlorine and ozone, but for iron and manganese removal, it has been reported to be as efficient and it requires considerably less equipment and capital investment. The dose of potassium permanganate, however, must be carefully controlled. Too little permanganate will not oxidize all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color. Permanganate can also form precipitates that cause mudball formations on filters. These are difficult to remove and compromise filter performance.

Ozone may be used for iron and manganese oxidation. Ozone may not be effective for oxidation in the presence of humic or fulvic materials. If not dosed carefully, ozone can oxidize reduced manganese to permanganate and result in pink water formation as well. Manganese dioxide particles, also formed by oxidation of reduced manganese, must be carefully coagulated to ensure their removal.

A low-cost method of providing oxidation is to use the oxygen in air as the oxidizing agent in a tray aerator. Water is simply passed down a series of porous trays to provide contact between air and water. No chemical dosing is required, which allows for unattended operation. This method is not effective for water in which the iron is complexed with humic materials or other large organic molecules. Oxygen is not a strong enough oxidizing agent to break the strong complexes formed between iron and manganese and large organic molecules. Furthermore, the rate of reaction between oxygen and manganese is very slow below pH values of 9.5.

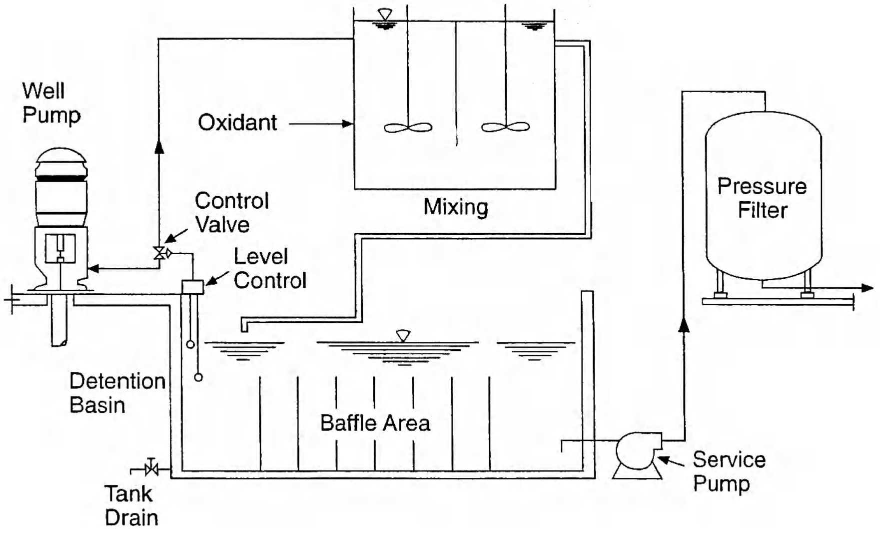


Figure 1. Chlorination, detention, and filtration (iron and manganese removal).

The presence of other oxidizable species in water hinders oxidation of the desired reduced compounds. Volatile organic chemicals, other organic compounds, or taste- and odor-causing compounds may result in an oxidant demand. This additional oxidant demand must be accounted for when dosing the oxidant. The expense of operation derives from the chemical use in most cases, and therefore is directly related to the source water quality.

Filtration

In general, manganese oxidation is more difficult than iron oxidation because the reaction rate is slower. A longer detention time (10 to 30 minutes) following chemical addition is needed prior to filtration to allow the reaction to take place.

There are different filtration media for the removal of iron and manganese, including manganese greensand, anthra/sand or iron-man sand, electromedia, and ceramic.

Manganese greensand is by far the most common medium in use for removal of iron and manganese through pressure filtration. Greensand is a processed material consisting of nodular grains of the zeolite mineral glauconite. The material is coated with manganese oxide. The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation-reduction reactions necessary for iron and manganese removal. This coating is maintained through either continuous or intermittent feed of potassium permanganate.

Anthra/sand (also iron-man sand) are other types of media available for removal of iron and manganese. They consist of select anthracite and sand with a chemically bonded manganese oxide coating. Unlike manganese greensand, these media are conditioned in the filter after media installation.

Electromedia provides a slightly different option from the manganese oxide coated media. This is a proprietary multi-media formulation which uses a naturally occurring zeolite and does not require potassium permanganate regeneration.

Finally, macrolite, unlike the other media discussed so far, is not a naturally occurring material which then undergoes processing for iron and manganese removal purposes. It is a manufactured ceramic material with a spherical shape and a rough, textured surface. The principal removal mechanism is physical straining rather than contact oxidation or adsorption.

Each medium has its advantages and disadvantages. Selection of a medium and oxidant should be based on pilot testing in which all necessary design criteria can be determined. Pressure filtration system manufacturers who offer the indicated media also offer fully automated systems.

ARE THERE ALTERNATIVE TREATMENTS?

Sequestration

Sequestration is the addition of chemicals to groundwater aimed at controlling problems caused by iron and manganese without removing them. These chemicals are added to groundwater at the well head or at the pump intake before the water has a chance to come in contact with air or chlorine. This ensures that the iron and manganese stays in a soluble form.

If the water contains less than 1.0 mg/L iron and less than 0.3 mg/L manganese, using polyphosphates followed by chlorination can be an effective and inexpensive method for mitigating iron and manganese problems. No sludge is generated in this method. Below these concentrations, the polyphosphates combine with the iron and manganese preventing them from being oxidized. Any of the three polyphosphates (pyrophosphate, tripolyphosphate, or metaphosphate) can be used.

To determine the best polyphosphate to use and the correct dosage, a series of samples at different concentrations may be prepared. Chlorine is added, and the samples are observed daily against a white background. The right polyphosphate dose is the lowest dose that does not noticeably discolor the water samples for four days.

Applying sodium silicate and chlorine simultaneously has also been used to sequester iron and manganese.

However, while this technique is reliable in the case of iron treatment, it has not been found to be effective in manganese control.

Ion Exchange

Ion exchange should be considered only for the removal of small quantities of iron and manganese because there is a risk of rapid clogging. Ion exchange involves the use of synthetic resins where a pre-saturant ion on the solid phase (the “adsorbent,” usually sodium) is exchanged for the unwanted ions in the water (see Ion Exchange and Demineralization Tech Brief #DWBLPE56). One of the major difficulties in using this method for controlling iron and manganese is that if any oxidation occurs during the process, the resulting precipitate can coat and foul the media. Cleaning would then be required using acid or sodium bisulfate.

Other

Systems that have a lime-soda ash softening plant do not need a separate iron and manganese removal plant. The high pH during softening allows rapid oxidation and precipitation of the iron and manganese as well as incorporation in the calcium and magnesium precipitates. Similarly, surface water treatment plants using coagulation, flocculation, sedimentation, and filtration also will remove iron and manganese as long as they make certain the iron and manganese get oxidized. Oxidation is sometimes a problem because of the presence of organic matter.

Finally, biological treatment methods are being pilot tested at different locations. Biological treatment methods are used extensively in European countries, such as the Netherlands, France, and Germany, and are advantageous primarily when water simultaneously contains iron, manganese, and ammonia.

HOW CAN IRON AND MANGANESE PROBLEMS BE MINIMIZED IN DISTRIBUTION MAINS?

Problems due to iron and manganese in distribution mains may be minimized by:

- prior removal by appropriate treatment,
- protecting iron/steel mains with bituminous linings, or using noncorrosive materials,
- avoiding dead-end mains,
- avoiding disturbances in the water flow, and
- flushing periodically.

WHERE CAN I FIND MORE INFORMATION?

Information in this fact sheet was primarily obtained from the following sources:

(1) American Water Works Association. 1998. *Water Treatment Plant Design*. Third Edition.

(2) American Water Works Association. 1990. *Water Quality 2nd Treatment*. Fourth Edition.

(3) Metcalf, B. M. 1998. “Pressure Filtration for Iron & Manganese Removal,” Proceedings of the New England Water Works Association Conference and Exhibition. Marlborough, MA.

(4) National Research Council. 1997. *Safe Water From Every Tap: Improving Water Service to Small Communities*. National Academy Press. Washington DC.

(5) Robinson, R. B. 1998. “State-of the-Art: Iron and Manganese Control,” Proceedings of the New England Water Works Association Conference and Exhibition. Marlborough, MA.

(6) U.S. Environmental Protection Agency. 1991. *Manual of Small Public Water Supply Systems*. EPA 570/9-91-003. Office of Water, Washington, DC.

(7) Vigneswaran, S., C. Visvanathan. 1995. *Water Treatment Processes: Simple Options*. CRC Press. New York, NY.

National Drinking Water Clearinghouse (NDWC) offers a Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS) database. This public reference database contains information about technologies in use at small water systems around the country. A database search could locate other small systems currently treating for iron and manganese.

For further information, call the NDWC at (800) 624-8301 or (304) 203-4191. Additional copies of Tech Brief fact sheets are free; however, postal charges are added to orders. To order, call the NDWC at (800) 624-8301 or (304) 293-4191. You may also order online at ndwc_orders@estd.wvu.edu, or download Tech Briefs from our Web site at http://www.ndwc.wvu.edu where they are available in the educational products section.

- Tech Brief: Disinfection, item #DWBLPE47;
- Tech Brief: Filtration, item #DWBLPE50;
- Tech Brief: Corrosion Control, item #DWBLPE52;
- Tech Brief: Ion Exchange and Demineralization, item #DWBLPE56;
- Tech Brief: Organics Removal, item #DWBLPE59;
- Tech Brief: Package Plants, item #DWBLPE63;
- Tech Brief: Water Treatment Plant Residuals Management, item #DWBLPE65
- Tech Brief: Lime Softening, item #DWBLPE67
- Tech Brief: Iron and Manganese Removal, item #DWBLPE70

EXTRATERRITORIAL LAND USE CONTROL TO PROTECT WATER SUPPLIES

Laurel Phoenix
Green Bay, Wisconsin

Cities continually need water to grow. If they are located near a river, lake, or groundwater source, they will use these closest sources first. Some cities, however, have needed to search for water far beyond their boundaries, typically looking for rivers, large lakes, or valleys suitable for damming to create reservoirs. Because these distant areas are in different political jurisdictions that may fight a city in its quest for water, a state may step in and give a city the power it needs to expropriate and subsequently control lands outside its municipal boundaries.

A city needing water from a new source may need extraterritorial control over land in that area in order to (1) establish the source, (2) maintain access to the source, and (3) maintain quality of the source. In establishing the source, a city can face numerous obstacles. There may be a small community using or living next to the water supply the city wants. It may not want to share that water or allow the city to put intake pipes into the water. It may worry that a drawdown of lake levels would change the shape of the shoreline, expose muddy littoral slopes (making it ugly), distance waterfront properties from the water, and make piers and docks useless. This would have a negative impact on property values around the lake. Future effects on property values would result if the city was given land use control authority in the watershed that would constrain the economic growth potential of the local community. Or what if the small community is in a valley bottom instead? It certainly will not want a dam and reservoir to drown its homes and businesses. Forcing an entire community to move not only destroys homes, businesses, farmlands, and forests, but also makes many local citizens lose their jobs and their social networks. Any community would naturally fight the forfeiture of its own potential economic growth to benefit a bigger city's economic growth.

The second step, maintaining access to the source, means that a city would need the right to travel over any properties necessary to maintain and repair miles of pipeline or to manage any dams.

It is the third step, maintaining quality of the source, which requires the most extraterritorial control of the source watershed. Different land uses create different nonpoint source pollution that can contaminate the source water. The city seeking the new water source will want to prevent watershed land uses that contaminate the source and require more money to treat the water. Inadequately treated municipal sewage, failing septic tanks, or farms with animals can all contribute *Escherichia coli (E. coli)* to the water source. Sediment from farm field erosion, steep building sites, or building too close to the water source can cause siltation of the reservoir and reduce the reservoir's storage capacity. Moreover, sediment adds to turbidity levels, and these total dissolved solids (TDS) can reach a high enough level that a drinking water treatment plant would have to shut down its intake pipes. Parasites such as *Cryptosporidium parvum* and *Giardia* spp., which cause cryptosporidiosis and giardiasis in humans, require extremely expensive filtration treatment, so cities that can keep a watershed very clean can obtain a filtration waiver from the Environmental Protection Agency (EPA) and avoid spending billions on filtration plants.

Because land use decisions most closely affect property values and the economic potential of a community, land use controls have historically been the right of local governments to decide. To give this decision-making power to another local government essentially gives the smaller community unequal rights in their state, a loss of control in determining their future, and a transfer of wealth to the larger city.

It is an extraordinary step for a state to give one local government extraterritorial control over another local government, as this gives the equivalent of limited state power to some local governments. Because of the critical nature of water supplies to cities, and because larger cities are a state's economic engines, a state will often pass legislation to allow establishment and access to a new water source. Some states have gone further to give extraterritorial land use control over communities in the source watershed to maintain the source water quality. To provide a few examples of extraterritorial land use controls, Boston, New York, and Syracuse are described here.

BOSTON

The Quabbin Reservoir is the largest and most recently developed water supply for the greater metropolitan area of Boston. The Swift River in western Massachusetts was impounded by a dam to flood a valley in the early 1930s. The Watershed Protection Act, 350 CMR 11 (to read the complete regulations, see http://www.mass.gov/mdc/350CMR11.html), delineates a variety of restrictions on land use in the four towns within the watershed in order to protect its water quality. Land has been categorized by proximity to a tributary or reservoir, presence of wetlands, areas overlying aquifers, and so on to distinguish the degree of regulation for each zone. The first buffer zone (within 400 ft of the reservoir or within 200 ft from a tributary or other surface water) is the Primary Protection Zone. No new construction, excavation, or grading is allowed. Dumping of any substance is illegal, and no new paving can be laid. Substances defined as pollutants cannot be manufactured, stored, applied, or dumped in this zone.

The second buffer zone is the Secondary Protection Zone. This includes vegetated wetlands, floodplain lands, land lying over selected aquifers, and any land between 200 and 400 ft of tributaries or surface waters. Development density is controlled (determined by X bedrooms per X acres), wetlands cannot be disturbed, and certain chemicals cannot be stored, used, or dumped. Sewage treatment facilities may not dump their effluent, leach fields must be at least 4 ft above the water table, liquid petroleum can only be stored in a structure that can hold 125% of the petroleum tank capacity, and this structure must be placed over a poured concrete floor. Storage or use of hazardous or solid waste beyond what a typical house would use is prohibited. Road salt, fertilizers, and pesticides must be stored indoors. No boat and car washing or servicing businesses are allowed, and no junkyards are allowed. The construction of impervious surfaces is limited to 10% of a lot. Recreational activities are limited in the land surrounding the reservoir. For example, hiking is allowed, but snowmobiles and off-road vehicles are not. Boats are not allowed on the lake, and no domestic animals or horseback riding are allowed.

NEW YORK

In 1905, the state legislated the creation of the New York City Board of Water Supply, which would be in charge of researching and developing bigger and cleaner water supplies for the city. New York City dammed several valleys in the Catskill mountains, inundating villages and farms. These dams were completed by 1927, and more dams were built in neighboring valleys that feed the Delaware River by the 1960s. All of these reservoirs were linked together by pipelines, and gravity flow delivered the water to the city boundaries. After years of contention between the watershed towns and New York City, the Final Rules and Regulations to protect the city's water supply became law on May 1, 1997 (to read the complete regulations, see http://www.ci.nyc.ny.us/html/dep/html/ruleregs/finalrandr.html). Because there is heavy pressure to develop land in these watersheds, these final rules and regulations list prohibited land uses, but the city agreed that it would never use the power of eminent domain to prevent new development in these areas. Rather, it would seek out willing sellers from which to purchase lands, and then it would leave these lands undeveloped. Development in these watersheds must be guided by proximity to water, slope of building lots, percentage of impervious area, and other requirements similar to that mentioned for the Quabbin watershed. Other pressures that New York City could have exerted were resolved by city-funded programs. For example, the city is paying to replace failing septics for houses and businesses. In addition, extra funding has been found to upgrade public sewage treatment plants to prevent their effluent from degrading the water quality of the reservoirs. Farms receive assistance on manure management and other farm activities that reduces their nutrient, sediment, and pesticide contributions to the reservoirs.

The New York City watershed agreement is distinct from how Boston's water authority controls the Quabbin watershed. The dynamics of the residents are different, as there are far more people living or wanting to live in the Catskill area. This means the Catskill residents have all the more potential money to lose if land use regulations in their watershed virtually eliminated the potential for economic growth.

SYRACUSE

The city of Syracuse, New York receives its water from Skaneateles Lake, one of the Finger Lakes of New York. Relative to Quabbin watershed or the Catskill watersheds, this lake lies in a much smaller watershed with a low-density population. There is a small but wealthy village that relies on tourism, a lake surrounded by large-lot estates, and a small amount of farmland. There are no industries or sewage treatment plants that discharge into this lake.

Syracuse has several tools to protect its water source. The watershed regulations (to read the complete regulations, see http://www.syracuse.ny.us/deptWater.asp), for example, allow Syracuse to test yearly for failing septic systems on every lakeshore property. The city also established two programs to protect water quality, the Skaneateles Lake Watershed Land Protection Program (SLWLPP) and the Skaneateles Lake Watershed Agricultural Program (SLWAP). The SLWLPP provides funds to buy permanent conservation easements from environmentally significant properties from willing sellers. The SLWAP helps farmers in the watershed create voluntary Whole Farm Plans that reduce nonpoint source pollution from these farms while saving farmers money.

THE CHOICES OF EXTRATERRITORIAL CONTROL

The ways in which these three cities exerted their extraterritorial control is influenced by how many citizens live in the watersheds now and how locals used their political voice to soften the heavy-handedness that total land use controls engender. Consequently, New York City and Syracuse had to develop more cooperative and voluntary solutions between municipalities to protect the water source without impoverishing the communities along their shores.

LEAK DETECTION AND WATER LOSS CONTROL

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Utilities can no longer tolerate inefficiencies in water distribution systems and the resulting loss of revenue associated with underground water system leakage. Increases in pumping, treatment and operational costs make these losses prohibitive. To combat water loss, many utilities are developing methods to detect, locate, and correct leaks.

Old and poorly constructed pipelines, inadequate corrosion protection, poorly maintained valves and mechanical damage are some of the factors contributing to leakage. One effect of water leakage, besides the loss of water resources, is reduced pressure in the supply system. Raising pressures to make up for such losses increases energy consumption. This rise in pressure makes leaking worse and has adverse environmental impacts.

Of the many options available for conserving water, leak detection is a logical first step. If a utility does what it can to conserve water, customers will tend to be more cooperative in other water conservation programs, many of which hinge on individual efforts. A leak detection program can be highly visible, encouraging people to think about water conservation before they are asked to take action to reduce their own water use. Leak detection is an opportunity to improve services to existing customers and to extend services to the population not served.

In general, a 10 to 20 percent allowance for unaccounted-for-water is normal. But a loss of more than 20 percent requires priority attention and corrective actions. However advances in technologies and expertise should make it possible to reduce losses and unaccounted-for-water to less than 10 percent. While percentages are great for guidelines, a more meaningful measure is volume of lost water. Once the volume is known, revenue losses can be determined and cost effectiveness of implementing corrective action can then be determined.

Figure 1. Shawn Menear, a graduate student in technology education at west virginia university, uses geophones to listen for water main leaks. Similar to a doctor or nurse's stethoscope, geophones are an inexpensive leak detection device used by water utilities.

BENEFITS OF LEAK DETECTION AND REPAIR

The economic benefits of leak detection and repair can be easily estimated. For an individual leak, the amount lost in a given period of time, multiplied by the retail value of that water will provide a dollar amount. Remember to factor in the costs of developing new water supplies and other "hidden" costs.

Some other potential benefits of leak detection and repair that are difficult to quantify include:

- increased knowledge about the distribution system, which can be used, for example, to respond more quickly to emergencies and to set priorities for replacement or rehabilitation programs;
- more efficient use of existing supplies and delayed capacity expansion;
- improved relations with both the public and utility employees;
- improved environmental quality;
- increased firefighting capability;
- reduced property damage, reduced legal liability, and reduced insurance because of the fewer main breaks; and
- reduced risk of contamination.

CAUSES OF LEAKS

Water produced and delivered to the distribution system is intended to be sold to the customer, not lost or siphoned from the distribution system without authorization. Not long ago, water companies sold water at a flat rate without metering. As water has become more valuable and metering technology has improved, more and more water systems in the U.S. meter their customers. Although all customers may be metered in a given utility, a fairly sizable portion of the water most utilities produce does not pass through customer meters. Unmetered water includes unauthorized uses, including losses from accounting errors, malfunctioning distribution system controls, thefts, inaccurate meters, or leaks. Some unauthorized uses may be identifiable. When they are not, these unauthorized uses constitute unaccounted-for water. Some unmetered water is taken for authorized purposes, such as fire fighting and flushing and blowoffs for water-quality reasons. These quantities are usually fairly small. The primary cause of excessive unaccounted-for water is often leaks.

CALCULATING UNACCOUNTED-FOR WATER

Unaccounted-for water is the difference between water produced (metered at the treatment facility) and metered use (i.e., sales plus non-revenue producing metered water). Unaccounted-for water can be expressed in millions of gallons per day (mgd) but is usually discussed as a percentage of water production:

$$\textbf{Unaccounted} - \textbf{for water}\ (\%) = \frac{(\text{Production} - \text{metered use}) \times 100\%}{(\text{Production})}$$

There are different types of leaks, including service line leaks, and valve leaks, but in most cases, the largest portion of unaccounted-for water is lost through leaks in the mains. There are many possible causes of leaks, and often a combination of factors leads to their occurrence. The material, composition, age, and joining methods of the distribution system components can influence leak occurrence. Another related factor is the quality of the initial installation of distribution system components. Water conditions are also a factor, including temperature, aggressiveness, and pressure. External conditions, such as stray electric current; contact with other structures; and stress from traffic vibrations, frost loads, and freezing soil around a pipe can also contribute to leaks. All water plants will benefit from a water accounting system that helps track water throughout the distribution system and identifies areas that may need attention, particularly large volumes of unaccounted-for water.

LEAK DETECTION AND REPAIR STRATEGY

There are various methods for detecting water distribution system leaks. These methods usually involve using sonic leak-detection equipment, which identifies the sound of water escaping a pipe. These devices can include pinpoint listening devices that make contact with valves and hydrants, and geophones that listen directly on the ground. In addition, correlator devices can listen at two points simultaneously to pinpoint the exact location of a leak. (See Figs. 1 and 2.)

Large leaks do not necessarily contribute to a greater volume of lost water, particularly if water reaches the surface; they are usually found quickly, isolated, and repaired. Undetected leaks, even small ones, can lead to large quantities of lost water since these leaks might exist for long periods of time. Ironically, small leaks are easier to detect because they are noisier and

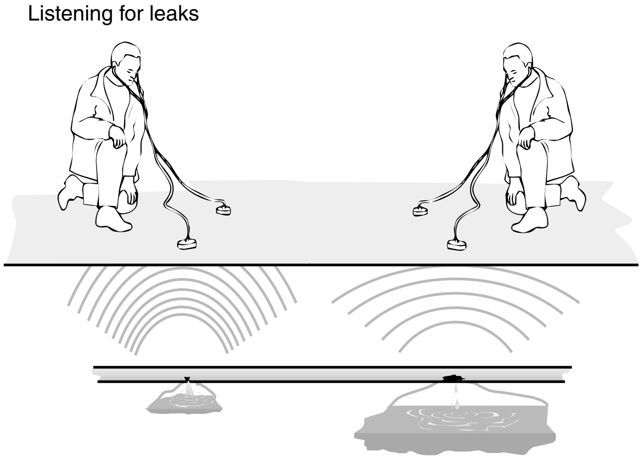

Figure 2. An important goal of leak detection is to find exactly where a leak is located. Typically, the louder the noise, the closer you are to the leak. Small leaks under high pressure usualy make more noise than larger leaks under low pressure. In fact, many large leaks make almost no sound whatsoever.

easier to hear using hydrophones. The most difficult leaks to detect and repair are usually those under stream crossings.

Leak detection efforts should focus on the portion of the distribution system with the greatest expected problems, including:

- areas with a history of excessive leak and break rates;
- areas where leaks and breaks can result in the heaviest property damage;
- areas where system pressure is high;
- areas exposed to stray electric current and traffic vibration;
- areas near stream crossings; and
- areas where loads on pipe exceed design loads.

Of course, detecting leaks is only the first step in eliminating leakage. Leak repair is the more costly step in the process. Repair clamps, or collars, are the preferred method for repairing small leaks, whereas larger leaks may require replacing one or more sections of pipe.

On average, the savings in water no longer lost to leakage outweigh the cost of leak detection and repair. In most systems, assuming detection is followed by repair, it is economical to completely survey the system every one to three years.

Instead of repairing leaking mains, some argue it is preferable to replace more leak-prone (generally older) pipes. Selecting a strategy depends upon the frequency of leaks in a given pipe and the relative costs to replace and repair them.

Deciding whether to emphasize detection and repair over replacement depends upon site-specific leakage rates and costs. In general, detection and repair result in an immediate reduction in lost water, whereas replacement will have a longer-lasting impact to the extent that it eliminates the root cause of leaks.

The most important factor in a leak detection and repair program is the need for accurate, detailed records that are consistent over time and easy to analyze. Records concerning water production and sales, and leak and break costs and benefits, will become increasingly important as water costs and leak and break damage costs increase and as leak detection and rehabilitation programs become more important. In order to optimize these programs by allocating funds in such a way that results in the greatest net benefits, adequate information is needed on which to base decisions and determine needs. Three sets of records should be kept: (1) monthly reports on unaccounted-for water comparing cumulative sales and production (for the last 12 months, to adjust discrepancies caused by the billing cycle); (2) leak-repair report forms; and (3) updated maps of the distribution system showing the location, type, and class of each leak.

COORDINATING LEAK DETECTION AND REPAIR WITH OTHER ACTIVITIES

In addition to assisting with decisions about rehabilitation and replacement, the leak detection and repair program can further other water utility activities, including:

- inspecting hydrants and valves in a distribution system;
- updating distribution system maps;
- using remote sensor and telemetry technologies for ongoing monitoring and analysis of source, transmission, and distribution facilities. Remote sensors and monitoring software can alert operators to leaks, fluctuations in pressure, problems with equipment integrity, and other concerns; and
- inspecting pipes, cleaning, lining, and other maintenance efforts to improve the distribution system and prevent leaks and ruptures from occurring. Utilities might also consider methods for minimizing water used in routine water system maintenance.

BEYOND LEAK DETECTION AND REPAIR

Detecting and repairing leaks is only one water conservation alternative; others include: meter testing and repair/replacement, rehabilitation and replacement programs, installing flow-reducing devices, corrosion control, water pricing policies that encourage conservation, public education programs, pressure reduction, requests for voluntary cutbacks or bans on certain water uses, and water recycling.

WHERE CAN I FIND MORE INFORMATION?

Jeffs, C., Lloyd C., and Pospishill D. 1989. *An Introduction to Water Loss and Leak Detection*. Duncan OK: National Rural Water Association.

Mays, W.L. 2000. *Water Distribution Systems Handbook*. American Water Works Association. New York: McGraw-Hill.

Moyer, E. M. 1985. *Economics of Leak Detection: A Case Study Approach*. Denver: American Water Works Association

Pask, David. 50 Percent Loss? How to Detect Small Utility Water Leaks. *On Tap*. Winter 1993. Morgantown WV: National Drinking Water Clearinghouse.

U.S. Environmental Protection Agency. 1998. *Water Conservation Plan Guidelines*. Washington, DC: Office of Water. EPA-832-D-98-001

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Tech Briefs, drinking water treatment fact sheets have been a regular feature in the National Drinking Water Clearinghouse (NDWC) newsletter *On Tap* for more than five years. Former NDWC Technical Assistance Coordinator Zacharia M. Lahlou, Ph.D, researches, compiles information, and writes these very popular items.

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Tech Brief: Corrosion Control, item #DWBLPE52;
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Tech Brief: Organics Removal, item #DWBLPE59;
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LIME–SODA ASH PROCESSES

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INTRODUCTION AND PROCESS OVERVIEW

As in other chemical water softening technologies, the objective of the lime–soda ash process is to precipitate polyvalent cations from solution by pH adjustment. In water treatment applications, Ca^{2+} and Mg^{2+} are the two major cations of concern, though Fe^{2+}, Fe^{3+}, Al^{3+}, and Mn^{2+} may also be present at problematic concentrations, depending on the properties of soil or geological material encountered by the surface or groundwater. Typically, a total hardness ranging from 75–120 mg/L as $CaCO_3$, is sought in domestic water softening.

Total [water] hardness (TH) is composed of carbonate and noncarbonate fractions, where carbonate hardness (CH) is the equivalent concentration (meq/L or mg/L as $CaCO_3$) of polyvalent cation species associated with carbonate ions [e.g., $Mg(HCO_3)_2$]. Similarly, noncarbonate hardness (NCH) is the equivalent concentration of all aqueous phase cations not associated with carbonate species, such as the "free" ions Ca^{2+}, Mg^{2+}, and Al^{3+}.

In this process, lime and soda ash are added to solution, Ca^{2+} precipitates as $CaCO_3(\downarrow)$, and Mg precipitates as $Mg(OH)_2(\downarrow)$. To precipitate $CaCO_3$, the pH of the water must be raised to approximately 10.3. Similarly, $Mg(OH)_2(\downarrow)$ forms when the pH is raised above 11. When there is not enough naturally occurring bicarbonate alkalinity (HCO_3^-) in water to form the $CaCO_3$ precipitate, alkalinity must be added (typically as Na_2CO_3).

CHEMICAL REACTIONS OF LIME–SODA ASH SOFTENING

Initially, any free acids in the water must be neutralized prior to raising the pH for cation precipitation. In natural waters, which are generally considered in equilibrium with the atmosphere, CO_2 and H_2CO_3 (carbonic acid) are the primary free acids of concern (1).

Typically, hydrated lime, $Ca(OH)_2$, is used to neutralize the weak acid, as presented in Equations 1 and 2. When added to water, lime initially dissociates into its constituent ions, Ca^{2+} and OH^-. Free calcium forms, so water hardness is actually increased. However, as the pH is raised, free calcium ions are used to form $CaCO_3(\downarrow)$, and the hardness imparted to the water by lime dissociation is removed.

$$\mathrm{Ca(OH)_2 + H_2O \longleftrightarrow Ca^{2+} + 2OH^- + H_2O} \quad (1)$$

$$\mathrm{CO_2 + Ca(OH)_2 \longleftrightarrow CaCO_3(\downarrow) + H_2O} \quad (2)$$

Following the neutralization of free acids, carbonate hardness due to calcium is removed, as presented in Equation 3. When the pH is less than 8.3, bicarbonate is the dominant carbonate species that contributes to alkalinity; thus, the dominant calcium carbonate species is $\mathrm{Ca(HCO_3)_2}$.

$$\mathrm{Ca^{2+} + 2HCO_3{}^- + Ca(OH)_2 \longleftrightarrow 2CaCO_3(\downarrow) + 2H_2O} \quad (3)$$

By adding hydrated lime, the pH is raised to ~10.3, which results in converting bicarbonate to carbonate ions and facilitates calcium precipitation as $\mathrm{CaCO_3}$ (limestone).

Similarly, carbonate hardness associated with magnesium is removed by raising the pH to ~11 and precipitating magnesium as a hydroxide; however, the process occurs in two steps because $\mathrm{MgCO_3}$ is soluble in water, as in Equations 4a and 4b.

$$\mathrm{Mg^{2+} + 2HCO_3{}^- + Ca(OH)_2 \longleftrightarrow MgCO_3 + CaCO_3(\downarrow) + 2H_2O} \quad (4a)$$

$$\mathrm{Mg^{2+} + CO_3{}^{2-} + Ca(OH)_2 \longleftrightarrow Mg(OH)_2(\downarrow) + CaCO_3(\downarrow)} \quad (4b)$$

At this point, the pH is ~11. Consequently, the pH does not need to be increased any further to enable the removal of noncarbonate hardness associated with calcium, $\mathrm{Ca^{2+}}$. However, carbonate must be added to the system to form the calcium carbonate precipitate. Carbonate is added as soda ash, and the following reaction occurs:

$$\mathrm{Ca^{2+} + Na_2CO_3 \longleftrightarrow CaCO_3(\downarrow) + 2Na^+} \quad (5)$$

Note that "free" $\mathrm{Na^+}$ ions do not contribute to water hardness.

When removing noncarbonate hardness due to magnesium, both lime and soda ash are required; lime is added to provide the $\mathrm{OH^-}$ ions necessary to precipitate Mg as $\mathrm{Mg(OH)_2(\downarrow)}$, and soda ash is needed to precipitate calcium.

$$\mathrm{Mg^{2+} + Ca(OH)_2 \longleftrightarrow Mg(OH)_2(\downarrow) + Ca^{2+}} \quad (6a)$$

$$\mathrm{Ca^{2+} + Na_2CO_3 \longleftrightarrow CaCO_3(\downarrow) + 2Na^+} \quad (6b)$$

After removing $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$ from solution, the pH is near 11, and $\mathrm{CO_2(g)}$ is added to reduce the pH to ~9.2–9.7 and thus, remove excess lime.

$$\mathrm{CO_2 + Ca(OH)_2 \longleftrightarrow CaCO_3(\downarrow) + H_2O} \quad (7a)$$

$$\mathrm{Mg(OH)_2(\downarrow) + CO_2 \longleftrightarrow MgCO_3 + H_2O} \quad (7b)$$

$\mathrm{CO_2(g)}$ is then added to reduce the water to a finished pH of ~8.6. (2,3).

Based on the relationships in Equations 1–7, the equivalent concentrations of lime and soda ash required are given by the following (2):

$$[\mathrm{Ca(OH)_2}] = [\mathrm{CO_2}] + [\mathrm{HCO_3{}^-}] + [\mathrm{Mg^{2+}}] + \text{excess} \quad (8)$$

$$[\mathrm{Na_2(CO_3)}] = [\mathrm{Ca^{2+}}] + [\mathrm{Mg^{2+}}] - \text{alkalinity} \quad (9a)$$

$$\text{Alkalinity} = [\mathrm{HCO_3{}^-}] + [\mathrm{CO_3{}^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \quad (9b)$$

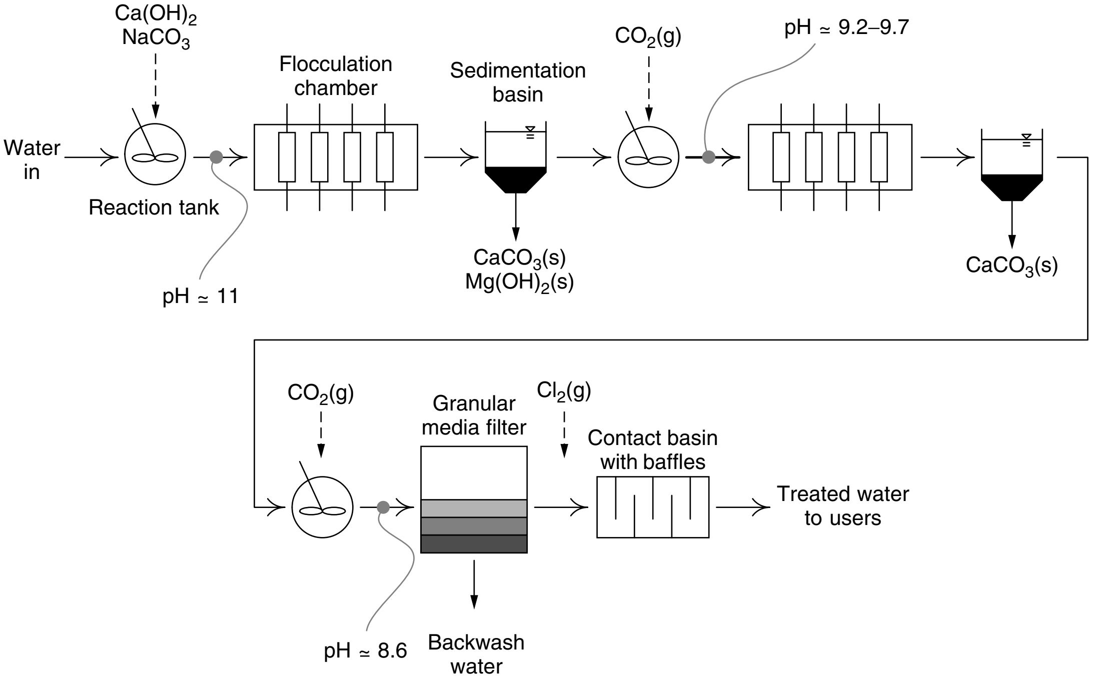

Figure 1. Schematic of typical layout of lime–soda ash softening process used in domestic water treatment.

PROCESS IMPLEMENTATION AND LIMITATIONS

The layout of a typical softening process in domestic water treatment is presented in (Fig. 1) (2). In this process, two flocculation basins and two sediment basins are required for the formation, precipitation, and subsequent removal of colloidal-particles. However, filtration is generally necessary after flocculation and sedimentation to remove the smallest particles that escape gravity settling. Due to the number of unit operations required in this process, capital costs can be high (2,3).

Further, Mg^{2+} is more expensive to remove than Ca^{2+}; thus, it is common to leave as much Mg in the water as feasible. Additionally, it is more costly to remove noncarbonate hardness than carbonate hardness because we must add $CO_3{}^{2-}$ (as Na_2CO_3; see Equation 6b) to facilitate the formation of the calcium carbonate precipitate. Consequently, as much noncarbonate hardness is left in the water as possible (2,3).

It is not possible to remove all Ca and Mg using lime–soda ash softening due to (1) the solubility of $CaCO_3(\downarrow)$ and $Mg(OH)_2(\downarrow)$, (2) limitations of mixing and contact, and (3) the lack of sufficient time for reaction kinetics to reach completion.

In general, the minimum calcium and magnesium hardnesses attainable in the lime–soda ash softening process are 30 and 10 mg/L as $CaCO_3$, respectively, though process economics is a major driving force in setting actual process end points (3). To attain treatment goals in a timely fashion, an excess of lime above stoichiometric requirements is supplied. Based on experience, a lime excess of $\sim$20 mg/L, as $CaCO_3$, is typically recommended. It has been found that magnesium concentrations in excess of 40 mg/L, as $CaCO_3$, cause scaling in domestic hot water heaters. However, due to the expense of Mg removal, treatment is not generally carried out to achieve a Mg concentration much lower than 40 mg/L, as $CaCO_3$. When it is necessary to remove magnesium to between 20 and 40 mg/L, as $CaCO_3$, an additional lime excess must be added equivalent to the amount of magnesium removed. However, through experience, it has been found that the addition of lime in excess of 40 mg/L, as $CaCO_3$, does not provide appreciably improved reaction kinetics. As a result, the application of other advanced unit operations such as ion exchange would be needed to reduce water hardness further (2). Further detailed discussion of lime–soda ash water softening processes is presented by Reh (4).

BIBLIOGRAPHY

1. Stumm, W. and Morgan, J. (1996). *Aquatic Chemistry*, 3rd Edn. John Wiley & Sons, New York.
2. Tchobanoglous, G. and Schroeder, E. (1987). *Water Quality*. Addison-Wesley, Reading, MA.
3. Reynolds, T. and Richards, P. (1995). *Unit Operations and Processes In Environmental Engineering*, 2nd Edn. PSW Publishing, Boston, MA.
4. Reh, C. (1978). Lime soda softening processes. In: *Water Treatment Plant Design for the Practicing Engineer*. R. Sanks (Ed.). Ann Arbor Science, Ann Arbor, MI.

LIME SOFTENING

National Drinking Water
Clearinghouse

Hard water can cause scaling problems in water heaters and soap does not lather well in hard water. Therefore, some water utilities soften water to improve its quality for domestic use. Lime softening is best suited to groundwater sources, which have relatively stable water quality. The combination of variable source water quality and the complexity of the chemistry of lime softening may make lime softening too complex for small systems that use surface water sources.

Although lime softening has been used successfully by groundwater systems serving fewer than 3,000 people, it is unlikely to be suitable for treating groundwater in systems serving 500 or fewer people unless those systems have some form of contract or satellite operation that would enable a trained operator to monitor the treatment process. Prefabricated lime softening equipment is available for small systems. Also, there is an American Water Works Association Standard for quicklime and hydrated lime (ANSI/AWWA B202-93) that provides purchasers, manufacturers, and suppliers with the minimum requirements, including physical, chemical, packaging, shipping, and testing requirements.

Either hydrated lime [$Ca(OH)_2$] or quicklime (CaO) may be used in the softening process. The choice depends upon economic factors, such as the relative cost per ton of the two materials as well as the size and equipment of the softening plant. Hydrated lime is generally used more in smaller plants because it stores better and does not require slaking (producing a chemical change in lime by combining it with water) equipment. On the other hand, quick-lime costs less per ton of available calcium oxide and is thus more economical for use in large plants.

Softened water has high causticity and scale-formation potential; hence, recarbonation is employed to reduce pH and mitigate scaling of downstream processes and pipelines. Onsite combustion generation of carbon dioxide (CO_2) or liquid CO_2 is the most common source of carbon dioxide for recarbonation.

WHAT IS HARD WATER?

"Hardness" in water is primarily the result of concentrations of calcium and magnesium. Thus, some water utilities remove calcium and magnesium to soften the water and improve its quality for domestic use. Other ions that produce hardness include iron, manganese, strontium, barium, zinc, and aluminum, but these ions are generally not present in significant quantities. Therefore, total hardness is usually defined as the sum of magnesium and calcium hardness in milligrams per liter (mg/L), as calcium carbonate ($CaCO_3$). Total hardness can also be differentiated into carbonate and noncarbonate hardness. Carbonate hardness is the portion of total hardness present in the form of bicarbonate salts [$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$] carbonate compounds ($CaCO_3$ and $MgCO_3$).

Noncarbonate hardness is the portion of calcium and magnesium present as noncarbonate salts, such as calcium sulfate ($CaSO_4$), calcium chloride ($CaCl_2$), magnesium sulfate ($MgSO_4$), and magnesium chloride (MgCl). The sum of carbonate and noncarbonate hardness equals total hardness.

What may be "hard" water in one area may be perfectly acceptable water in another area. In general, the degree of hardness is classified as follows:

Hardness	mg/L as $CaCO_3$
Soft	0 to 75
Moderate	75 to 150
Hard	150 to 300
Very hard	Above 300

Source: *Water Treatment Plant Design*, 1998.

For most applications, total hardness of 120 mg/L or less and magnesium hardness of 40 mg/L or less appear to be acceptable design criteria for softening facilities.

HOW DOES THE LIME-SOFTENING PROCESS WORK?

In the lime-softening process, the pH of the water being treated is raised sufficiently to precipitate calcium carbonate and, if necessary, magnesium hydroxide. The normal pH of water is between 6.5–8.5. In small systems, lime softening is typically practiced by adding hydrated lime to raw water to raise the pH to approximately 10. This removes calcium carbonate, essentially limestone. If magnesium removal is also required, the pH during softening needs to be closer to 11. Lime-softening systems need not be pilot tested for small systems using groundwater sources. Jar testing to determine appropriate process pH and chemical doses is sufficient. Doses of these chemicals should not change greatly over time unless the groundwater is subject to periodic infiltration by surface water that changes in quality. Lime-softening systems do need to be pilot tested if used on surface water sources with variable quality.

WHAT PRETREATMENT IS USED?

The principal types of pretreatment used before lime softening are aeration and presedimentation.

Aeration may be used to remove carbon dioxide from the source water before softening. This is only applicable to groundwaters where carbon dioxide concentrations are relatively high. Lime removal of carbon dioxide in source water adds to operation costs because of chemical expenses and increased calcium carbonate residuals.

Induced draft or open tray aeration is often used and may reduce the carbon dioxide level to 10 mg/L or less. Aeration also oxidizes iron and manganese; clogging of the aeration tray is a problem.

Presedimentation is used primarily by those plants treating high turbidity surface waters.

WHAT ARE THE MONITORING AND OPERATING REQUIREMENTS?

Regulatory monitoring requirements for lime softening plants depend on whether the source water is surface water or groundwater. Process monitoring requirements should focus on measurement of pH, hardness, and alkalinity for plants treating groundwater. In addition, filtered water turbidity monitoring is needed at the plants treating surface water for compliance purposes, as well as to manage filter operation.

One of the difficult aspects of lime softening is the operation and maintenance of lime feeders and lines carrying lime slurry to the point of application. In addition, plant operators must understand lime softening chemistry. Measurement of pH must be accurate, and the operator must know that the pH meter is properly calibrated. Failure to maintain the proper pH in softened water prior to filtration at a lime softening plant could result in precipitation or excess lime in the filter beds and formation of calcium carbonate deposits within the filters.

WHAT ARE THE CHEMICAL REQUIREMENTS?

The amount of lime required to remove carbonate hardness and magnesium can be calculated using in the following equation:

$$\begin{aligned}\mathrm{CaO(lb/mil\ gal)} &= 10.6\ \mathrm{CO_2(mg/L)} + 4.7[\mathrm{alkalinity(mg/L)} \\ &\quad + \mathrm{magnesium\ hardness(mg/L)} + \mathrm{X}]\end{aligned}$$

Where CaO is 100 percent pure, CO_2 is expressed as CO_2, alkalinity is expressed as $CaCO_3$, and X is the required excess hydroxide alkalinity in mg/L as $CaCO_3$. The magnesium hardness shown is the amount to be removed by softening, and not the amount present. Desired excess alkalinity can be determined from the magnesium hydroxide solubility relationship: it is typically in the range of 30 to 70 mg/l and is often estimated at 50 mg/L expressed as $CaCO_3$.

WHAT ARE OTHER SOFTENING ALTERNATIVES?

The selection of lime, lime-soda ash, or caustic soda softening is based on cost, total dissolved solids criteria, sludge production, carbonate and noncarbonate hardness, and chemical stability. Water containing little or no noncarbonate hardness can be softened with lime alone. However, water with high noncarbonate hardness may require both lime and soda ash to achieve the desired finished water hardness. Softening with lime or lime-soda ash is generally less expensive than caustic softening. Caustic soda softening increases the total dissolved solids of treated water, while lime and lime-soda ash softening often decrease total dissolved solids. Caustic soda softening produces less sludge than lime and lime-soda ash softening. Caustic soda does not deteriorate during storage, while hydrated lime may absorb carbon dioxide and water during storage, and quicklime may slake in storage causing feeding problems. The final selection is

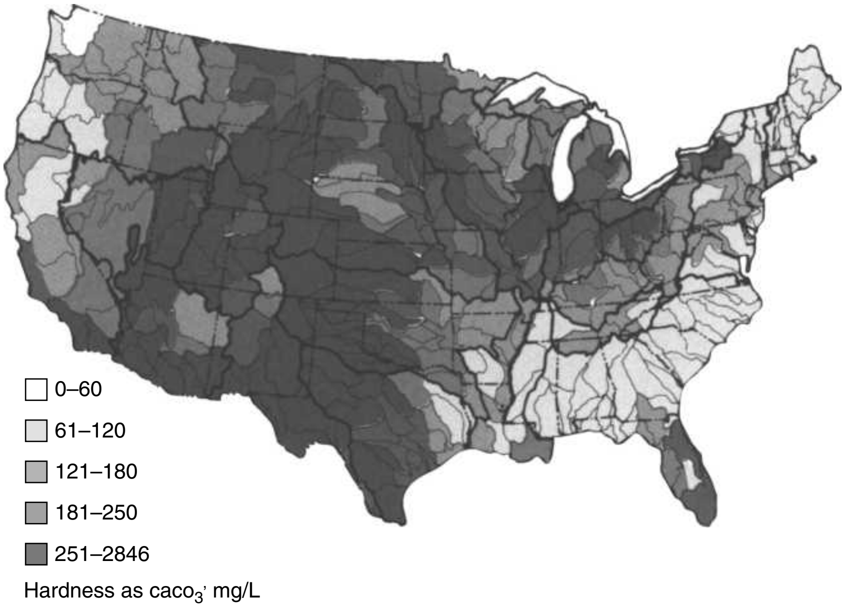

Figure 1. Average water hardness in the continental united states. Courtesy of the U.S. Geological Survey, Report 78-200.

generally based on cost, water quality, and owner and operator preference.

WHAT ARE THE BENEFITS OF SOFTENING?

Potential benefits of softening water at a central treatment plant include the following:

- reducing dissolved minerals and scale-forming tendencies,
- reducing consumption of household cleaning agents,
- removing radium 226 and 228,
- removing arsenic and uranium,
- removing heavy metals,
- supplementing disinfection and reducing algal growths in basins,
- removing certain organic compounds and reducing total organic carbon (TOC),
- removing silica and fluoride,
- removing iron and manganese,
- reducing turbidity of surface waters in conjunction with the hardness precipitation process,
- increasing the Langelier Saturation Index, useful for corrosion control under some conditions, and
- possibly removes *Giardia Lamblia* cysts.

ARE THERE CONCERNS ABOUT SOFT WATER?

In most cases, for consumer use, relatively soft water is preferable; however, it does have several disadvantages. Excessively soft water can cause corrosion in pipes. This corrosion can shorten the service life of pipes and household appliances and can result in toxic materials, such as lead and cadmium, being dissolved in drinking water. The decision to soften a water supply depends completely on the community. Drinking water regulations do not generally require softening.

WHAT ABOUT LIME SOFTENING RESIDUALS?

All water softening plants, large or small, are now required to refrain from directly discharging any wastes—liquid or solid—into rivers or streams. Where abandoned stone quarries, sand and gravel pits, or coal mines are available nearby, it may be possible to dispose of the sludge for many years without any serious difficulty. In areas where there are abandoned coal-strip mines, pumping the sludge into these areas may be a logical and convenient solution. If acid waters are leaching out of the mine into the watershed, as many such mines do, the waste sludge can help in abating serious stream pollution by neutralizing the acid water. Such neutralization may offer a great potential savings in material treatment cost to the state.

Selection of lime, lime-soda ash, or caustic soda chemical precipitation process must adequately address the disposal of generated sludges. Ultimate disposal of lime or caustic sludges now includes options, such as discharge to sanitary sewers, drying lagoons, and land application.

In some cases, sludge is discharged directly into a community's sewage system. Such a discharge must be done with the approval of the municipal sewage department, since not all systems can accommodate this alkaline waste, at least in the volume produced. In other instances, the discharge of such sludge could prove beneficial in neutralizing other acid trade wastes entering the same system. A few small plants are permitted to discharge directly into the community's storm sewer system, although this method has been phased out in most cases.

Lagooning is another practical solution. If the sludge can be dried to approximately 50 percent moisture content in lagoons, the annual requirement will be approximately

0.5 to 1.0 acre-feet per 100 mg/L hardness removed for every million gallons per day (MGD). Also, multiple lagoons used on a fill and let dry sequence, or filling from one end and withdrawing or decanting from the other, often result in better drying of the sludge.

Increasing ingenuity is necessary for sludge disposal, since lagooning, one of the most common practices, is becoming less frequent due to the dearth of available land and soaring land costs. Therefore, other methods are being increasingly employed.

An attractive method for a water plant located in a farming area is to use land application of the sludge on farm fields where the soil pH is too low for optimal plant growth. In addition to providing a desirable pH for plant growth, lime-softening sludge is generally a pure source of calcium carbonate with varying small amounts of magnesium hydroxide and provides an effective source of liming material for farmers. It has a neutralizing value for soil acids in excess of most agricultural liming materials.

WHERE CAN I FIND MORE INFORMATION?

Information in this fact sheet was primarily obtained from the following sources:

(1) Pizzi, Nicholas G. 1995. *Hoover's Water Supply and Treatment*. Twelfth Edition by Bulletin 211. National Lime Association, Kendall/Hunt Publishing Company, Arlington, VA 22203.
(2) American Water Works Association. 1984. *Introduction to Water Treatment. Principles and Practices of Water Supply Operations*.
(3) National Lime Association at http://www.lime.org/.
(4) National Research Council. 1997. *Safe Water From Every Tap: Improving Water Service to Small Communities*. National Academy Press. Washington D.C.
(5) *Technology Transfer Handbook: Management of Water Treatment Plant Residuals*. American Association of Civil Engineers Manuals and Reports on Engineering Practice No. 88, AWWA Technology Transfer Handbook, U.S. EPA/625/R-95/008.
(6) American Water Works Association. 1990. *Water Quality and Treatment: A Handbook of Community Water Supplies*. Fourth Edition.
(7) American Water Works Association and American Society of Civil Engineers. 1998. *Water Treatment Plant Design*. McGraw-Hill, New York, NY.
(8) Vigneswaran, S., C. Visvanathan. 1995. *Water Treatment Processes: Simple Options*. CRC Press. New York, NY.

Also, the National Drinking Water Clearinghouse (NDWC) Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS) is a public reference database that contains information about technologies in use at small water systems around the country.

For further information, call the NDWC at (800) 624-8301 or (304) 293-4191. Additional free copies of Tech Brief fact sheets are available from the NDWC at the above numbers or you may download Tech Briefs from our Web site at http://www.ndwc.wvu.edu. You may also order via e-mail at ndwc_orders@ndwc.wvu.edu.

Tech Brief: Disinfection, *item #DWBLPE47*
Tech Brief: Filtration, *item #DWBLPE50*
Tech Brief: Corrosion Control, *item #DWBLPE52*
Tech Brief: Ion Exchange and Demineralization, *item #DWBLPE56*
Tech Brief: Organics Removal, *item #DWBLPE59*
Tech Brief: Package Plants, *item #DWBLPE63*
Tech Brief: Management of Water Treatment Plant Residuals, *item #DWBLPE65*
Tech Brief: Lime Softening, *item #DWBLPE67*

ION EXCHANGE—USE OF MAGNETIC ION EXCHANGE RESIN FOR DOC REMOVAL

Marin Slunjski
Orica Watercare
Regency Park, SA, Australia

BACKGROUND

Conventional treatment by flocculation has a low efficiency of around 30% for DOC removal, although this can be increased to 50% by enhanced coagulation. Alternative treatment processes more effective at DOC removal include granular-activated carbon (GAC) adsorption and membrane filtration technologies, specifically nanofiltration. The latter process requires a pretreatment stage to remove suspended solids prior to membrane filtration.

ION EXCHANGE FOR DOC REMOVAL

Much of the DOC is acidic and amenable to removal by ion exchange. The DOC molecules are large (apparent molecular weight from 0.5 kD to more than 10 kD) and have a high negative charge density (10–15 meq/g DOC).

MIEX® resin is very small, five times smaller than conventional resins. This allows it to be easily dispersed in water. It is a macroporous, strong base anion exchange resin that, together with its small size, facilitates rapid DOC exchange during both DOC removal from water and resin regeneration.

The reaction mechanism is shown in Fig. 1. The resin is suspended in water containing low concentrations of DOC and other inorganic anions. The resin's affinity for the DOC molecules shifts the equilibrium to DOC uptake. The reaction is very efficiently reversed by treating the resin with a solution of high chloride concentration, such as brine.

This resin is specially formulated to include a magnetic component that allows individual resin beads to interact like small magnets, a feature that is the basis for the unique handling characteristics of the MIEX® resin and for the innovative engineering of this ion exchange process.

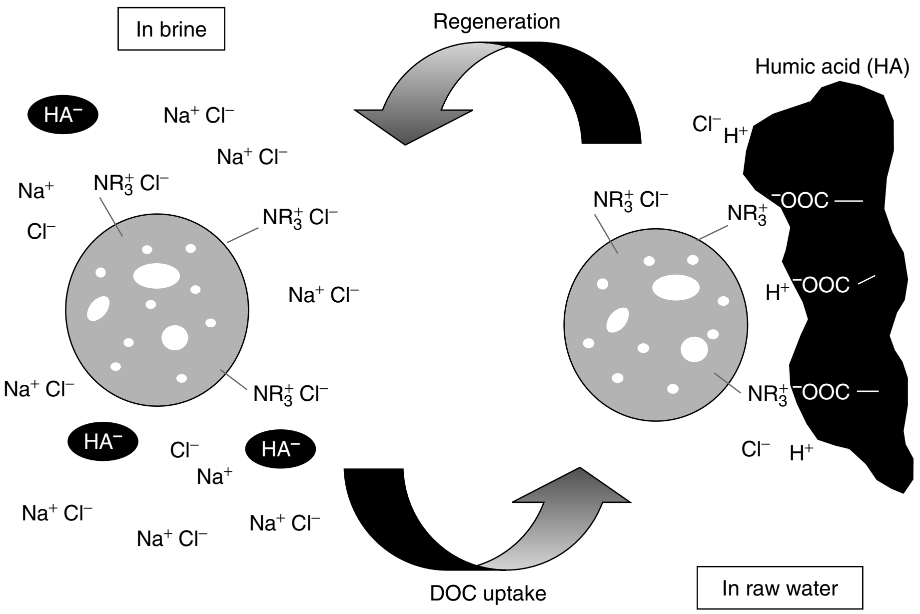

Figure 1. Standard DOC exchange mechanism.

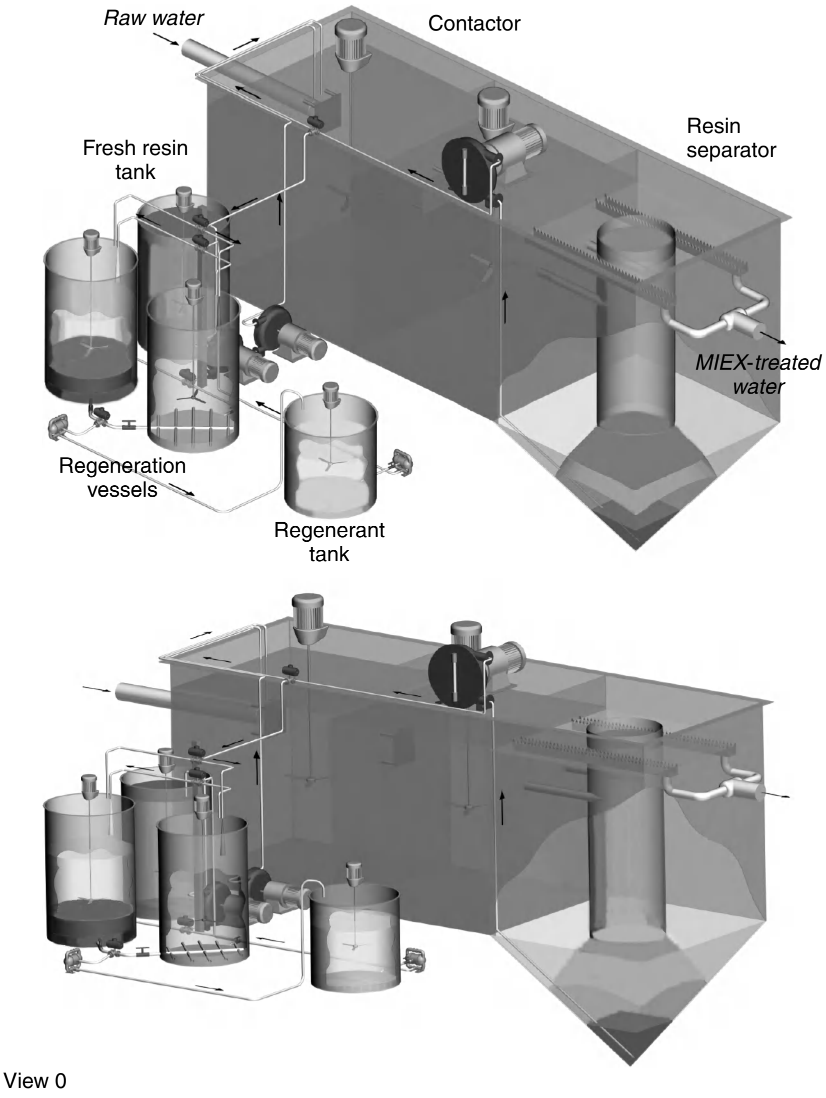

Figure 2. Diagram of 1-mL/day (0.265 mgd) MIEX® resin plant.

MIEX® RESIN IN DRINKING WATER TREATMENT

The MIEX® resin treatment process employs conventional water treatment plant facilities, including a stirred resin contact tank and gravity settlers, as shown in Fig. 2. The resin is dosed into raw/untreated water at a concentration required to achieve a specific water quality. Resin concentrations are in the range of 5–20-mL settled resin per L water (1.25–5.0-g dry weight resin per L). The retention time in the flow-through contacting tanks ranges from 10 to 30 minutes, which is sufficient to achieve more than 50% DOC removal.

The suspension of resin in water from the contacting tanks flows by gravity into a separator. The separator feed well is designed to provide conditions that promote agglomeration of individual resin beads under their magnetic forces. The agglomerates formed are heavy enough to settle to the bottom of the separator against water upflow rates between 5 and 15 $m^3/m^2/h$ (2–6 gpm/ft^2). In this process, more than 99.95% of the resin fed into the separator is recovered in the concentrated (~300 mL-settled resin per L) separator underflow referred to as resin recycle.

In addition to keeping the plant footprint small, the high upflow rate in the resin separator is required to flush out effectively turbidity introduced into the MIEX® plant with raw water. Because a small amount of the resin attrited by pumping and mixing is carried over from the separator with treated water, turbidity increases through the MIEX® process by about 1–2 NTU.

The resin recycle from the separator is directed back to the contacting tanks for another DOC uptake cycle. To maintain the resin's capacity for DOC removal, a small amount of the recycled resin, typically 10% of the total resin flow, is continuously diverted to resin regeneration and is replaced by the same amount of fresh (regenerated) resin. In this way, each resin bead is, on average, contacted by water 10–20 times before being diverted to regeneration.

The DOC-laden resin is stored in a regeneration vessel until a preset settled resin volume is reached. This triggers switching over the resin off-take to the second regeneration

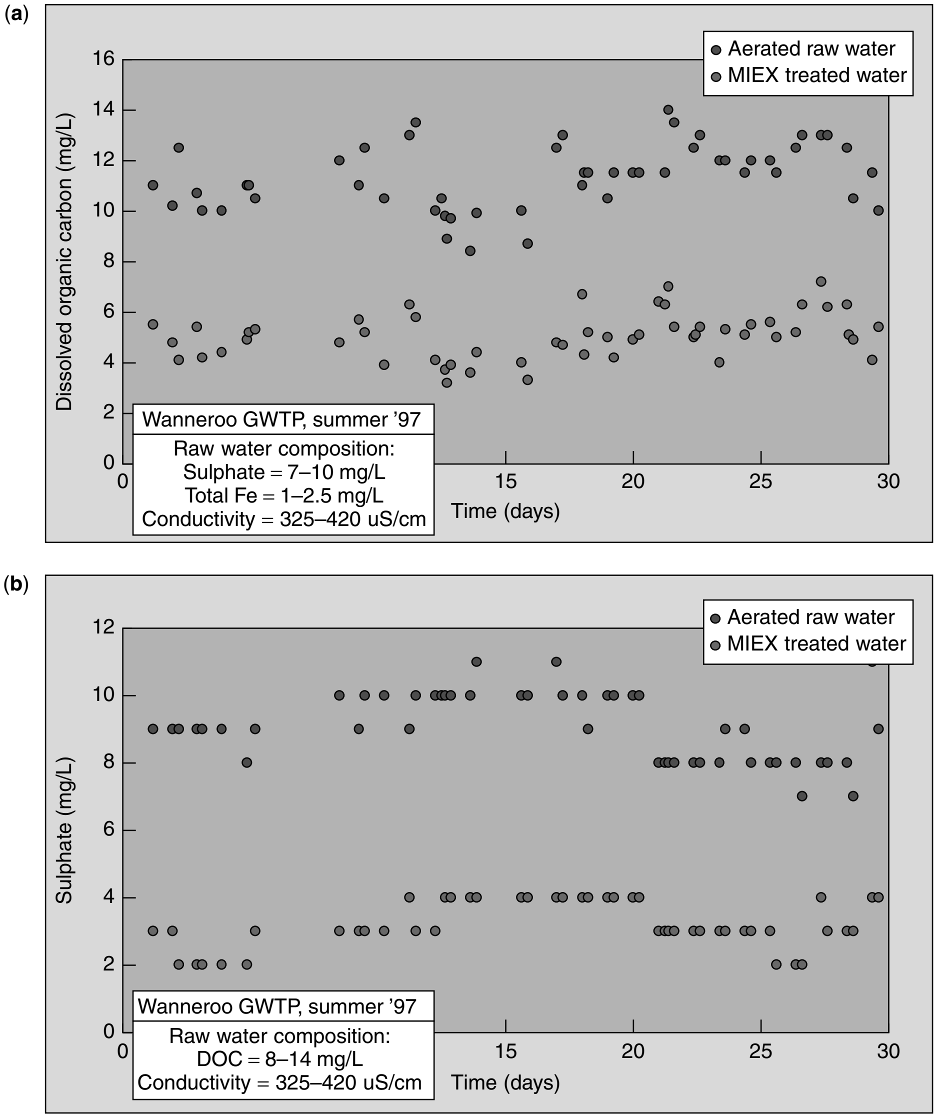

Figure 3. DOC and sulfate removal results.

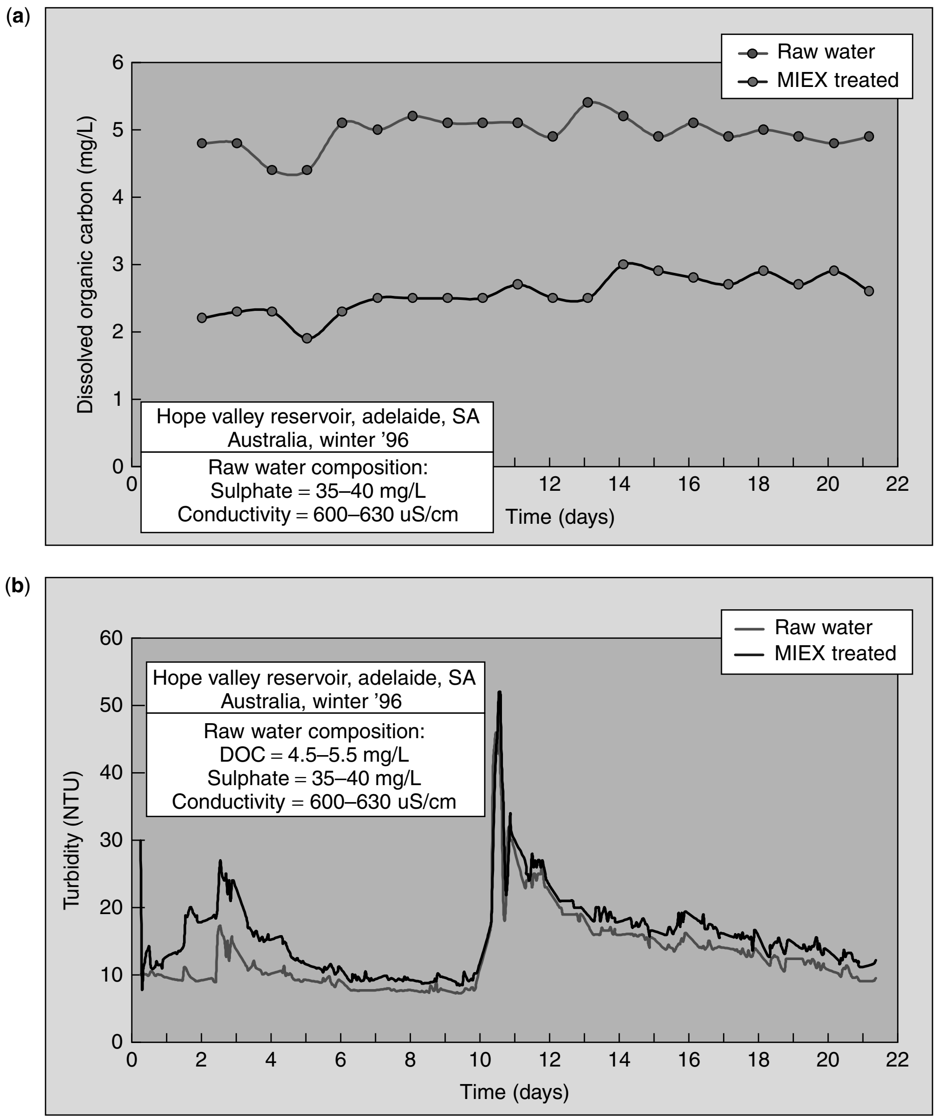

Figure 4. Effect of turbidity on MIEX® resin DOC removal.

vessel, and the start of regeneration in the full vessel. The regeneration is a sequential process comprising draining of carrier water, mixing resin with regenerant, draining of used regenerant, optional rinsing of regenerated resin with water, resuspending of regenerated resin in water, and transferring it into the fresh resin tank.

The basic regenerant is 120-g/L NaCl solution dosed at 3:1 brine to resin volume. Depending on the raw water quality, in some cases, pH modified regenerations using small additions of NaOH and HCl are beneficial. The consumption of salt for regeneration and waste regenerant production is minimized by reusing the regenerant a number of times. Salt usage is from 50-kg to 80-kg NaCl per mL water treated depending on conditions, and salt is adjusted after each use.

RESULTS OF MIEX® TREATMENT

Due to the steady-state nature of operation, this process produces water of constant quality. The high resin preference for DOC anions removes no other anions (bicarbonate, nitrate, etc.), except for sulfate removed in appreciable quantities (Fig. 3).

DOC removal is undisturbed by excursions of raw water turbidity, as shown in Fig. 4. This process is not designed to remove turbidity and may actually contribute 1–2 NTU due to a small amount of resin carryover (Fig. 4b).

Under typical process conditions, MIEX® resin preferentially removes the smaller molecular weight (MW) fraction of DOC. This makes it complementary to alum coagulation, which is known to be more efficient in removing the larger MW fraction of DOC, as shown in Fig. 5.

Pretreatment with MIEX® resin usually results in 50–60% DOC removal. This in turn results in even higher reductions in the alum dose required for turbidity removal. Alum used for turbidity removal will remove a further 20–30% DOC. The combined MIEX®/low-dose alum treatment can remove an overall 80–90% DOC. The low residual DOC levels result in a 50–60% reduction in chlorine demand compared with using

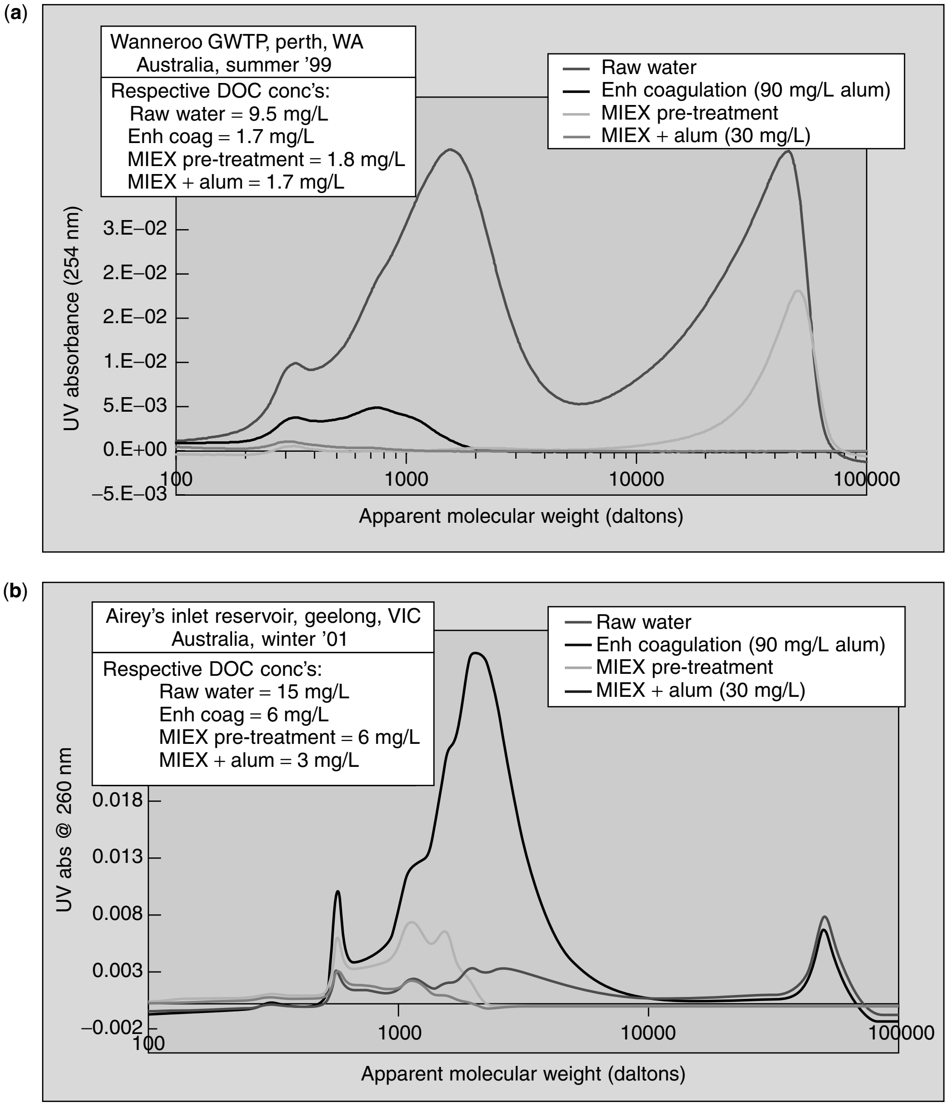

Figure 5. Effect of MIEX® on NOM's apparent molecular weight.

only conventional alum treatment. However, the main benefit of more efficient DOC removal from the combined MIEX®/coagulation process is the reduction in disinfection byproducts formed (Fig. 6).

PROCESS CAPITAL AND OPERATING COSTS

The MIEX® plant uses conventional water treatment infrastructure and equipment. There is no need for pressure columns or complicated piping/valve arrangements. Due to the high settler loading rate, the plant footprint is small, and the production rate high—the average water retention time in the plant is in the range of 40 min to 1 h.

Furthermore, the plant requires only 10% of the resin inventory compared with a conventional system based on the 10–15 min empty EBCT[3] generally recommended for DOC removal (1). This results in further reductions in plant capital costs. There is also no need for periodical replacement of the complete resin inventory, as it is continuously refreshed with small additions of makeup resin.

The main operating cost is resin makeup, the replacement of resin carried over from the separator. The actual resin loss is a physical parameter determined by the plant design and operating conditions. At a separator rise rate of 7 m/h, the loss rate is estimated at 4.5-L settled resin per mL treated water (4.5 gal/mg).

Another significant cost is salt for resin regeneration. Depending on the regeneration process design and raw water quality, the actual salt consumption ranges between 50- and 300-kg NaCl per mL treated water (420–2500 lb/mg). Because only small amounts of NaOH and HCl are used for occasional pH modified regenerations, these chemical costs are minor. The MIEX® plant power consumption is about 50 kW per mL treated water (190 kW/MG).

Finally, there may be some costs for disposal of spent regenerant. This waste stream can be as small as 50–200 L per mL water treated (gal/mg) based on a

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[3] EBCT—empty bed contact time: time to treat the amount of water equal to the resin bed volume.

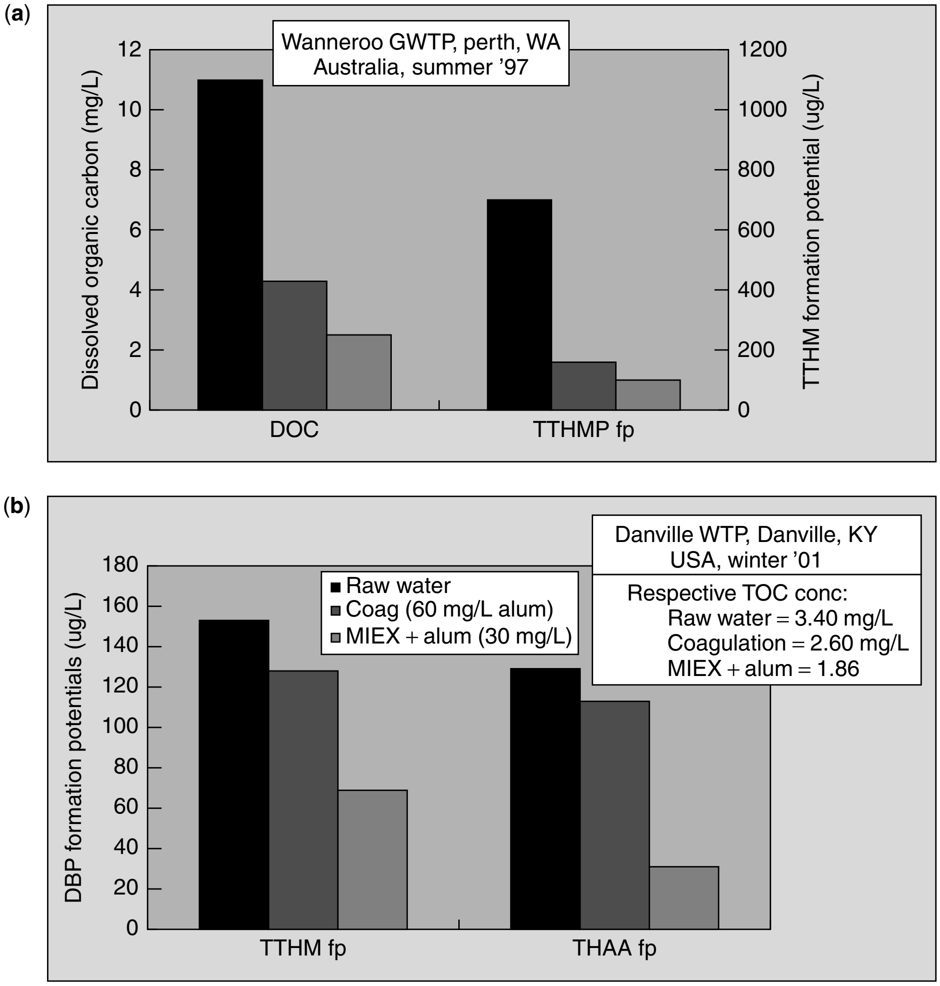

Figure 6. Effect of MIEX® on disinfection byproduct formed.

spent brine concentration of 30-g/L DOC and depending on the amount of DOC removed from raw water by the MIEX® resin. There are a number of disposal options available—sewering, deep well injection, deep ocean outfalls, and evaporation, depending on a particular plant site.

In conclusion, the process based on the MIEX® resin represents a simple, economical option for upgrading water treatment plants to improve removal of DOC and disinfection byproduct precursors. The process can easily be combined with an existing coagulation treatment plant either as an add-on greenfield plant or retrofitted into the existing infrastructure.

It is also possible to combine the MIEX® resin process as the single color/DOC removing step followed by turbidity removal using microfiltration (1,2). This solution is particularly attractive as a "chemical-free" water treatment process.

BIBLIOGRAPHY

1. Fettig, J. (1999). Removal of humic substances by adsorption/ion exchange. In: *IWSA/IAWQ Conference Proceedings: Removal of Humic substances from Water*, H. Ødegaard (Ed.). Trondheim, Norway, June 24–26, pp. 185–194.
2. Morran, J., Drikas, M., Hepplewhite, C., and Pelekani, C. (2001). *MIEX® and Microfiltration—A Winning Alliance*, in Conference Proceedings OzWater 2001, April 1–4, Canberra, Australia.
3. Bourke, M., Harrison, S., Long, B., and Lebeau, T. (2001). *MIEX® Resin Pretreatment Followed by Microfiltration as an Alternative to Nanofiltration for DBP Precursor Removal*, in AWWA 2001 Membrane Technology Conference Proceedings, March 4–7, San Antonio, TX.

READING LIST

Ødegaard, H., Eikebrokk, B., and Storhaug, R. (1999). Processes for the Removal of Humic Substances from Water—An Overview Based on Norwegian Experience. In: *IWSA/IAWQ Conference Proceedings: Removal of Humic substances from Water*. H. Ødegaard (Ed.). June 24–26, Trondheim, Norway, pp. 43–52.

Potts, J., Wessels, L.P., and Van Paassen, W.C. (2000). Ion exchange for colour and total carbon removal in combination with dead-end nano-filtration for reuse of regenerate. In: *Proceedings from the Conference on Membranes in Drinking and Industrial Water Production*, Oct. 3–6, Paris, France, published by Deasalination Publications, L'Aquila, Italy, Vol. 1, pp. 241–246.

MEMBRANE FILTRATION

National Drinking Water
Clearinghouse

A membrane or, more properly, a semipermeable membrane, is a thin layer of material capable of separating substances when a driving force is applied across the membrane.

Once considered a viable technology only for desalination, membrane processes are increasingly employed for removal of bacteria and other microorganisms, particulate material, and natural organic material, which can impart color, tastes, and odors to the water and react with disinfectants to form disinfection byproducts (DBP). As advancements are made in membrane production and module design, capital and operating costs continue to decline.

The pressure-driven membrane processes discussed in this fact sheet are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

MEMBRANE FILTRATION: ALTERNATIVE TO CONVENTIONAL FILTRATION

Membrane filtration systems' capital costs, on a basis of dollars per volume of installed treatment capacity, do not escalate rapidly as plant size decreases. This factor makes membranes quite attractive for small systems. In addition, for groundwater sources that do not need pretreatment, membrane technologies are relatively simple to install, and the systems require little more than a feed pump, a cleaning pump, the membrane modules, and some holding tanks. According to a 1997 report by the National Research Council, most experts foresee that membrane filtration will be used with greater frequency in small systems as the complexity of conventional treatment processes for small systems increases.

NEW REGULATIONS FAVOR MEMBRANE TECHNOLOGIES

Membrane processes have become more attractive for potable water production in recent years due to the increased stringency of drinking water regulations. Membrane processes have excellent separation capabilities and show promise for meeting many of the existing and anticipated drinking water standards. The Surface Water Treatment Rule (SWTR) and the anticipated Groundwater Disinfection Rule have led to the investigation of UF and MF for turbidity and microbial removal. The new Disinfectants/Disinfection Byproduct (D/DBP) rules have increased interest in NF and UF membranes for DBP precursor removal.

Potable water treatment has traditionally focused on processes for liquid-solid separation rather than on processes for removing dissolved contaminants from water. Thus, the effect of the 1996 Safe Drinking Water Act (SDWA) amendments has been to encourage water treatment professionals to consider the more unconventional treatment processes, such as membrane technologies, alone, or in conjunction with liquid-solid separation, to meet current regulations.

COMPARING MEMBRANE FILTRATION SYSTEMS

While all types of membranes work well under proper conditions, choosing the most appropriate membrane for a given application still remains crucial (see Fig. 1). In many cases, selection is complicated by the availability of new types of membranes, applications, or by site-specific conditions. Bench and pilot tests are powerful tools for situations where process risks and uncertainties exist or the cost impacts from problems are potentially high.

Membrane classification standards vary considerably from one filter supplier to another. What one supplier sells as a UF product, another manufacturer calls a NF system. It is better to look directly at pore size, molecular weight cutoff (MWCO), and applied pressure needed when comparing two membrane systems.

MWCO, which can be regarded as a measure of membrane pore dimensions, is a specification used by membrane suppliers to describe a membrane's retention capabilities.

MICROFILTRATION (MF)

MF is loosely defined as a membrane separation process using membranes with a pore size of approximately 0.03 to 10 microns, a MWCO of greater than 100,000 daltons, and a relatively low feedwater operating pressure of approximately 100 to 400 kPa (15 to 60 psi). Representative materials removed by MF include sand, silt, clays, *Giardia lamblia* and *Cryptosporidium* cysts, algae, and some bacterial species (see Fig. 2 and Table 1). MF is not an absolute barrier to viruses; however, when used in combination with disinfection, MF appears to control these microorganisms in water.

The primary impetus for the more widespread use of MF has been the increasingly stringent requirements for removing particles and micro-organisms from drinking water supplies. Additionally, there is a growing emphasis on limiting the concentrations and number of chemicals that are applied during water treatment. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination.

Another application for the technology is for removal of natural or synthetic organic matter to reduce fouling potential. In its normal operation, MF removes little or no organic matter; however, when pretreatment is applied, in-creased removal of organic material, as well as a retardation of membrane fouling can be realized.

Two other applications involve using MF as a pretreatment to RO or NF to reduce fouling potential. Both RO and NF have been traditionally employed to desalt or remove hardness from groundwater.

Process

MF membranes provide absolute removal of particulate contaminants from a feed stream by separation based

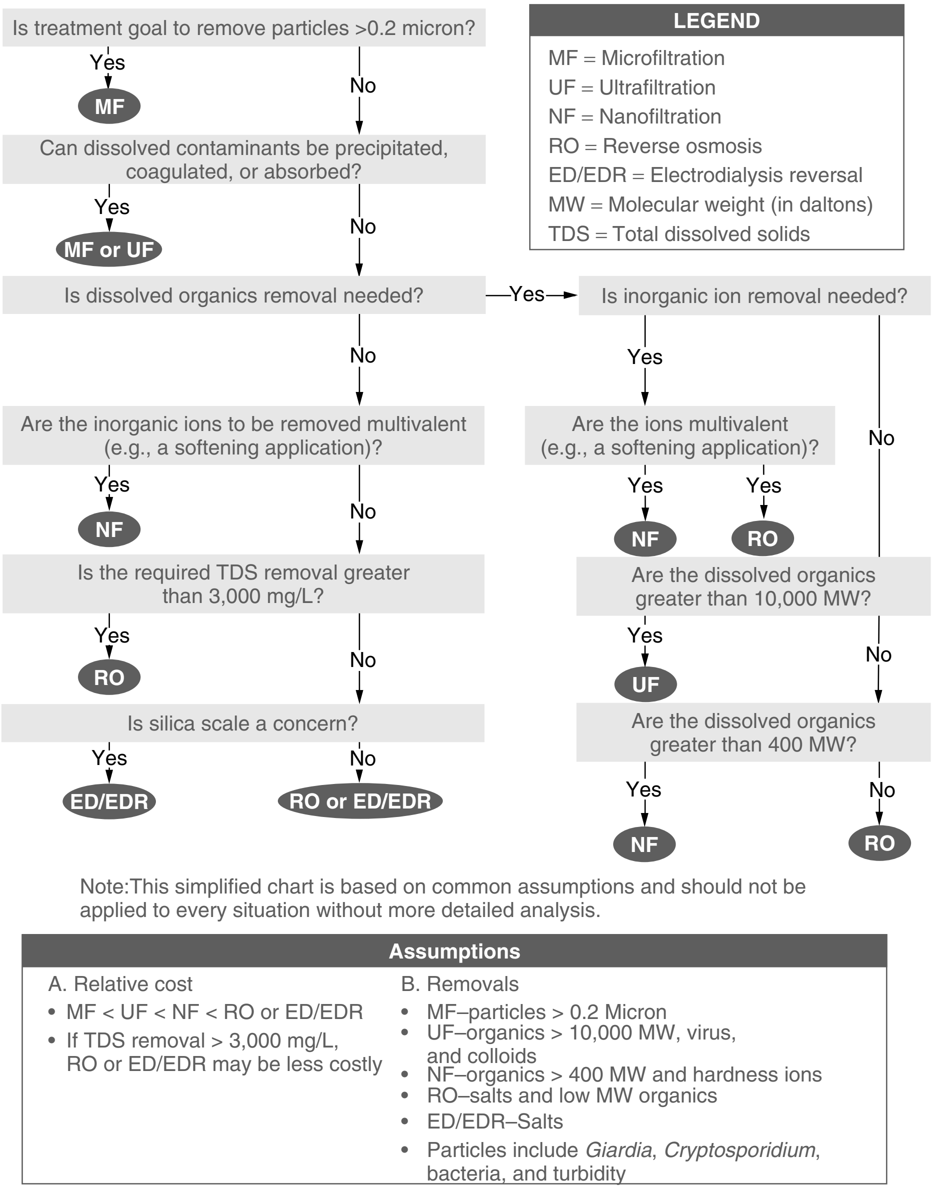

Figure 1. Generalized membrane process selection chart. *Reprinted from* Proceedings of the 1993 Membrane Technology Conference, *by permission.Copyright* © 1993, *American Water Works Association*.

on retention of contaminants on a membrane surface. It is the "loosest" of the membrane processes, and as a consequence of its large pore size, it is used primarily for removing particles and microbes and can be operated under ultralow pressure conditions.

In the simplest designs, the MF process involves prescreening raw water and pumping it under pressure onto a membrane. In comparison to conventional water clarification processes, where coagulants and other chemicals are added to the water before filtration, there are few pretreatment requirements for hollow-fiber systems when particles and microorganisms are the target contaminants.

Prefilters are necessary to remove large particles that may plug the inlet to the fibers within the membrane module. More complex pretreatment strategies are sometimes employed either to reduce fouling or enhance the removal of viruses and dissolved organic matter. In such cases, pretreatment by adding coagulants or powdered activated carbon (PAC), has been employed. In some cases, the cake layer built up on the membrane during the water production cycle can remove some organic materials.

It may be necessary to adjust the feedwater pH by chemical dosing prior to membrane filtration in order to maintain the pH within the recommended operating range for the membrane material employed. It should be noted that pH adjustment is not required for scaling control, since MF membranes do not remove uncomplexed dissolved ions.

MF membranes, under the most conservative conditions, appear to act as an absolute barrier to selected bacteria and protozoan cysts and oocysts. Unlike UF however, MF does not remove appreciable densities of viruses. Therefore, it is necessary to complement MF with a post-membrane disinfection process. Chemical disinfection may

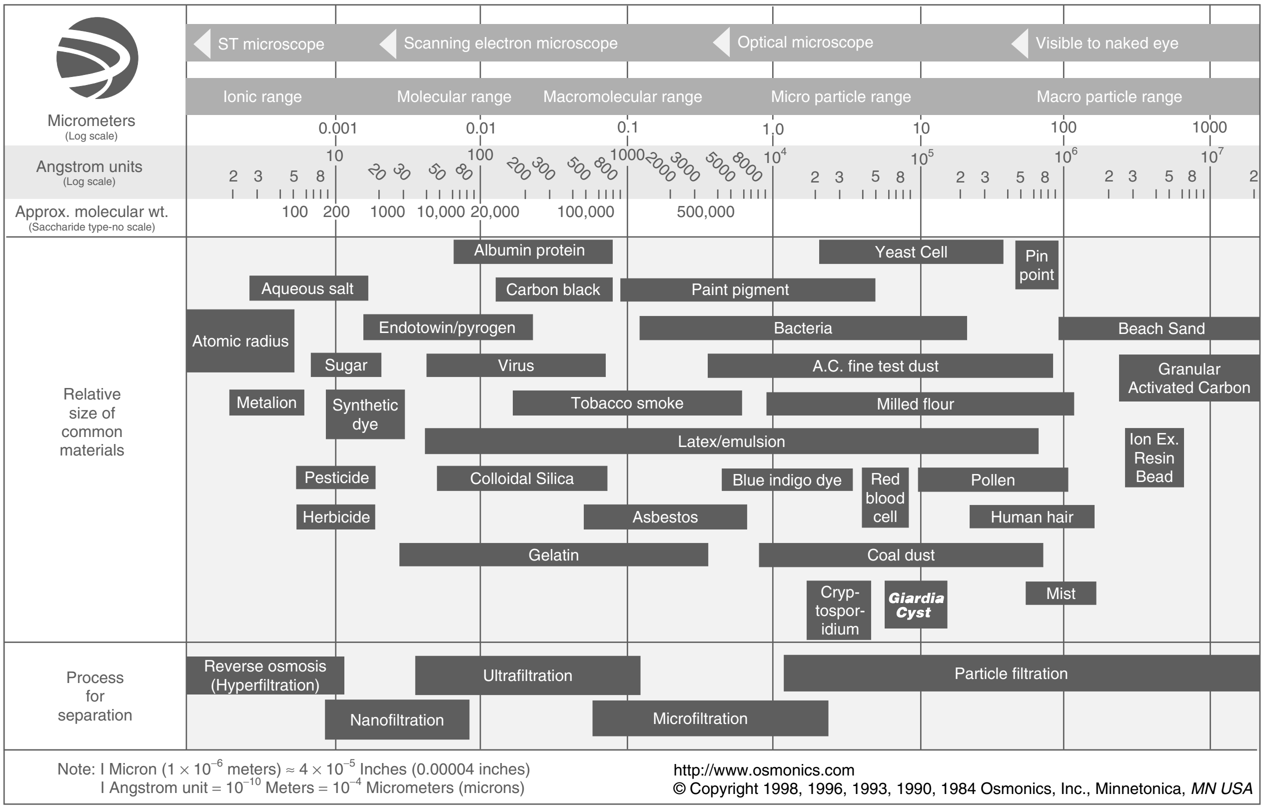

Figure 2. The filtration spectrum. *Reprinted courtesy of Osmonics, Inc., Minnetonka, MN.*

Table 1. Surface Water Treatment Compliance Technology: Membrane Filtration

Unit Technologies	Removals: Log Giardia & Log Virus	Raw Water, Pretreatment & Other Water Quality Issues
Microfiltration (MF)	Very effective Giardia, >5–6 log; Partial removal of viruses (disinfect for virus credit).	High quality or pretreatment required. Same note regarding TOC.
Ultrafiltration (UF)	Very effective Giardia, >5–6 log; Partial removal of viruses (disinfect for virus credit).	High quality or pretreatment required (e.g., MF). TOC rejection generally low, so if DBP precursors are a concern, NF may be preferable.
Nanofiltration (NF)	Very effective, absolute barrier (cysts and viruses).	Very high quality or pretreatment required (e.g., MF or UF to reduce fouling/extend cleaning intervals). See also RO pretreatments, below.
Reverse Osmosis (RO)	Very effective, absolute barrier (cysts and viruses).	May require conventional or other pretreatment for surface water to protect membrane surfaces: may include turbidity or Fe/Mn removal; stabilization to prevent scaling; reduction of dissolved solids or hardness; pH adjustment.

Source: U.S. Environmental Protection Agency, 1998.

be employed by applying chlorine, chlorine dioxide, or chloramines; however, long contact times are required to inactivate viruses.

Equipment

For municipal-scale drinking water applications, the commercially available membrane geometries that are the most commonly employed are spiral wound, tubular, and hollow capillary fiber. However, spiral-wound configurations are not normally employed for MF due to the flat-sheet nature of the membrane, which presents difficulties in keeping the membrane surface clean. Unlike spiral-wound membranes, hollow-fiber and tubular configurations allow the membrane to be backwashed, a process by which fouling due to particulate and organic materials is controlled.

Membrane “package” plants are normally employed for plants treating less than one million gallons per day (mgd). The components of the plant may include prescreens, a feed pump, a cleaning tank, an automatic gas backwash system, an air compressor, a membrane integrity monitor, a backwash water transfer tank, a pressure break reservoir, an air filter for the gas backwash, controls for the programmable logic controller, and a coalescer.

Operation and Maintenance

In MF, there are two methods for maintaining or re-establishing permeate flux after the membranes are fouled:

- Membrane backwashing: In order to prevent the continuous accumulation of solids on the membrane surface, the membrane is backwashed. Unlike backwashing for conventional media filtration, the backwashing cycle takes only a few minutes. Both liquid and gas backwashing are employed with MF technology. For most systems, backwashing is fully automatic. If backwashing is incapable of restoring the flux, then membranes are chemically cleaned. The variables that should be considered in cleaning MF membranes include: frequency and duration of cleaning, chemicals and their concentrations, cleaning and rinse volumes, temperature of cleaning, recovery and reuse of cleaning chemicals, neutralization and disposal of cleaning chemicals.
- Membrane pretreatment: Feedwater pretreatment can be employed to improve the level of removal of various natural water constituents. It is also used to increase or maintain transmembrane flux rates and/or to retard fouling. The two most common types of pretreatment are coagulant and PAC addition.

ULTRAFILTRATION (UF)

UF involves the pressure-driven separation of materials from water using a membrane pore size of approximately 0.002 to 0.1 microns, an MWCO of approximately 10,000 to 100,000 daltons, and an operating pressure of approximately 200 to 700 kPa (30 to 100 psi). UF will remove all microbiological species removed by MF (partial removal of bacteria), as well as some viruses (but not an absolute barrier to viruses) and humic materials (see Fig. 2 and Table 1). Disinfection can provide a second barrier to contamination and is therefore recommended.

The primary advantages of low-pressure UF membrane processes compared with conventional clarification and disinfection (postchlorination) processes are:

- No need for chemicals (coagulants, flocculants, disinfectants, pH adjustment);
- Size-exclusion filtration as opposed to media depth filtration;
- Good and constant quality of the treated water in terms of particle and microbial removal;
- Process and plant compactness; and
- Simple automation.

Fouling is the limiting phenomenon responsible for most difficulties encountered in membrane technology for water treatment. UF is certainly not exempt from this fouling control problem. Therefore, membrane productivity is still an important subject, which should be thoroughly researched in order to have a better understanding of this phenomenon and its mechanisms.

Process

UF is a pressure-driven process by which colloids, particulates, and high molecular mass soluble species are retained by a process of size exclusion, and, as such, provides means for concentrating, separating into parts, or filtering dissolved or suspended species. UF allows most ionic inorganic species to pass through the membrane and retains discrete particulate matter and nonionic and ionic organic species.

UF is a single process that removes many water-soluble organic materials, as well as microbiological contaminants. Since all UF membranes are capable of effectively straining protozoa, bacteria, and most viruses from water, the process offers a disinfected filtered product with little load on any post-treatment sterilization method, such as UV radiation, ozone treatment, or even chlorination.

Unlike RO, the pretreatment requirement for UF is normally quite low. Fortunately, due to the chemical and hydrolytic stability of UF membrane materials, some of the pretreatments essential for RO membranes, such as adjustment of pH or chlorine concentration levels, do not apply. However, it may be necessary to adjust the pH to decrease the solubility of a solute in the feed so that it may be filtered out.

UF is designed to remove suspended and dissolved macromolecular solids from fluids. The commercially available modules are therefore designed to accept feedwaters that carry high loads of solids. Because of the many uses for UF membranes, pilot studies are normally conducted to test how suitable a given stream is for direct UF.

Water containing dissolved or chelated iron and manganese ions needs to be treated by an adequate oxidation process in order to precipitate these ions prior to UF membrane filtration, as with all membrane processes. This is recommended to avoid precipitation of iron and manganese in the membrane, or even worse, on the permeate side of the membrane (membrane fouling during the backwash procedure). Preoxidation processes generally used include aeration, pH adjustment to a value greater than eight, or addition of strong oxidants, such as chlorine, chlorine dioxide, ozone, or potassium permanganate.

Natural organic matter (NOM) is of great importance in potential fouling of the UF membrane and, consequently, in permeate flux that can be used under normal operating conditions. Thus, it is an interesting design option to use PAC or coagulants to pretreat the water to remove NOM and, consequently, decrease the surface of membrane needed.

Equipment

UF membranes can be fabricated essentially in one of two forms: tubular or flat-sheet.

Package plants, skid-mounted standard units that allow significant cost savings, are usually employed for plants treating less than 1.5 mgd. The primary skid-mounted system components may include an auto-cleaning prefilter, raw water pump, recirculation pump, backwash pump, chlorine dosing pump for the backwash water, air compressor (valve actuation), chlorine tank, chemical tank (detergent), programmable logic controller with program and security sensor (high pressure, low level, etc.)

Operation and Maintenance

The UF membrane plant may be divided into several subcategories:

- Raw water intake and pressure pumps;
- Pretreatment, which includes prescreening, prefiltration, and pH adjustment (if required) or any of the needed pretreatments;
- UF units;
- Chemical cleaning station, backwash station (which uses chlorinated product water), chlorine station, conditioner/preservative station; and
- Line for discharging or treatment of back wash water.

Operation and performance of a UF membrane plant are greatly influenced by raw water quality variations. Turbidity as well as Total Organic Carbon (TOC) of the raw water are water quality parameters of major importance that drive operation mode and membrane flux for all the UF plants presently in operation worldwide.

NANOFILTRATION (NF)

NF membranes have a nominal pore size of approximately 0.001 microns and an MWCO of 1,000 to 100,000 daltons. Pushing water through these smaller membrane pores requires a higher operating pressure than either MF or UF. Operating pressures are usually near 600 kPa (90 psi) and can be as high as 1,000 kPa (150 psi). These systems can remove virtually all cysts, bacteria, viruses, and humic materials (see Fig. 2 and Table 1). They provide excellent protection from DBP formation if the disinfectant residual is added after the membrane filtration step. Because NF membranes also remove alkalinity, the product water can be corrosive, and measures, such as blending raw water and product water or adding alkalinity, may be needed to reduce corrosivity. NF also removes hardness from water, which accounts for NF membranes sometimes being called "softening membranes." Hard water treated by NF will need pretreatment to avoid precipitation of hardness ions on the membrane.

More energy is required for NF than MF or UF, which has hindered its advancement as a treatment alternative.

Process

NF membranes have been observed to operate on the principle of diffusion rather than sieving as with MF and UF membranes.

Operation and Maintenance

Operational parameters of membranes include the physical and chemical properties of the membrane, the pore size or molecular weight cut-off (MWCO), and configuration.

REVERSE OSMOSIS (RO)

RO systems are compact, simple to operate, and require minimal labor, making them suitable for small systems. They are also suitable for systems where there is a high degree of seasonal fluctuation in water demand.

RO can effectively remove nearly all inorganic contaminants from water. RO can also effectively remove radium, natural organic substances, pesticides, cysts, bacteria, and viruses (see Fig. 2 and Table 1). RO is particularly effective when used in series. Water passing through multiple units can achieve near zero effluent contaminant concentrations. Disinfection is also recommended to ensure the safety of water.

Some of the advantages of RO are:

- Removes nearly all contaminant ions and most dissolved non-ions,
- Relatively insensitive to flow and total dissolved solids (TDS) level, and thus suitable for small systems with a high degree of seasonal fluctuation in water demand,
- RO operates immediately, without any minimum break-in period,
- Low effluent concentration possible,
- Bacteria and particles are also removed, and
- Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications.

Some of the limitations of RO are:

- High capital and operating costs,

- Managing the wastewater (brine solution) is a potential problem,
- High level of pretreatment is required in some cases,
- Membranes are prone to fouling, and
- Produces the most wastewater at between 25–50 percent of the feed.

Process

RO removes contaminants from water using a semipermeable membrane that permits only water, and not dissolved ions (such as sodium and chloride), to pass through its pores. Contaminated water is subject to a high pressure that forces pure water through the membrane, leaving contaminants behind in a brine solution. Membranes are available with a variety of pore sizes and characteristics.

Equipment

Typical RO units include raw water pumps, pretreatment, membranes, disinfection, storage, and distribution elements. These units are able to process virtually any desired quantity or quality of water by configuring units sequentially to reprocess waste brine from the earlier stages of the process. The principal design considerations for reverse osmosis units are:

- operating pressure,
- membrane type and pore size,
- pretreatment requirements, and
- product conversion rate (the ratio of the influent recovered as waste brine water to the finished water).

WASTE STREAM DISPOSAL

Waste stream disposal is a significant problem in many areas. Unlike conventional treatment processes, in which approximately 5 to 10 percent of the influent water is discharged as waste, membrane processes produce waste streams amounting to as much as 15 percent of the total treated water volume. (See Table 2.) Because little or no chemical treatment is used in a membrane system, the concentrate stream usually contains only the contaminants found in the source water (although at much higher concentrations), and for this reason the concentrate can sometimes be disposed of in the source water. Other alternatives include deep well injection, dilution and spray irrigation, or disposal in the municipal sewer. These alternatives are usually necessary for NF wastes, which usually contain concentrated organic and inorganic compounds. Regardless of the type of membrane, disposal must be carefully considered in decisions about the use of membrane technology. Applicable local discharge regulations must be respected.

MEMBRANE INTEGRITY TESTING

One of the most critical aspects of employing membrane technology is ensuring that the membranes are intact and

Table 2. Surface Water Treatment Compliance Technology: Membrane Filtration

Unit Technologies	Complexity: Ease of Operation (Operator Skill Level)	Secondary Waste Generation	Other Limitations/ Drawbacks
Microfiltration	Basic: increases with pre/post-treatment and membrane cleaning needs.	Low-volume waste may include sand, silt, clay, cysts, and algae.	Disinfection required for viral inactivation.
Ultrafiltration	Basic: increases with pre/post-treatment and membrane cleaning needs.	Concentrated waste: 5 to 20 percent volume. Waste may include sand, silt, clays, cysts, algae, viruses, and humic material	Disinfection required for for viral inactivation.
Nanofiltration	Intermediate: increases with pre/post-treatment and membrane cleaning needs.	Concentrated waste: 5 to 20 percent volume.	Disinfection required under regulation, and recommended as a safety measure and residual protection.
Reverse Osmosis	Intermediate: increases with pre/post-treatment and membrane cleaning needs.	Briney waste. High volume, e.g., 25 to 50 percent. May be toxic to some species.	Bypassing of water (to provide blended/stabilized distributed water) cannot be practiced at risk of increasing microbial concentrations in finished water. Post-disinfection required under regulation, is recommended as a safety measure and for residual maintenance. Other post-treatments may include degassing of CO_2 or H_2S, and pH adjustment.

Source: U.S. Environmental Protection Agency, 1998.

continuing to provide a barrier between the feedwater and the permeate or product water. There are several different methods that can be employed to monitor membrane integrity, including:

- Turbidity monitoring,
- Particle counting or monitoring,
- Air pressure testing,
- Bubble point testing,
- Sonic wave sensing, and
- Biological monitoring.

WHERE CAN I FIND MORE INFORMATION?

(1) American Water Works Association and American Society of Civil Engineers. 1998. *Water Treatment Plant Design*. New York: McGraw-Hill.

(2) Bergman, A.R. and J.C. Lozier, 1993. Membrane Process Selection and the Use of Bench and Pilot Tests. *Membrane Technology Conference Proceedings*, Baltimore: American Water Works Association.

(3) Jacangelo, J.G., J-M. Laine, E.W. Cummings, A. Deutschmann, J. Mallevialle, M.R. Wiesner. 1994. *Evaluation of Ultrafiltration Membrane Pretreatment and Nanofiltration of Surface Waters*. Denver: American Water Works Association and AWWA Research Foundation.

(4) Jacangelo, J.G., S. Adham, J-M. Laine. 1997. *Membrane Filtration for Microbial Removal*. Denver: American Water Works Association Research Foundation and American Water Works Association.

(5) Mallevialle, J., P.E. Odendaal, and M.R. Wiesner, 1996. *Water Treatment Membrane Processes*. New York: McGraw-Hill.

(6) National Research Council. 1997. *Safe Water From Every Tap*. Washington, D.C.: National Academy Press.

(7) U.S. Environmental Protection Agency. 1990. *Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities*. Washington, D.C.: Office of Water. EPA/625/5-90/025.

(8) U.S. Environmental Protection Agency. 1989. *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Washington, D.C.: Office of Water. EPA/625/4-89/023.

(9) U.S. Environmental Protection Agency. 1998. *Small System Compliance Technology List for the Surface Water Treatment Rule and Total Coliform Rule*. Washington, D.C.: Office of Water. EPA/815/R/98/001.

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- Tech Brief: Disinfection, item #DWBLPE47;
- Tech Brief: Filtration, item #DWBLPE50;
- Tech Brief: Corrosion Control, item #DWBLPE52;
- Tech Brief: Ion Exchange and Demineralization, item #DWBLPE56;
- Tech Brief: Organics Removal, item #DWBLPE59;
- Tech Brief: Package Plants, item #DWBLPE63;
- Tech Brief: Water Treatment Plant Residuals Management, item #DWBLPE65;
- Tech Brief: Lime Softening, item #DWBLPE67;
- Tech Brief: Iron and Manganese Removal, item #DWBLPE70;
- Water Conservation Measures Fact Sheet, item #DWBLPE74; and
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For further information, comments about this fact sheet, or to suggest topics, call Lahlou at one of the above numbers or contact him via e-mail at mlahlou2@wvu.edu.

WATER METERS

Zane Satterfield
Vipin Bhardwaj
NDWC Engineering Scientist

Any viable business must be able to determine how much product it is making and selling and if that product is profitable. Water is a business. And, the best way for a water utility to measure or account for the water produced and then sold is by using water meters. This Tech Brief, discusses the different types of meters, their applications, and their importance for a water utility business.

WHY ARE METERS IMPORTANT?

Water meters are important to a utility for several reasons:

1. They make it possible to charge customers in proportion to the amount of water they use.
2. They allow the system to demonstrate accountability.
3. They are fair for all customers because they record specific usage.
4. They encourage customers to conserve water (especially as compared to flat rates).
5. They allow a utility system to monitor the volume of finished water it puts out.
6. They aid in the detection of leaks and waterline breaks in the distribution system.

A system without meters is like a taxi without a fare counter. Without a meter, it costs the same to drive around the block as it does from New York to Los Angeles.

TYPES OF METERS

Meters are classified into two basic types: positive displacement and velocity. Each of these meter types has variations, leading to the perception that there are several different kinds. Meters that feature both positive displacement and velocity are known as compound meters. The unit of measurement is usually in gallons but sometimes in cubic feet.

POSITIVE DISPLACEMENT METERS

In this type of meter, a known volume of liquid in a tiny compartment moves with the flow of water. Positive displacement flow meters operate by repeatedly filling and emptying these compartments. The flow rate is calculated based on the number of times these compartments are filled and emptied. The movement of a disc or piston drives an arrangement of gears that registers and records the volume of liquid exiting the meter. There are two types of positive displacement meters: nutating disc and piston.

Nutating disc meters have a round disc that is located inside a cylindrical chamber. The disc is mounted on a spindle. The disk nutates, or wobbles, as it passes a known volume of liquid through the cylindrical chamber. The rotating motion of the disk is then transmitted to the register that records the volume of water that went through the meter (see Fig. 1 below).

Piston meters have a piston that oscillates back and forth as water flows through the meter. A known volume of water is measured for each rotation, and the motion is transmitted to a register through an arrangement of magnetic drive and gear assembly.

Positive displacement meters are sensitive to low flow rates and have high accuracy over a wide range of flow rates. Positive displacement meters are used in homes, small businesses, hotels, and apartment complexes. They are available in sizes from 5/8” to two inches.

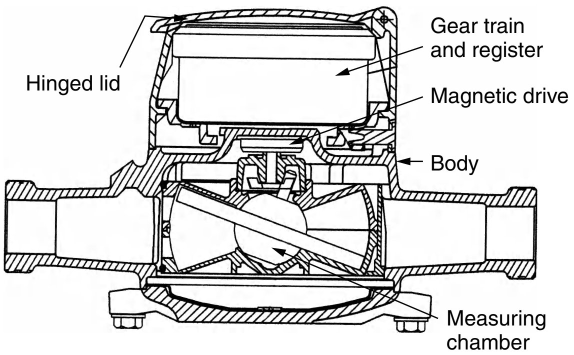


Figure 1. Nutating-disk meter with plastic housing. *Source*: AmericanWater Works Association. *Water Transmission and Distribution. Principles and Practices of Water Supply Operations*, 2nd Edition.

VELOCITY METERS

Velocity meters operate on the principle that water passing through a known cross-sectional area with a measured velocity can be equated into a volume of flow. Velocity meters are good for high flow applications.

Velocity meters come in different types, including turbine, multi-jet, propeller, ultrasonic, venture, and orifice meters. These meters are available in sizes of two inches and larger with the exception of multi-jet meters, which are between 5/8” and two inches.

Turbine meters have a rotating element that turns with the flow of water. Volume of water is measured by the number of revolutions by the rotor.

Venturi meters have a section that has a smaller diameter than the pipe on the upstream side. Based on a principle of hydraulics, as water flows through the pipe, its velocity is increased as it flows through a reduced cross-sectional area. Difference in pressure before water enters the smaller diameter section and at the smaller diameter “throat” is measured. The change in pressure is proportional to the square of velocity. Flow rate can be determined by measuring the difference in pressure. Venturi meters are suitable for large pipelines and do not require much maintenance.

Orifice meters work on the same principle as venturi meters, except that, instead of the decreasing cross-sectional area, there is a circular disk with a concentric hole. Flow rate is calculated similarly to the venturimeter by measuring the difference in pressures.

Ultrasonic meters send sound waves diagonally across the flow of water in the pipe. Changes in the velocity of water are converted electronically to change in flow rate.

Magnetic meters have an insulated section through which water flows. The flow of water induces an electrical current that is proportional to the velocity and hence the flow rate.

Propeller meters have a fan-shaped rotor that spins with the flow of water. A recorder is attached to the rotor to register the readings.

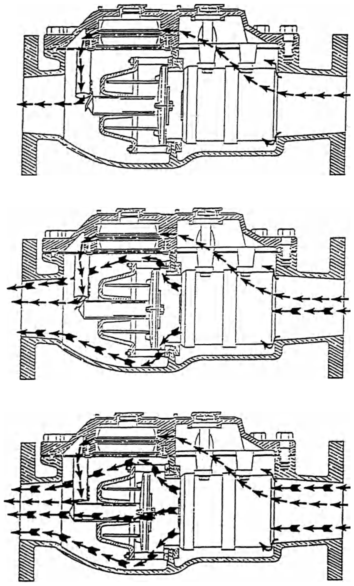
Multi-jet meters have tangential openings in a chamber to direct the water flow across a rotor with many vanes. Flow is measured proportional to the speed of the rotor.

COMPOUND METERS

In some cases, it is necessary to have a combination meter—both a positive displacement meter and velocity meter installed together—to be able to measure high and low flows. Low flows are measured through positive displacement while high flows are measured by velocity. A valve arrangement directs flows into each part of the meter (see Fig. 2).

METER INSTALLATION

Meters are installed either in outdoor meter pits (also known as meter wells) or inside the building served. Although it is common to have a meter installed in the basement, it is better to have the meter located at the curb or property line because of easy access for reading or maintenance. It is sometimes difficult to gain access to the



Low flow: All of the water passes through the nutating disk measuring element.

Crossover: As the control valve opens under higher flow rates, water passes through both measuring elements while the disk-side throttling begins.

Full flow: At high flow rates the control valve is fully open. The bulk of the water passes through the turbine measuring element, and the disk-side is throttled to a minimal amount.

Figure 2. Compound meter. *Source*: American Water Works Association, *Water Transmission and Distribution, Principles and Practices of Water Supply Operations*, 2nd Edition.

residence or building when no one is there. Nevertheless, it may be necessary due to extreme cold weather to have the meter located indoors to prevent frost damage. Large meters are usually installed in concrete or block vaults preferably out of traffic areas, but they also can be installed inside.

General guidelines for installing meters are:

- In outdoor meter pits, the face of the meter should be between 18 and 24 inches from the ground surface or top of the meter pit lid.
- Meter pits or wells should have six to 12 inches of gravel at the bottom to help with drainage.
- Large meter pits should have a drain or a sump pump if a drain is not possible. There should never be standing water in a meter pit or well.
- If at all possible, the meter pit or well should not be located in an area prone to flooding.
- The meter setting should have a shut-off valve on both sides of the meter (i.e., the customer's side and the water main side).
- If possible, the meter should be installed in a horizontal position.
- The meter should be easily accessible for service, inspection, and reading even if meter reading is via remote sensing equipment.
- Protect the meter from freezing.
- Always be mindful of public safety. Don't have the meter lid sticking up or have it too low so that it creates a hole.
- Install seals on the meter to reduce tampering and indicate when tampering does occur.

The following suggestions apply to larger meter vaults or pits:

- Large meter pits should also have a drain or a sump pump if a drain is not possible. There should never be standing water in a meter pit or well.
- To prevent disruption of service when replacing or repairing large meters, there should be a bypass that can also be metered. Having the bypass metered would be similar to a manifold set-up where you have two or more meters in parallel making service of one meter easy without service disruption or lost revenue.
- Large meter installations should have good structural support to prevent stress on the water line. Also there should be at least 10 times the pipe diameter of straight pipe before the meter and five times the pipe diameter of straight pipe after the meter.
- Some large meters recommend or require a strainer to be installed ahead of the meter.
- With large meters that are located in concrete vaults or pits, ideally, the meter face should be located over the hatchway to help with reading the meter, possibly reading the meter without even entering the pit. This will also help in lifting the meter from the pit. Remember, if the meter reader has to enter the meter vault or pit, this is considered a confined space entry and the proper safety procedures must be followed.

Small meter installation is easier with a meter yoke (also known as a meter setter). Meter yokes have different configurations and can have any combination of built-in check valves, regulators, and lockable shutoff valves. Utilities should have their own set specifications with illustrations depicting proper meter installations.

METER READING

There are two common types of water meter registers: circular and straight. Either of the meters can be manufactured to read in gallons or cubic feet. The circular register is somewhat more difficult to read.

The straight register is what is seen on newer meters and is read like a car's odometer. On some larger meters there will be a multiplier on the register face or the meter itself. The multiplier will be noted as 10X, 100X, or 1000X depending on the size of the meter. The multiplier indicates that the meter reader must multiply what is read by the number noted 10, 100, or 1,000. For example, if the register displays the number 975 and the multiplier is 10X, then the meter reading is 9750 gallons.

There are several different ways meter reading can be accomplished.

- Direct read is, as the name suggests, an individual directly reading the register.
- Remote reading is done through an electronic signal, usually with a wire to a separate station where the individual could either direct read or touch read.
- Touch read or plug-in readers use a handheld device that takes the electronic signal from plugging-in or touching the remote station and translates it into the number of gallons used. The remote station can even be on top of the meter pit lid. The readings are stored

on the hand-held device until the meter reader gets back to the office to be downloaded to a computer.

- A newer development is automatic meter reading, which enables the meter reader to drive down the street and obtain the readings from the meters usually through radio transmission.

SELECTING A METER

Meters are selected using several factors: flow rate, size of pipe, pressure loss and safety considerations, such as fire service regulations. For sizes of one inch and smaller and low flow rates, positive displacement types of meters are common. For residential uses, 5/8” or 3/4” meters are used.

For medium flows, such as in apartment buildings, businesses, and public buildings, positive displacement meters in sizes of 1”, 11/2”, or two inches are used. In sizes of two and three inches, either, displacement, multi-jet, or turbine types of meters can be used. In the three- to four-inch size range, the meter type depends on the average flow rate. If the flow rate is between five and 35 percent of maximum flow rate, the positive displacement type is better. If the flow rates are going to be 10 to 15 percent of the maximum capacity, a turbine type should be used. If close accuracy at low flows is important, but large flows also have to be measured, a compound meter is best.

For large flows, velocity meters are more appropriate. Turbine meters are suitable for large flows where minimum flow rate is above 10 to 20 percent of maximum rating. Turbine meters have low pressure loss at high flow rates. Propeller meters are suitable for large mainlines or for pump station discharge.

METER TESTING AND MAINTENANCE

For meters to be effective, they must accurately read the amount of water flowing through them. Proper testing and maintenance procedures should be in place to assure accuracy.

Master meters—meters at the treatment plant that measure the largest water volumes—are the highest priority in the meter testing and maintenance program. These meters determine how much water is produced or sold and should be tested once a year. (More often if large amounts of water are measured through the meter.)

Industrial and commercial meters are the second testing and maintenance priority in the system. “The most expensive water loss in the distribution system is associated with under registration of industrial and commercial water meters, rather than leaks,” says Jeff Bennett utility inspector with the West Virginia Public Service Commission. “Lost water sales are lost revenue at the retail rate. Lost water due to leaks is only the loss of the cost to produce the water.”

Bennett also points out, “a two-inch meter will, at a minimum, provide as much revenue as eight residential meters, while a six-inch meter will provide at least as much revenue as 50 residential meters. Since large meters provide considerably more revenue per meter, it only makes ‘cents’ to test them more frequently.”

Meters larger then two inches are usually tested in-place using a calibrated field test meter. To be able to field test a meter, there must be a tap and an isolation valve immediately downstream from the meter. This temporary connection can be made with a fire hose. Even new meters should be tested.

Master meters in water plants are, in some cases, difficult or impossible to test using a field test meter. In these situations, a draw-down test can be conducted, which involves comparing a known volume of water pumped out of a tank (clearwell) to the volume recorded on the meter being tested.

Although residential meters may be the final priority in the testing and maintenance program, in small systems, they may be the most important. The residential meters can be broken down to the ones that have high usage and the ones that don’t. It only makes sense to concentrate on residential meters that have high usage because of a big family or multiple occupants compared to residential meters that never reach the minimum bill because of single occupancy of an elderly person.

The majority of residential meters are the positive displacement type, which almost always slow down when they are worn or encrusted by minerals or debris. With residential meters, the testing program should either consist of periodic testing on a test bench or a complete change-out program.

Residential meters should be checked, cleaned, and calibrated every seven to 10 years or as indicated by your state primacy agency. If your system does not have a meter test bench, check with a neighboring system or shop around for a company that can do testing on a certified test bench.

Testing and maintenance of the meters depends on the quality and quantity of the water. If adverse conditions, such as high minerals or large flows are encountered, meters will require more frequent attention. Water that has high levels of minerals will affect the operation of a meter over time. This should be taken into account with a system’s preventive maintenance program by cleaning the meter to extend its life and to improve the accuracy of the meter.

Maintenance requirements will vary depending upon the material used in the meter components. Although plastic meters are less expensive, more maintenance and more frequent replacement may be necessary.

If your water system does not have any meters for residential connections, and you want to start metering it, a typical cost would be $280 for connection (house). The price breaks down as follows:

• Direct read 5/8” meter	**$40**
• Tandem meter setter (yoke) able to accept regulator	**$90**
• Pressure regulator (3/4” typical size)	**$40**
• Meter well (pit)	**$25**
• Meter frame and lid	**$35**
• Corporation-stop	**$15**
• 6” service saddle	**$35**
• Total for each connection	**$280**

If the system has 200 residential connections, the total material cost would be $56,000. With a meter life expectance of 15 years, it would take less than $1.50 per connection per month to recoup the cost.

If your system already has meters, but doesn't have a good maintenance program, here is an example of revenue lost due to a slow residential meter (assuming a 4,500 gallons per month rate at a cost of $25.00):

Loss with a meter 3 percent slow = $0.75 per month or $9.00 per year **for one meter**.

Loss with a meter 5 percent slow = $1.25 per month or $15.00 per year **for one meter**.

In some small systems, city buildings, golf courses, municipal swimming pools, and even the water plant are not charged. These connections should be metered to account for all treated water.

Keep in mind that if your system has a sewer utility, the loss is compounded, because most sewer utilities rely on water meters to bill for the sewer service. In these cases having an inaccurate water meter will have a direct impact on sewer revenue.

READING LIST

American Water Works Association. 1996. *Water Transmission and Distribution, Principles and Practices of Water Supply Operations*, 2nd Edn. AWWA, Denver.

American Water Works Association. 1986. *Water Meters—Selection, Installation, Testing, and Maintenance*, 3rd Edn. AWWA, Denver.

Bennett, Jeff. Unpublished. *"Water Metering" and "Meter Testing Programs."* White papers for the Public Service Commission of West Virginia.

MICROBIOLOGICAL CONCERNS OF DRINKING WATER DISTRIBUTION SYSTEMS

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Drinking water in a distribution system may contain microbes that enter the distribution system through treatment breakthrough, regrowth, or contamination of water in the system. The majority of these organisms are harmless. However, pathogenic organisms may also be present. A number of waterborne disease outbreaks related to distribution systems have been reported. Many factors contribute to the regrowth and contamination of drinking water in distribution systems. This article discusses the factors that contribute to microbial regrowth and contamination of distribution systems. To ensure protection of public health, these factors should be adequately addressed to safeguard drinking water from contamination in distribution systems.

INTRODUCTION

The purpose of a drinking water distribution system is to deliver water that is safe and acceptable in odor, taste, and appearance. Most drinking water utilities rely on the "multiple-barrier concept" as the guiding principle for providing safe water. Traditionally, the barriers have included (1) source water protection; (2) coagulation, flocculation, and sedimentation; (3) filtration; (4) disinfection; and (5) protection of water in the distribution system. These barriers are used to duplicate microbial removal capabilities by succeeding process steps so that sufficient backup systems are available to permit continuous operation in the face of normal mechanical failures. The distribution system is considered the final and one of the most important barriers in the multiple-barrier concept for providing safe drinking water.

After the treatment process, the microbiological quality of drinking water is at its highest; however, as the treated water travels through the distribution system, the microbiological quality of the water may deteriorate through three basic mechanisms: (1) breakthrough from treatment plants, (2) microbial growth/regrowth, and (3) contamination within the distribution system. This article discusses the microbiological concerns of drinking water distribution systems.

OUTBREAKS FROM DISTRIBUTION SYSTEM DEFICIENCIES

From 1971 to 1998, 619 drinking waterborne disease outbreaks were reported in the United States due to microbiological, chemical, or unknown etiology (1). Of the 619 waterborne disease outbreaks, 113 outbreaks and 21,058 reported cases of illness or 13 deaths were from distribution system contamination. Increasingly, concern has been raised regarding the adequacy of distribution system barriers. Distribution system deficiencies were associated with 30.3% of the community outbreaks (1). Lippy and Waltrip (2) reported that nearly 37% of the community outbreaks from 1946 to 1980 were due to failures of a distribution system. Craun and McCabe (3) reported that distribution system deficiencies accounted for most of the waterborne hepatitis outbreaks (10 out of 17 outbreaks) in public water systems from 1946 to 1970. Contamination of mains during construction or repair and cross-connections were cited as some of the primary causes of distribution deficiencies. In recent years, waterborne disease outbreaks due to distribution system deficiencies have had disastrous consequences. For example, an outbreak of hemorrhagic *Escherichia coli* serotype 0157:H7 occurred in Cabool, MO during December 1989 and January 1990 and resulted in 243 cases of diarrhea and 4 deaths (4). It was concluded that the illness was caused by contaminants that entered the distribution system through two major pipe breaks and 43 service meter failures that occurred during unusually cold weather.

ETIOLOGICAL AGENTS OF OUTBREAKS RELATED TO DRINKING WATER DISTRIBUTION SYSTEMS

Microbiological and chemical contaminants were associated with 75 and 38 outbreaks, respectively, for the 113 reported outbreaks caused by distribution system deficiencies from 1971 to 1998 (1). Of the outbreaks caused by microbial contaminants, bacteria were responsible for 21%, protozoa for 17%, viruses for 8%, and unknown etiological agents for 54% of outbreaks (Fig. 1). The bacterial agents identified were *Salmonella, E. coli* 0157:H7, *Shigella, Campylobacter, Salmonella typhimurium,* and *Vibrio cholerae*. The protozoan agents identified were *Giardia* and *Cyclospora*. Viruses identified were norovirus and hepatitis A.

MICROBIAL OCCURRENCE IN THE DISTRIBUTION SYSTEM

Drinking water in a distribution system may contain many microbes that enter the system through treatment breakthrough, regrowth, or contamination of water in the system. The majority of these organisms are harmless and not many have the potential to be pathogenic. However, pathogens may also pass into drinking water in a distribution system. Two types of pathogens may be present in the drinking water—primary pathogens (those that inhabit the gastrointestinal tract) and opportunistic pathogens (microorganisms that may exist as part of a normal body microflora but under certain conditions may cause disease in compromised hosts such as immunocompromised individuals). Primary pathogens include *Salmonella, E. coli* 0157, *Shigella, Yersinia, Campylobacter*, enteric viruses, and protozoan parasites such as *Giardia* and *Cryptosporidium*. These organisms may cause a variety of diseases including gastroenteritis, typhoid, paratyphoid fever, dysentery, cholera, hepatitis, paralysis, and meningitis.

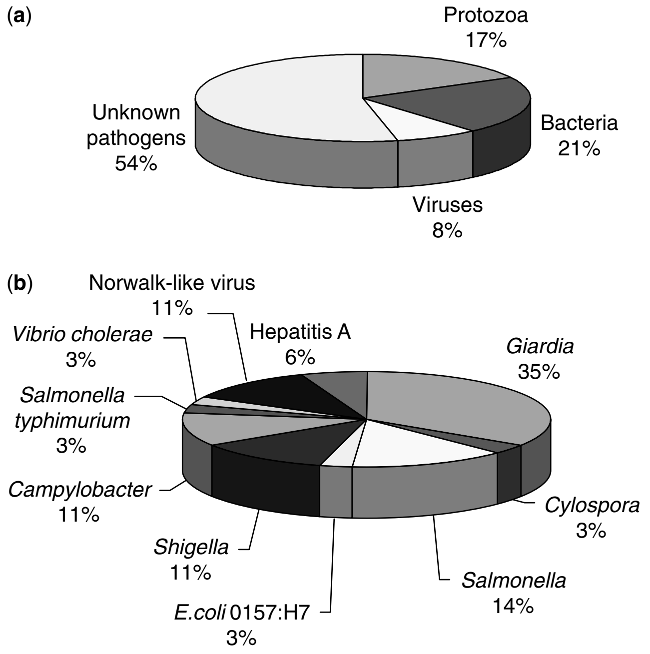

Figure 1. (**a**) Etiological agents for U.S. waterborne disease outbreaks caused by distribution system deficiencies from 1971–1998; (**b**) percent of outbreaks caused by the specific microbial etiology from 1971–1998. Data from Reference 1.

Opportunistic pathogens that may occur in a drinking water distribution system include *Klebsiella pneumoniae, Pseudomonas aeruginosa, Legionella pneumophila, Aeromonas hydrophila, Citrobacter spp., Enterobacter spp., Moraxella spp., Mycobacterium avium* complex, *Staphylococcus aureus*, fungi, and yeast (4,5). These organisms may cause diseases such as pneumonia, meningitis, septicemia, gastrointestinal illness, and respiratory tract infection.

Factors Contributing to Distribution System Contamination

Because of the expansive nature of a distribution system, that has many miles of pipe, storage tanks, and interconnections with industrial users, opportunities for contamination do exist. A list of possible sources of distribution system contamination is presented in Table 1. Cross-connections are recognized as a major risk to water quality, but their probability of occurrence is low due to vigilant cross-connection control programs. However, complete cross-connection control is difficult to achieve, and many systems face challenges in maintaining an effective cross-connection control program in the face of dwindling resources and personnel cutbacks.

Inadequate separation of water mains and sewers may contribute to distribution system contamination through broken or leaking water mains. Engineering standards call for a separation of 10 ft between drinking water and sewer pipelines, although separations can be as little as 18 inches if the pipelines are placed on different levels (6). In saturated soil, microbes can move several meters in short periods of time (7). This transport could be aided by water flowing out of the sewer line. Because it is not uncommon for water systems to lose more than 10% of total production through leaks in pipelines (8), opportunities exist for water to intrude through these portals.

Despite the best efforts to repair main breaks using good sanitary procedures, main breaks are an opportunity

Table 1. Sources of Distribution System Contamination

- Cross-connection
- Inadequate separation of water main and sewer
- Contamination of broken or leaking water main
- Contamination of mains during construction/repair
- Back-siphonage
- Contamination of distribution storage
- Intrusion of contaminants due to pressure transients

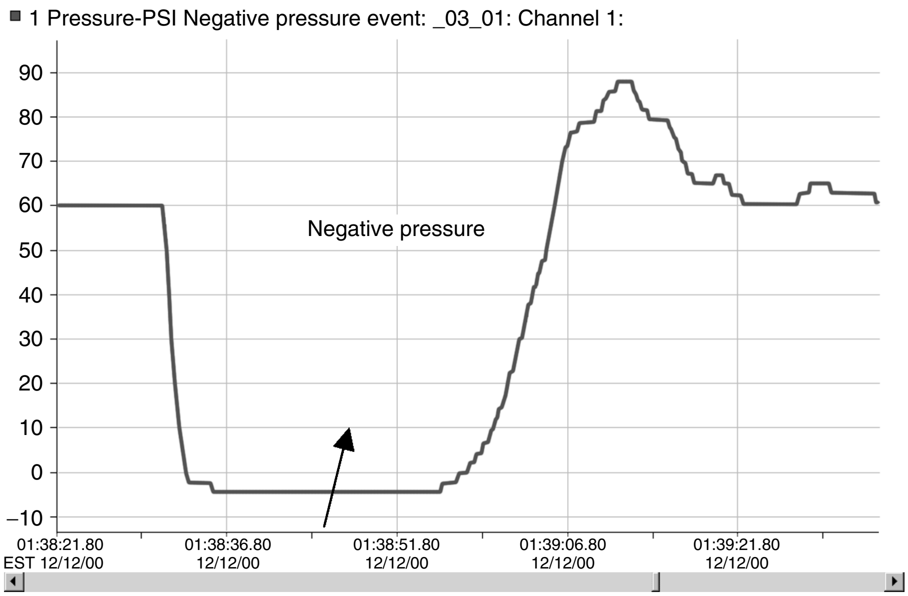

Figure 2. A negative pressure transient in a drinking water distribution system following a power outage. The negative pressure lasted approximately 22 seconds before static pressures were restored.

for contaminants to enter a distribution system. Utilities typically isolate the affected section, super chlorinate, and flush the repaired pipe. However, flushing velocities may not always be achievable to remove all contaminated debris, and microbiological tests to check the final water quality may not detect contaminating organisms. McFeters et al. (9) reported high levels of injured coliform bacteria, not detectable by standard coliform techniques, following the repair of a main break. Resampling at the site 1 week later showed high levels of the coliform bacteria, detectable only using m-T7 agar, a medium specially designed to recover chlorine-injured coliforms.

Installation of backflow devices to prevent the entry of contaminated water is an important distribution system barrier. Due to cost considerations, backflow devices are primarily installed on commercial service lines where the facility uses potentially hazardous substances (4). Examples of such facilities include hospitals, mortuaries, dry cleaners, and industrial users. It is not common that all service connections have backflow devices, so the possibility of back-siphonage exists at these points. In addition, installation of backflow devices for all service connections would make routine checking of the devices nearly impossible and without routine inspection, the proper functioning of the units cannot be determined. Even when backflow devices have been installed, contamination has occurred. The failure of a backflow check valve allowed water stored for fire protection to enter the Gideon, Missouri, distribution system (4). A broken vent in the storage tank allowed birds to enter and contaminate the water with *Salmonella*. Three people died due to *Salmonella* infection.

Pressure transients in drinking water pipelines are caused by an abrupt change in the velocity of water. These events are also termed “surges” or “water hammer.” These pressure transients are waves that have both positive and negative amplitude. They can draw transient negative pressures in a distribution system that last only for seconds and may not be observed by conventional pressure monitoring. Circumstances that produce these pressures waves may commonly occur in every water system. Because these waves travel through the distribution system, the transient negative pressure wave can momentarily draw water back into the pipe at any point where water is leaking out of the system. Depending on the size of the leaks, the volume of intrusion can range from one to hundreds of gallons (10,11). A negative pressure surge in a distribution system has been documented (12). A negative pressure surge wave was observed following a power outage that suddenly shut down a pumping station (Fig. 2). The rapid change in water velocity resulted in a negative pressure that lasted for approximately 22 seconds until static pressures were restored. Pressure transients can be caused by main breaks, sudden change in demand, uncontrolled pump starting or stopping, opening and closing of a fire hydrant, power failure, air valve slam, flushing operations, feed tank draining, and other conditions.

If pathogens are present at the exterior of the distribution pipelines, they may enter into the system due to hydraulic pressure gradients or during construction, repair, cross-connections, and conditions or activities where the system is open to the atmosphere or the environment. Karim et al. (12) reported the presence of microbial indicator and pathogens adjacent to distribution systems. Total coliform and fecal coliform bacteria were detected in water and soil samples adjacent to distribution systems in about half of the samples, indicating the presence of fecal contamination (Fig. 3). *Bacillus* was found in almost all the samples, which is not a surprise because it is a normal soil organism. Viruses were detected using culturable methods in 12% of the soil and water samples and by molecular methods in 19% of the soil samples and 47% of the water samples. When these data are combined, 56% of the samples were positive for viruses

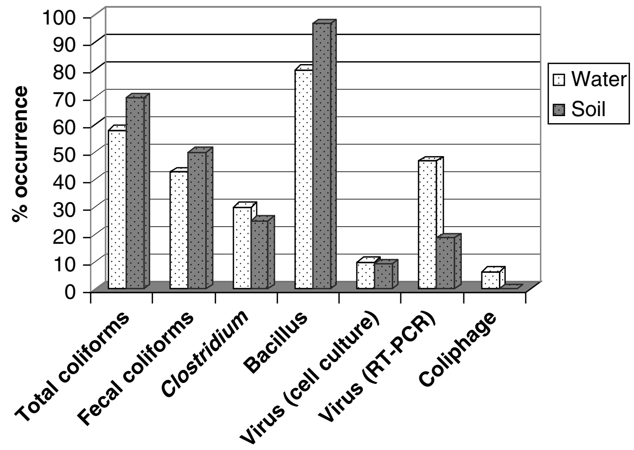

Figure 3. Occurrence of microorganisms in water and soil samples adjacent to distribution system pipelines.

either in the water or the soil. Sequence analysis showed that these viruses were predominantly enteroviruses (the vaccine strain of poliovirus), but Norwalk and hepatitis A viruses were also detected, providing clear evidence of human fecal contamination immediately exterior to the pipe. This data suggest that opportunities could exist for pathogens to intrude into the distribution system and emphasize the need to maintain an effective disinfectant residual in all parts of the distribution system (13).

MICROBIAL REGROWTH IN A DISTRIBUTION SYSTEM

Recent studies have examined data from more than 90 water systems to determine the factors that contribute to microbial growth in drinking water (14,15). These studies have shown that the occurrence of coliform bacteria can be related to the following factors: filtration, temperature, disinfectant type and residual, assimilable organic carbon (AOC) level, corrosion control, and pipe material selection.

Filtration

Four unfiltered surface water systems included in a study (14) accounted for 26.6% of the total number of bacterial samples collected but represented 64.3% (1013 of 1576) of the positive coliform samples. Although the results do not suggest that treatment was inadequate (e.g., coliforms were not related to breakthrough of treatment barriers), the data suggested that filtration may be an important factor in preventing coliform regrowth. Following the study, one of the systems installed filtration, and distribution system coliform levels were reduced by a factor of 3 during the following 18-month interval.

Temperature

Temperature is an important factor in microbial growth. On average, the occurrence of coliform bacteria was significantly higher when water temperatures were >15 °C. (14). However, the minimum temperature at which microbial activity was observed varied from system to system. Systems that typically experienced cold water had increases in coliform occurrences when water temperatures ranged near 10 °C. The strains of coliform bacteria in these systems may be better adapted to grow at lower temperatures (psychrophiles).

Disinfectant Residual and Disinfectant Level

Maintenance of a disinfectant residual throughout a distribution system is intended to produce conditions unfavorable for bacterial survival in drinking water. Choosing the appropriate disinfectant or improper application of disinfectant can affect bacterial growth conditions. For filtered systems, there was a difference between systems that maintained free chlorine residual and systems that used chloramines (14). For systems that used free chlorine, 0.97% of 33,196 samples contained coliform bacteria, whereas 0.51% of 35,159 samples from chloraminated systems contained coliform bacteria (statistically different at $p < .0001$). The average density of coliform bacteria was 35 times higher in free chlorinated systems compared to chloraminated water [0.60 colony forming units (cfu)/100 mL for free chlorinated water, compared to 0.017 cfu/100 mL for chloraminated water]. Previous research hypothesized that chloramines may be better able to penetrate into distribution system biofilms and inactivate attached bacteria (16,17).

In addition to the type of disinfectant used, the residual maintained at the end of the distribution system was also associated with coliform occurrences (14). Systems that maintained dead-end free chlorine levels <0.2 mg/L or monochloramine levels <0.5 mg/L had substantially more coliform occurrences than systems that maintained higher disinfectant residuals. However, systems that had high AOC levels needed to maintain high disinfectant residuals to control coliform occurrences. Therefore, maintenance of a disinfectant residual alone did not ensure that treated waters would be free of coliform bacteria.

AOC Level

The combined results from two surveys of AOC levels in North American drinking water systems are shown in (Fig. 4) (14,15). The levels (summarized as the geometric mean based on 12 to 36 samples) range from 20 to 214 μg/L. The results also indicate that the majority of the total AOC results from the growth of the test organism,

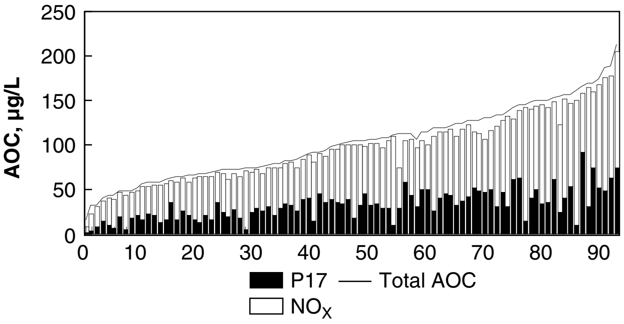

Figure 4. AOC levels in 94 North American water systems.

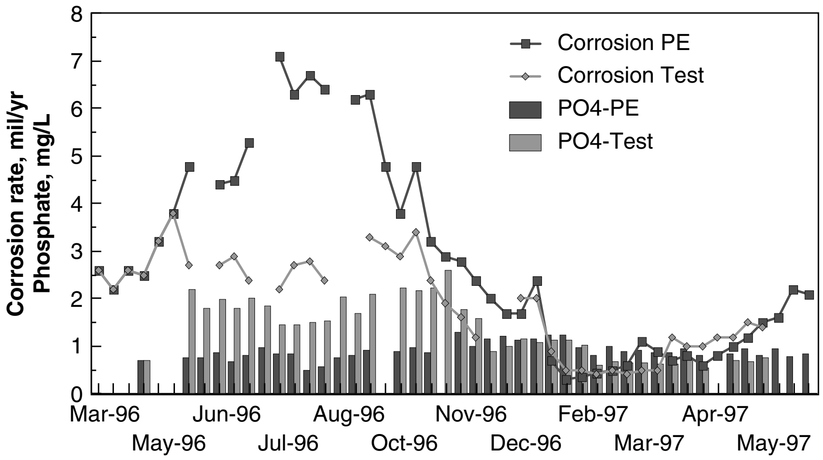

Figure 5. Increasing phosphate levels can reduce corrosion rates.

Spirillum sp., strain NOX. This $\mathrm{AOC_{NOX}}$ fraction is influenced by disinfection practices (chlorine, ozone, etc.) and suggests that changes in these practices (i.e., the type of disinfectant, the point of application, dose) can impact AOC levels in finished drinking water.

High levels of AOC can stimulate bacterial growth in distribution system biofilms. On average, free chlorinated systems with AOC levels greater than 100 μg/L had 82% more coliform positive samples, and the coliform densities were 19 times higher than in free chlorinated systems that had average AOC levels less than 99 μg/L. However, high levels of AOC alone do not dictate the occurrence of coliform bacteria in drinking water; they are only one factor.

Corrosion Control and Pipe Materials

Most systems do not measure corrosion rates on a daily basis, so this parameter is difficult to evaluate on a full scale. However, recent research has demonstrated that corrosion of iron pipes can influence the effectiveness of chlorine-based disinfectants in inactivating biofilm bacteria (17,18). Therefore, the choice of pipe material and the accumulation of corrosion products can dramatically impact the ability to control the effects of biofilms in drinking water systems.

Figure 5 shows the average monthly corrosion rates [in mils (thousandths of an inch) per year] in a system in Illinois. The conventional plant effluent corrosion rate showed marked seasonal variations. Corrosion rates were highest during the summer months when, traditionally, coliform occurrences the highest. Similar seasonal variations have been observed in other systems (19). This variation in rates of corrosion is important because the corrosion products react with residual chlorine and prevent the biocide from penetrating the biofilm and controlling bacterial growth. Studies have shown that free chlorine is impacted to a greater extent than monochloramine, although the effectiveness of both disinfectants is impaired if corrosion rates are not controlled (17,18). Increasing the phosphate-based corrosion inhibitor dose, especially during the summer months, can help reduce corrosion rates. In full-scale studies, systems that used a phosphate-based corrosion inhibitor had lower coliform levels than systems that did not control corrosion (14).

CONCLUSION

Drinking water in a distribution system may contain microbes that enter the distribution system through treatment breakthrough, regrowth, or contamination of water in the system. The majority of these organisms are harmless. However, pathogenic organisms may also be present in drinking water. A number of waterborne disease outbreaks related to distribution systems have been reported. Factors that may contribute to distribution system contamination include cross-connections, inadequate separation of water mains and sewers, contamination of broken or leaking water main, contamination of mains during construction/repair, back-siphonage, contamination of distribution storage, and intrusion of contaminants due to pressure transients. Factors that may contribute to regrowth include filtration, temperature, disinfectant type and residual, assimilable organic carbon (AOC) level, corrosion control, and pipe material selection. To ensure the protection of public health, these factors should be adequately addressed to safeguard drinking water from contamination in a distribution system.

BIBLIOGRAPHY

1. Craun, G. and Calderon, R. (2001). Waterborne disease outbreaks caused by distribution system deficiencies. *JAWWA* **93**(9): 64–75.
2. Lippy, E.C. and Waltrip, S.C. (1984). Waterborne disease outbreaks—1946–1980: A thirty-five year perspective. *JAWWA* **76**: 60–67.
3. Craun, G.F. and McCabe, L.J. (1973). Review of the causes of waterborne disease outbreaks. *JAWWA* **65**: 74–84.
4. Geldreich, E.E. (1996). *Microbial Quality of Water Supply in Distribution Systems*. Lewis, Boca Raton, FL.
5. Geldreich, E.E. (1990). Microbiological quality control in distribution systems. In: *Water Quality and Treatment*. F.W. Pontius (Ed.). American Water Works Association. McGraw-Hill, New York, Chap. 18.
6. *Recommended Standards for Water Works*. (1992). *Great Lakes Upper Mississippi River Board of State Public Health*

& Environmental Managers. Health Education Services, Albany, NY.

7. Abu-Ashour, J., Joy, D.M., Lee, H., Whiteley, H.R., and Zelin, S. (1994). Transport of microorganisms through soil. *Water Air Soil Pollut.* **75**: 141–158.
8. American Water Works Association and American Water Works Association Research Foundation. (1992). *Water Industry Database: Utility Profiles*. AWWA, Denver, CO.
9. McFeters, G.A., Kippen, J.F., and LeChevallier, M.W. (1986). Injured coliforms in drinking water. *Appl. Environ. Microbiol.* **51**: 1–5.
10. Funk, J.E., Van Vuuren, S.J., Wood, D.J., Lecherallier, M., and Freidman, M. (1999). Pathogen intrusion into water distribution system due to transients. *Proceedings of the 3rd ASME/JSME Joint Fluid Engineering Conference*, July 18–22 San Francisco, CA.
11. LeChevallier, M.W. (1999). The case for maintaining a disinfectant residual. *JAWWA* **91**(6): 86–94.
12. Karim, M.R., Abbaszadegan, M., and LeChevallier, M. (2003). Potential for pathogen intrusion during pressure transients. *JAWWA* **95**(5): 134–146.
13. LeChevallier, M.W., Gullick, R.W., and Karim, M.R. (in press). The potential for health risks from intrusion of contaminants into the distribution system from pressure transients. *J. Water Health.*
14. LeChevallier, M.W., Welch, N.J., and Smith, D.B. (1996). Full scale studies of factors related to coliform regrowth in drinking water. *Appl. Environ. Microbiol.* **62**(7): 2201–2211.
15. Volk, C., Welch, N., and LeChevallier, M. (1996). *Survey of Assimilable Organic Carbon and Coliform Regrowth in the American Water System*. American Water Works Service Company, Inc., Voorhees, NJ.
16. LeChevallier, M.W., Lowry, C.D., and Lee, R.G. (1990). Disinfecting biofilms in a model distribution system. *JAWWA* **82**(7): 87–99.
17. LeChevallier, M.W. (1991). Biocides and the current status of biofouling control in water systems. *Proc. Int. Workshop Ind. Biofouling Biocorrosion*. Springer-Verlag, Germany, pp. 113–132.
18. LeChevallier, M.W., Lowry, C.D., Lee, R.G., and Gibbon, D.L. (1993). Relationship between iron corrosion and disinfection of biofilm bacteria. *JAWWA* **85**(7): 111–123.
19. Norton, C.D. and LeChevallier, M.W. (1997). Chloramination: Its effect on distribution system water quality. *JAWWA* **89**(7): 66–77.

NITRIFICATION OF POTABLE WATER USING TRICKLING FILTERS

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INTRODUCTION

It is well established that nitrogen in the form of ammonia must be removed from wastewater before it is disposed of, as well as from potable water before it can be consumed. When ammonia is discharged to an aquatic environment, it leads to oxygen consumption (nitrogenous oxygen demand) that causes fish death. Furthermore, ammonia must be removed before water is disinfected with chlorine because ammonia reacts with chlorine and produces chloramines, which have been found to be carcinogenic (1,2).

Ammonia may be removed chemically or biologically. Nitrification, the key biological process for ammonia oxidation, is carried out by two different nitrifying bacteria (aerobic, autotrophs), *Nitrosomonas* and *Nitrobacter*. The overall reaction may be written as:

$$\mathrm{NH_4}^+ + 2\mathrm{O_2} \rightarrow \mathrm{NO_3}^- + \mathrm{H_2O} + 2\mathrm{H}^+ \tag{1}$$

According to this reaction, it takes 4.57 g of oxygen to oxidize 1 g of $\mathrm{NH4^+{-}N}$. The two bacterial groups are each responsible for a single step in the oxidation of ammonia to nitrate, according to the following reaction scheme:

Nitrosomonas:

$$\mathrm{NH_4}^+ + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{NO_2}^- + 2\mathrm{H}^+ + \mathrm{H_2O} \tag{2}$$

Nitrobacter:

$$\mathrm{NO_2}^- + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_3}^- \tag{3}$$

Nitrification is typically used for tertiary treatment of wastewater and for pretreatment of potable water. Nitrifying bacteria are characterized by low specific growth rates. Trickling filters provide a support medium for biofilm growth, thus allowing the possibility of maintaining nitrifying bacteria at high hydraulic loadings. Wastewater treatment using biofilms grown on support media was the first continuous flow bioprocess employed by sanitary engineers nearly a century ago. As the wastewater flows over the biological slime in a nitrifying trickling filter, ammonia as well as dissolved oxygen diffuse into the biofilm where they are metabolized by the bacteria. The essential processes are mass transport and bioconversion. Modern trickling filters often use plastic support media that attain better performance but at a substantially higher cost than filters based on rock. Nitrification of potable water is a relatively new process, and only limited information is available. Pozzuolana and Biolite filters have been used to nitrify potable water (3).

Trickling filter operation is based on the following principles: The organic material present in the wastewater is degraded by a population of microorganisms attached to the filter medium (Fig. 1). Organic material from the liquid is adsorbed onto the biological film or slime layer. In the outer portions of the biological slime layer (0.1 to 0.2 mm), the organic material is degraded by aerobic microorganisms. As the microorganisms grow, the thickness of the slime layer increases, and the diffused oxygen is consumed before it can penetrate the full depth of the slime layer. Thus, an anaerobic environment is established near the surface of the medium. As the slime layer increases in thickness, the adsorbed organic matter is metabolized before it can reach the microorganisms near the medium face. As a result of having no external organic source available for cell carbon, the microorganisms near the medium face enter into an endogenous phase of growth and lose their ability to cling to the medium surface. The liquid then washes the slime off the medium, and a new slime layer starts to grow (Fig. 1). This phenomenon of losing the slime layer is called "sloughing" and is primarily a function of the organic and hydraulic loading on the filter. In modern trickling filters, the hydraulic loading rate is adjusted to maintain a slime layer of uniform thickness (4).

THE EFFECT OF SUPPORT MATERIAL ON NITRIFYING TRICKLING FILTERS FOR POTABLE WATER TREATMENT

The advantages of trickling filters include low maintenance, inexpensive installation, and great tolerance of variations in hydraulic and organic loads. As mentioned earlier, the bacteria responsible for oxidizing ammonia to nitrate are autotrophic organisms that have very slow specific growth rates. Thus, their stabilization on a support material and the development of biofilm structures enables the permanent existence of these organisms in the filter and the possibility of maintaining nitrifying bacteria at high hydraulic loadings. The filter medium is of such great importance for the function of biofilters that several experiments have been carried out to study and compare different filter media types (5,6). The support materials used in trickling filters are either granulated or fixed media. Granulated media are small separate elements (rock, gravel, sand, and plastic elements); fixed media consist of larger constructions with connected areas. Several factors are important in the function of trickling filters, but the most important is selection of the appropriate filter medium. Among the selection criteria for filter media in trickling filters are void ratio, specific surface area, homogeneous water flow, and cost.

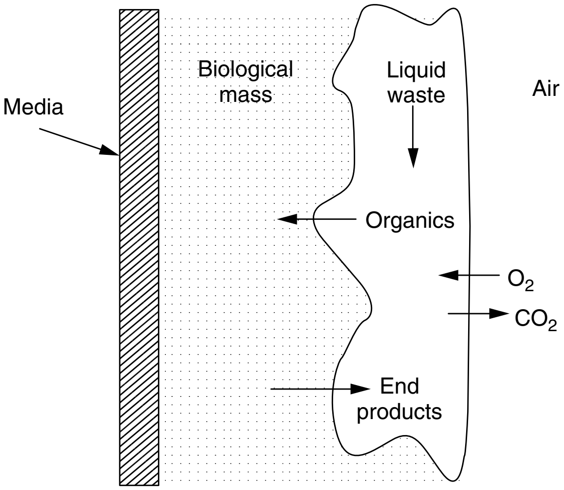

Figure 1. Schematic of the cross section of a biofilm in a trickling filter.

The use of plastic filter media drastically increases the installation cost of a nitrifying trickling filter. Plastic filter media are specially designed to provide high void space and high specific surface area. Thus, they are very attractive for wastewater treatment, where the high organic and ammonia load and the presence of suspended solids leads to the formation of very thick biofilm structures (150–2000 μm) (7, 8). To reduce the cost of the process in this case, we can use large diameter gravel instead of plastic media, resulting in low specific surface area and consequently huge constructions.

For potable water, the ammonia load is rather low (usually 0.5–2 mg/L) almost without any organic load and with a very low concentration of suspended solids. As a result, the biofilm remains very thin (50–200 μm) (9), and the use of small gravel becomes feasible thus resulting in higher specific surface areas and very compact constructions; the use of small gravel enables more area for biofilm growth per volume unit in a trickling filter. Hence, the use of small-sized gravel is very attractive due to the minimal cost of this material and its availability. On the other hand, small-sized gravel leads to small void ratios and all the problems mentioned before.

Quartz sand was the first material used for filtration and is still the basic material in many existing filters. Sand may be combined with anthracite, garnet, and schists of varying porosity, provided that these materials have low friability and low loss in acid (3). Gravels consist mainly of calcitic and silicic salts. For trickling filters, and sand filters, the use of silicic materials is the most common.

INFLUENCE OF RECIRCULATION ON THE EFFICIENCY OF A NITRIFYING TRICKLING FILTER FOR POTABLE WATER TREATMENT

Recirculation in biological filter process is usually considered to reduce nutrient loading on the filter, increase the wettability of the filter, and result in a more even bioconversion along the filter depth. Vayenas and Lyberatos (10) studied the influence of recirculation on the efficiency of a pilot-scale nitrifying trickling filter for potable water treatment. This filter exhibited excellent performance for the ammonia concentrations usually encountered in potable water even for high values of hydraulic loading (9). The pilot-scale filter has, of course, limitations on ammonia and hydraulic loading. For high hydraulic loading (680 m^3/m^2 d), the filter floods; for high ammonia concentration (above 5 mg/L), pore clogging due to bacterial mass becomes a serious problem and the filter requires frequent backwashing.

Experimental results and model predictions showed that for low hydraulic loading (110 m^3/m^2 d), recirculation leads to lower filter efficiency even for high inlet ammonia concentrations. For intermediate hydraulic loading (225 m^3/m^2 d) and for low inlet ammonia concentrations (2 mg/L), recirculation leads to inferior performance, whereas for high inlet ammonia concentration (15 mg/L), the filter performance is improved and the recycle ratio increases. Finally, for high hydraulic loading (450 m^3/m^2 d), recirculation improves the filter efficiency for any values of ammonia concentration and recycle ratio. The higher the recycle ratio, the better the filter performance.

These results are expected because essentially complete conversion is obtained for low loadings. Recirculation evens out ammonia concentrations along the filter depth and leads to higher effluent concentrations. For high loadings, lower overall conversions are expected in the absence of recirculation. In these instances, recirculation leads to better exploitation of the total filter depth. In conclusion, recirculation can improve the efficiency of the filter only for high or intermediate values of hydraulic loading and high ammonia concentrations.

IRON AND MANGANESE INHIBITION OF BIOLOGICAL AMMONIA REMOVAL FROM POTABLE WATER

Water sources that contain ammonia often may also contain iron and manganese. Ammonia, iron, and manganese may be removed chemically or biologically from a water supply. Biological removal of these pollutants is preferable because there is no need to add extra chemicals and the volume of the sludge generated is appreciably smaller and hence easier to handle (3). The simultaneous biological removal of the three elements is very difficult mainly due to the different redox potential values needed to oxidize them. Gouzinis et al. (11) studied the simultaneous removal of ammonia, iron, and manganese from potable water using a pilot-scale trickling filter and the influences these pollutants have on filter performance and efficiency. They concluded that iron has a strong negative effect on ammonia removal whereas ammonia has very low impact on iron removal. They also concluded that for low ammonia concentrations (1 mg/L), the presence of manganese does affect ammonia removal. The influence of manganese becomes sensible at an ammonia concentration of 2 mg/L; at higher ammonia concentrations, manganese strongly affects ammonia removal. The main conclusion of that work was that iron should be removed before ammonia and manganese oxidation. For low iron concentrations, oxidation by extended aeration can reduce iron, and subsequent biological ammonia and manganese removal can be carried out without any problems. For higher iron concentrations, an initial biological iron oxidation stage should be necessary.

MODELING AND DESIGN OF NITRIFYING TRICKLING FILTERS FOR POTABLE WATER TREATMENT

The design of trickling filters is much more difficult than design for homogeneous processes (e.g., activated sludge process) because design engineers must take extra care with respect to the attachment of microorganisms to the surface of the filter medium, the filter medium's influence on the process, nutrient and oxygen transport from the air and the liquid phase through the biofilm structure, biomass detachment, pore clogging and filter flooding, and filter backwash.

The design of biological trickling filters was initially based on empirical or semiempirical models. For many years, design engineers had limited success in applying fairly simple design equations to modeling trickling filter performance. The first approaches were based on NRC equations (12), Eckenfelder's equation (13), or Atkinson's model (14). Later, detailed mathematical steady-state models for describing the biofilm processes were proposed by Vaughan and Holder (15), Benefield and Molz (16), Logan et al. (17) and Gujer and Boller (18). These models were more accurate and offered a better understanding of the mechanisms of biofilm development, but there was still uncertainty in the model parameter values.

Vayenas and Lyberatos (9) developed a simple steady-state model for ammonia removal from potable water that predicts the ammonia concentration profile and the mean biofilm thickness profile along the filter depth. The model considers that the filter may be divided into a number of equal size compartments, for each of which homogeneous conditions may be assumed. The model also considers a somewhat different mechanism for biofilm development because ammonia concentrations in potable water are usually low and sloughing is not so intense as in wastewater treatment. It is worth noting that the model includes analytical recursive equations concerning ammonia concentration and predicts filter performance very well for all operating conditions that were tested. Figure 2 presents a typical ammonia concentration profile along the filter depth and the corresponding model predictions.

The dynamics of nitrifying trickling filters can be divided into fast and slow modes. Slow modes are caused by the growth and decay of the organisms

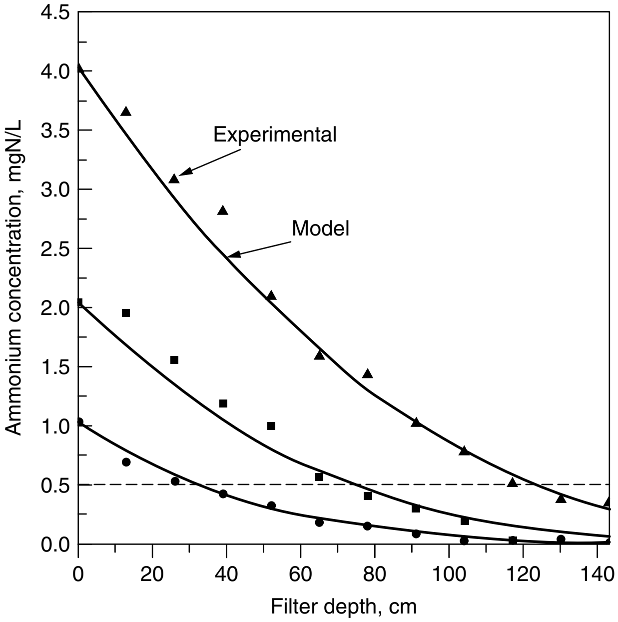

Figure 2. Experimental data and model predictions based on the model of Vayenas and Lyberatos (9) for an ammonia concentration profile in a pilot-scale nitrifying trickling filter for potable water treatment (hydraulic loading 225 m^3/m^2 d) (19).

in the biofilm; fast modes are caused mainly by the hydraulics and mass transfer resistances in the biofilm (20,21). The fast dynamics of nitrifying trickling filters for tertiary wastewater has been described by Kissel et al. (22), Wanner and Gujer (23), and Wik (20,21), and experimental evidence has been presented by Wik (20,21).

Vayenas et al. (24) developed a dynamic model to describe nitritification and nitratification in trickling filters. Their results showed that after an organic or hydraulic loading shock, nitrifying trickling filters reach a new steady state for ammonia-, nitrite-, and nitrate nitrogen concentrations in only a few minutes, whereas biofilm thickness requires a very long time to reach steady state (Fig. 3).

Additionally, Vayenas et al. (24) predicted the biofilm thickness and concentration profiles of ammonia, nitrite, and nitrate inside the biofilm structure (Fig. 4).

Recently, Tekerlekopoulou and Vayenas (25), using the steady-state version of the dynamic model of Vayenas et al. (24), constructed the operating diagram of a nitrifying trickling filter, thus defining the operating conditions for complete and safe nitrification (Fig. 5).

Figure 5 contains the three critical lines of 0.5, 0.1, and 10 mg/L for ammonia-, nitrite-, and nitrate-nitrogen (26). The diagram in (Fig. 5) is the operating diagram of the system and shows the effect of inlet ammonia concentration and hydraulic load on ammonia-, nitrite- and nitrate-nitrogen concentrations. The operating diagram is particularly useful when one wants to compare experimental observations made in a bioreactor with the predictions of a mathematical model describing the system. In the various regions of the operating diagram, different behaviors of the system are observed. In the diagram shown in (Fig. 5), there are six regions in each of which one or more of the ammonia-, nitrite-, and nitrate-nitrogen concentrations is below the maximum permitted limit, as shown below:

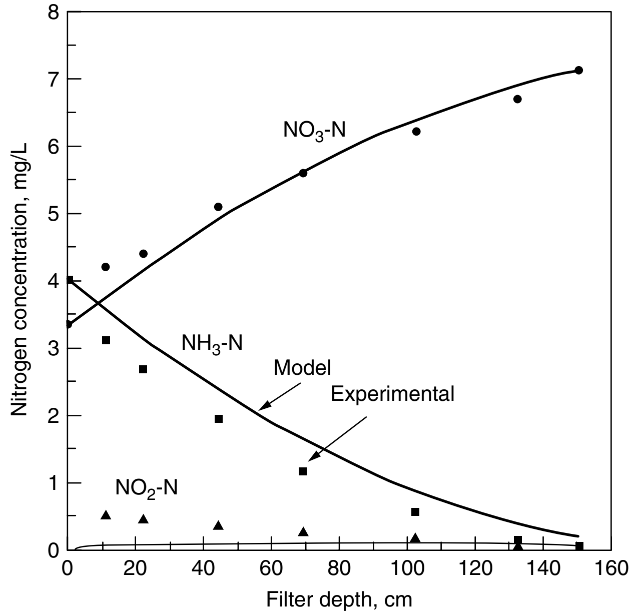

Figure 3. Predicted and experimental concentration profiles of ammonia-, nitrite- and nitrate-nitrogen (hydraulic loading: 225 m^3/m^2 d; feed concentrations: $NH_3 - N = 4$ mg/L, $NO_2 - N = 0$ mg/L, and $NO_3 - N = 3.36$ mg/L) (24).

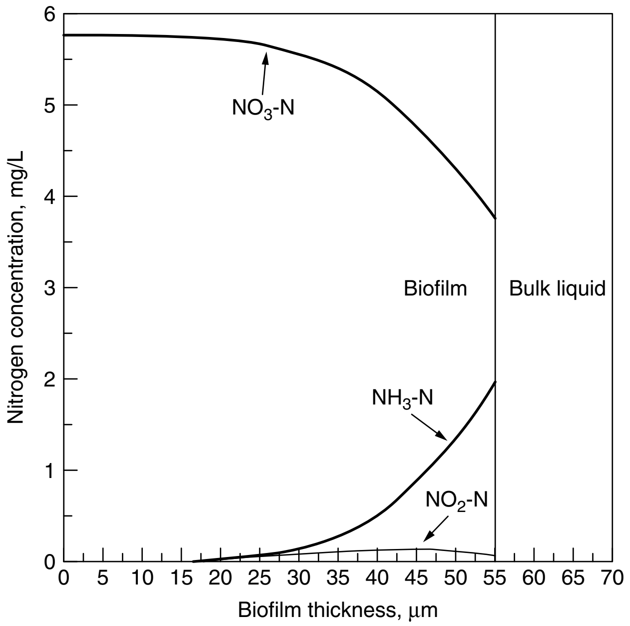

Figure 4. Ammonia-, nitrite-, and nitrate nitrogen concentration profiles along the biofilm thickness near the top of the filter (hydraulic loading: 225 m^3/m^2 d: feed concentrations: $NH_3 - N = 3$ mg/L, $NO_2 - N = 0$ mg/L, and $NO_3 - N = 3.36$ mg/L) (24).

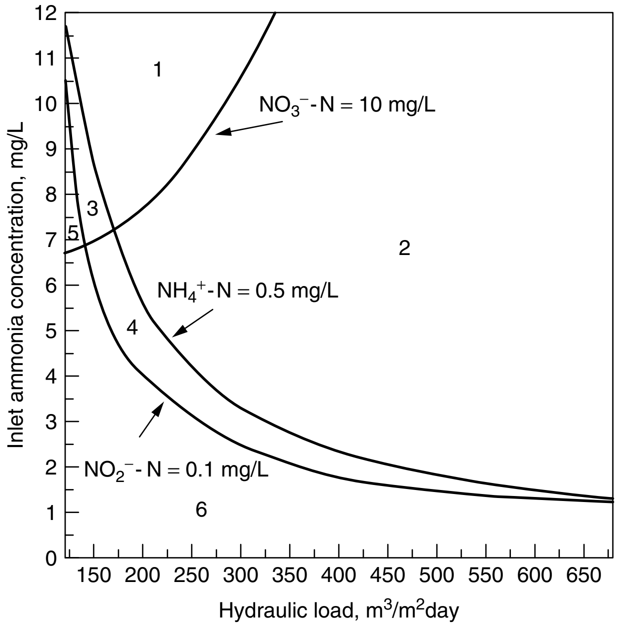

Figure 5. Operating diagram of a pilot-scale nitrifying trickling filter (25).

Region 1. All outlet concentrations are above the maximum permitted limits
Region 2. Outlet NO^{-}_{3}-N concentration below the maximum permitted limit
Region 3. Outlet NH^{+}_{4}-N concentration below the maximum permitted limit
Region 4. Outlet NH^{+}_{4}-N and NO^{-}_{3}-N below the maximum permitted limits
Region 5. Outlet NH^{+}_{4}-N and NO^{-}_{2}-N below the maximum permitted limits
Region 6. All outlet concentrations are below the maximum permitted limits

According to (Fig. 5), to achieve complete nitrification, one should combine the operating conditions so that the system would always remain in Region 6. The operating diagram of the system provides an overview of the process limitations where the areas of safe/complete nitrification operation are defined. According to the operating diagram, complete nitrification at low flow rates can be achieved even for ammonia feed concentrations up to about 6.5 mg/L, whereas at high flow rates, complete nitrification is possible only for ammonia feed concentrations up to about 2 mg/L.

BIBLIOGRAPHY

1. Duddles, A.G., Richardson, E.S., and Barth, I.E. (1974). Plastic medium trickling filters for biological nitrogen control. *J. Water Pollut. Control Fed.* **46**: 937–946.
2. Bull, R.J., Gerba, C., and Trussel, R.R. (1990). Evaluation of the health risks associated with disinfection. *Crit. Rev. Environ. Control* **20**: 77–114.
3. Degremont (1991). *Water Treatment Handbook*, 6th Edn. Lavoisier, Paris.
4. Metcalf and Eddy. (1991). *Wastewater Engineering, Treatment, Disposal, Reuse*, 3rd Edn. McGraw-Hill, New York, pp. 404–406.
5. Krüner, G. and Rosenthal, H. (1983). Efficiency of nitrification in trickling filters using different substrates. *Aquaculture Eng.* **2**: 49–67.
6. Lekang, O. and Kleppe, H. (2000). Efficiency of nitrification in trickling filters using different filter media. *Aquaculture Eng.* **21**: 181–199.
7. Gullicks, H.A. and Cleasby, J.L. (1986). Design of trickling filter nitrification towers. *J. Water Pollut. Control Fed.* **58**(1): 60–67.
8. Hao, O.J., et al. (1991). Biological fixed-film systems. *Res. J. Water Pollut. Control Fed.* **63**(4): 388–394.
9. Vayenas, D.V. and Lyberatos, G. (1994). A novel model for nitrifying trickling filters. *Water Res.* **28**(6): 1275–1284.
10. Vayenas, D.V. and Lyberatos, G. (1995). On the design of nitrifying trickling filters for potable water treatment. *Water Res.* **29**(4): 1079–1084.
11. Gouzinis, A., Kosmidis, N., Vayenas, D.V., and Lyberatos, G. (1998). Removal of Mn and simultaneous removal of NH_3, Fe and Mn from potable water using a trickling filter. *Water Res.* **32**(8): 2442–2450.
12. National Research Council. (1946). Sewage treatment at military installations. Report of the subcommittee on sanitary engineering. *Sewage Works J.* **18**(5): 787.
13. Eckenfelder, W.W. (1963). Trickling filtration design and performance. *Trans. Am. Soc. Civ. Eng.* **128**: 394–398.
14. Atkinson, B., Davies, I.J., and How, S.Y. (1974). The overall rate of substrate uptake by microbial films, parts I and II. *Trans. Inst. Chem. Eng.* **52**: 248–260.
15. Vaughan, G.M. and Holder, G.A. (1984). Substrate removal in the trickling filter process. *J. Water Pollution Control Fed.* **56**: 417–423.
16. Logan, E.B., Hermanowich, W.S., and Parker, S.D. (1987). A fundamental model for trickling filter process design. *J. Water Pollut. Control Fed.* **59**: 1029–1042.
17. Benefield, L. and Molz, F. (1984). Mathematical simulation of a biofilm process. *Biotechnol. Bioeng.* **27**: 921–931.
18. Gujer, W. and Boller, M. (1986). Design of a nitrifying tertiary trickling filter based on theoretical concepts. *Water Res.* **20**(11): 1353–1362.
19. Tekerlekopoulou, A.G., Dermou, E., and Vayenas, D.V. (2004). *The effect of support material and ammonia shock load on nitrifying trickling filters performance for potable water treatment* (submitted).
20. Wik, T. (1999). Adsorption and denitrification in nitrifying trickling filters. *Water Res.* **33**(6): 1500–1508.
21. Wik, T. (1999). Rational transfer function models for nitrifying trickling filters. *Water Sci. Technol.* **39**(4): 121–128.
22. Kissel, J.C., McCarty, P.L., and Street, R.L. (1984). Numerical simulation of mixed culture biofilm. *J. Environ. Eng.* **110**(2): 393–411.
23. Wanner, O. and Gujer, W. (1986). A multispecies biofilm model. *Biotechnol. Bioeng.* **28**: 314–328.
24. Vayenas, D.V., Pavlou, S., and Lyberatos, G. (1997). Development of a dynamic model describing nitrification and nitratification in trickling filters. *Water Res.* **31**(5): 1135–1147.
25. Tekerlekopoulou, A.G. and Vayenas, D.V. (2003). Operational and design considerations of a trickling filter for ammonia removal from potable water. *Environ. Modelling Assessment* **8**(2): 55–62.
26. *EEC-Official Journal of the European Communities*, No 80/779, August 30, 1980.

ORGANIC REMOVAL

National Drinking Water
Clearinghouse

Some small drinking water systems face contamination of raw water by natural or synthetic organic chemicals (SOCs). Natural organic materials might be present in water supplies, especially from surface water sources. Dissolved organics may cause taste, odor, or color problems in a community's drinking water, resulting in consumer complaints. Sources of SOCs include leaking underground gasoline/storage tanks, agricultural runoff containing herbicides or pesticides, solid waste or hazardous waste landfills, and improperly disposed chemical waste. The technologies most suitable for organic contaminant removal in drinking water systems are granular activated carbon (GAC) and aeration.

GAC has been designated by the U.S. Environmental Protection Agency (EPA) as the best available technology (BAT) for synthetic organic chemical removal. Various kinds of GAC are available for removing organics from drinking water. The most frequently used carbon in U.S. treatment plants is coal-based carbon because of its hardness, adsorption capacity, and availability. Some peat and lignite carbons have been used also.

Aeration systems that might be suitable for small drinking water systems include packed column aeration, diffused aeration, and multiple-tray aeration. Recent technologies that use aeration for organics removal include mechanical aeration, catenary grid, and Higee aeration.

Table 1 presents operational conditions for the organics treatment technologies most suitable for small systems.

Table 1. Organic Treatment Technologies Suitable for Small Systems

Technology	Level of Operational Skill Required	Level of Maintenance Required	Energy Requirements
Granular Activated Carbon (GAC)	Medium	Low	Low
Packed Column Aeration (PCA)	Low	Low	Varies
Diffused Aeration	Low	Low	Varies
Multiple-Tray Aeration	Low	Low	Low
Mechanical Aeration	Low	Low	Low
Catenary Grid	Low	Low	High
Higee Aeration	Low	Medium	High

Source: U.S. Environmental Protection Agency, 1989.

SOME TECHNOLOGIES FOR ORGANIC REMOVAL IN SMALL SYSTEMS:

A. Activated Carbon

Description. Activated carbon is carbon that has been exposed to very high temperatures, creating a vast network of internal pores.

Two types of activated carbon, granular and powdered, have been used widely in drinking water treatment. Powdered activated carbon (PAC), which is most often used for taste and odor control, is added directly to the raw water and removed by settling in sedimentation basins.

GAC removes many organic contaminants as well as taste and odor from water supplies.

Performance/Advantages. Organics that are readily adsorbed by activated carbon include:

- aromatic solvents (benzene, toluene, nitrobenzenes);
- chlorinated aromatics (PCBs, chlorobenzenes, chloroaphthalene);
- phenol and chlorophenols;
- polynuclear aromatics (acenaphthene, benzopyrenes);
- pesticides and herbicides (DDT, aldrin, chlordane, heptachlor);
- chlorinated aliphatics (carbon tetrachloride, chloroalkyl ethers); and
- high molecular weight hydrocarbons (dyes, gasoline, amines, humics).

Limitations. Organics that are poorly adsorbed by activated carbon include:

- alcohols;
- low molecular weight ketones, acids, and aldehydes;
- sugars and starches;
- very high molecular weight or colloidal organics; and
- low molecular weight aliphatics.

GAC is not effective in removing vinyl chloride from water. In addition, because of the long empty bed contact time (EBCT) required, radon removal at the treatment plant scale is not feasible. However, at the residential scale, GAC systems are cost-effective for radon removal.

Several operational and maintenance factors affect the performance of GAC. Contaminants in the water can occupy GAC adsorption sites, whether they are targeted for removal or not. Also, adsorbed contaminants can be replaced by other contaminants with which GAC has a greater affinity. Therefore, the presence of other contaminants might interfere with the removal of the contaminants of concern.

A significant drop in the contaminant level in influent water will cause a GAC filter to desorb, or slough off, adsorbed contaminants because GAC is an equilibrium process. As a result, raw water with frequently changing contaminant levels can result in treated water of unpredictable quality.

Bacterial growth on the carbon is another potential problem. Excessive bacterial growth may cause clogging and higher bacterial counts in the treated water. Bacterial levels in the treated water must be closely monitored, and the final disinfection process must be carefully controlled.

Process. Activated carbon removes contaminants through adsorption, primarily a physical process in which dissolved contaminants adhere to the porous surface of the carbon particles. The adsorption process can be reversed relatively easily. The ease of reversing adsorption is another key factor in activated carbon's usefulness because it facilitates the recycling or reuse of the carbon.

GAC can be used as a replacement for existing media (such as sand) in a conventional filter, or it can be used in a separate contactor (a vertical steel pressure vessel used to hold the activated carbon bed).

GAC contactors require monitoring to ensure that they work effectively. A GAC monitoring system should include:

- laboratory analysis of treated water to ensure that the system is removing organic contaminants,
- monitoring of headloss (the amount of energy used by water in moving from one point to another) through the contactors to ensure that backflushing (reversing

the flow to remove trapped material) is performed at appropriate times,

- bacteria monitoring of the contactor's effluent (since bacteria can grow rapidly within the activated carbon bed),
- turbidity monitoring of the contactor's effluent (to determine if suspended material is passing through GAC bed).

After a period of months or years, depending on the concentration of contaminants, the surface of the pores in the GAC can no longer adsorb contaminants. The carbon must then be replaced. The GAC vendor will be able to provide guidance concerning when to replace the GAC. Disposing of carbon with contaminants that are classified as hazardous wastes will dramatically increase disposal costs.

Equipment/Design. The typical GAC unit can be similar in design to either gravity or pressure filters. In some communities, the sand in existing filters has been either partially or completely replaced with GAC. Media depth of up to 10 feet is needed to ensure adequate removal of potentially harmful organic contaminants. Activated carbon filters can be designed to treat hydraulic loadings of 2 to 10 gallons per minute per square foot (gpm/ft^2). Sufficient detention time in the filter must be provided to achieve the desired level of the organic contaminant removal. The detention time is determined by the volume of the GAC filter divided by the flow rate. This is referred to as the EBCT since the volume of carbon in the bed is not considered. For adequate removal of most organic contaminants to occur, the EBCT should be about 10 minutes. EBCTs less than 7.5 minutes are generally ineffective.

GAC is available in different grades of effectiveness. Low-cost carbon requires a lower initial capital outlay but must be replaced more often, resulting in higher operating costs.

B. Aeration

Description. Aeration, also known as air stripping, mixes air with water to volatilize contaminants (turn them to vapor). The volatilized contaminants are either released directly to the atmosphere or treated and released. Aeration is used to remove volatile organic chemicals and can also remove radon.

Equipment. A small system might be able to use a simple aerator constructed from relatively common materials instead of a specially designed aerator system. Examples of simple aerators include:

- a system that cascades the water or passes it through a slotted container,
- a system that runs water over a corrugated surface, or
- an airlift pump that introduces oxygen as water is drawn from a well.

Other Aeration Types

Packed Column Aeration. Packed column aeration (PCA) or packed tower aeration (PTA) is a waterfall aeration process that drops water over a medium within a tower to mix the water with air. The medium is designed to break the water into tiny droplets and to maximize its contact with tiny air bubbles for removal of the contaminant. Air is also blown in from underneath the medium to enhance this process (see Fig. 1).

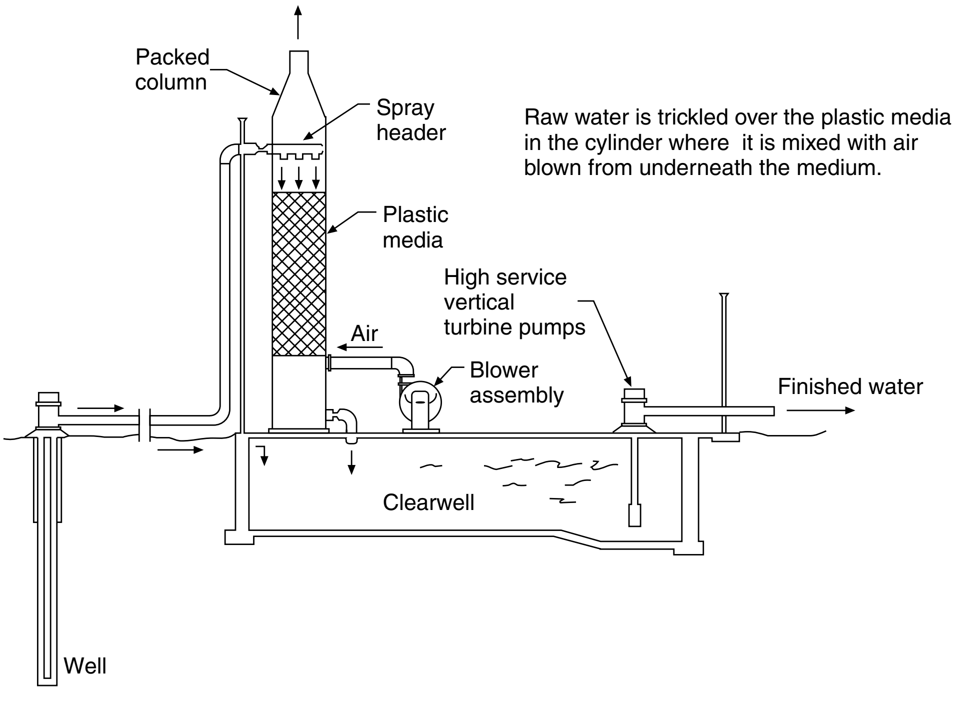

Figure 1. Packed tower aeration system.

Systems using PCA may need pretreatment to remove iron, solids, and biological growth to prevent clogging of the packing material. Post treatment such as the use of a corrosion inhibitor, may also be needed to reduce corrosive properties in water due to increased dissolved oxygen from the aeration process.

Packed columns usually operate automatically and need only daily visits to ensure that the equipment is running satisfactorily. Maintenance requirements include servicing pump and blower motors and replacing air filters on the blower, if necessary.

PCA exhaust gas may require treatment to meet air emissions regulations, which can significantly increase the costs of this technology.

Diffused Aeration. In a diffused aeration system, a diffuser bubbles air through a contact chamber for aeration. The diffuser is usually located near the bottom of the chamber. The air introduced through the diffuser, usually under pressure, produces fine bubbles that create water-air mixing turbulence as they rise through the chamber.

The main advantage of diffused aeration systems is that they can be created from existing structures, such as storage tanks. However, they are less effective than packed column aeration, and usually are employed only in systems with adaptable existing structures.

Multiple Tray Aeration. Multiple tray aeration directs water through a series of trays made of slats, perforations, or wire mesh. A blower introduces air from underneath the trays.

Multiple tray aeration units have less surface area than PCA units. This type of aeration is not as effective as PCA and can experience clogging from iron and manganese, biological growth, and corrosion problems.

Multiple tray aeration units are readily available from package plant manufacturers.

Mechanical Aeration. Mechanical aeration uses mechanical stirring mechanisms to mix air with the water. These systems can effectively remove volatile organic chemicals (VOCs).

Mechanical aeration units need large amounts of space because they demand long detention times for effective treatment. As a result, they often require open-air designs, which can freeze in cold climates. These units also can have high energy requirements. However, mechanical aeration systems are easy to operate and are less susceptible to clogging from biological growth than PCA systems.

Catenary Grid. Catenary grid systems are a variation of the packed column aeration process. The catenary grid directs water through a series of wire screens mounted within the column. The screens mix the air and water in the same way as packing materials in PCA systems.

These systems can effectively remove VOCs. They have higher energy requirements than PCA systems, but their more compact design lowers their capital cost relative to PCA.

Higee Aeration. Higee aeration is another variation of the PCA process. These systems pump water into the center of a spinning disc of packing material, where the water mixes with air.

Higee units require less packing material than PCA units to achieve the same removal efficiencies. Because of their compact size, they can be used in limited spaces and heights. Current Higee systems are best suited for a temporary application of less than 1 year with capacities up to 380 liters (100 gallons) per minute.

WHERE CAN I FIND MORE INFORMATION?

Information in this fact sheet was primarily obtained from three documents:

- *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. EPA/625/4-89/023;
- *Small Community Water and Wastewater Treatment*, EPA/625/R-92/010; *and*
- *Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities*, EPA/625/5-90/025.

All publications can be ordered free from the U.S. Environmental Protection Agency Office of Research and Development at (513) 569-7562.

The NDWC offers these documents as well, but at a cost to help recover photocopying and other expenses. *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*, item #DWBKDM04, a 209-page book, costs $30.05. *Small Community Water and Wastewater Treatment*, item #DWBKRE03, a 95-page book, costs $ 13.65. The third book, *Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities*, item #DWBKGN09, an 82-page publication, costs $11.82. Shipping and handling charges apply.

Also, the NDWC's Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS) is a public reference database that contains information about technologies in use at small water systems around the country. For further information on accessing or ordering RESULTS, call the NDWC at (800) 624-8301 or (304) 293-4191.

For additional free copies of Tech Brief fact sheets *call the NDWC at one of the numbers above. You may also download Tech Briefs from our Web site at* http://www.ndwc.wvu.edu.

- Tech Brief: Organic Removal, *item #DWBLPE59*;
- Tech Brief: Ion Exchange and Demineralization, *item #DWBLPE56*;
- Tech Brief: Corrosion Control, *item #DWBLPE52*;
- Tech Brief: Filtration, *item #DWBLPE50*; or
- Tech Brief: Disinfection, *item #DWBLPE47*.

OZONE

National Drinking Water
Clearinghouse

New water treatment goals for disinfection byproducts (DBP) and for microbial inactivation will increase the need to consider new disinfection technologies. Ozone is an attractive alternative. This technology has evolved and improved in recent years, thereby increasing its potential for successful application. It is important to note that ozone, like other technologies, has its own set of advantages and disadvantages that show up in differing degrees from one location to the next

WHAT IS OZONE?

Ozone is a colorless gas that has an odor most often described as the smell of air after a spring electrical thunderstorm. Some people also refer to the odor as similar to the smell of watermelons. Ozone (O_3) is an extremely unstable gas. Consequently, it must be manufactured and used onsite. It is the strongest oxidant of the common oxidizing agents. Ozone is manufactured by passing air or oxygen through two electrodes with high, alternating potential difference.

WHAT REGULATIONS GOVERN OZONE?

In the next century, small water systems will need to use disinfection methods that are effective for killing pathogens without forming excessive DBP. Disinfection byproduct compliance is more likely to be a problem for small water systems treating surface water than for those treating groundwater because surface water sources tend to contain more natural organic matter that forms byproducts when mixed with disinfectants. In August 1997, the U.S. Environmental Protection Agency (EPA) listed ozone as a “compliance” in the requirements of the Surface Water Treatment Rule for all three sizes of small drinking water systems.

ADVANTAGES

Using ozone to treat water has many advantages, including the following:

- Possesses strong oxidizing power and requires short reaction time, which enables the germs, including viruses, to be killed within a few seconds;
- Produces no taste or odor;
- Provides oxygen to the water after disinfecting;
- Requires no chemicals;
- Oxidizes iron and manganese;
- Destroys and removes algae;
- Reacts with and removes all organic matter;
- Decays rapidly in water, avoiding any undesir able residual effects;
- Removes color, taste, and odor; and
- Aids coagulation.

LIMITATIONS

The use of ozone to treat water has some limitations:

- Toxic (toxicity is proportional to concentration and exposure time);
- Cost of ozonation is high compared with chlorination;
- Installation can be complicated;
- Ozone-destroying device is needed at the exhaust of the ozone-reactor to prevent toxicity and fire hazards;
- May produce undesirable aldehydes and ketones by reacting with certain organics;
- No residual effect is present in the distribution system, thus postchlorination is required;
- Much less soluble in water than chlorine; thus special mixing devices are necessary; and
- It will not oxidize some refractory organics or will oxidize too slowly to be of practical significance.

DISINFECTION

Design of an ozone system as primary treatment should be based on simple criteria, including ozone contact concentrations, competing ozone demands, and a minimum contact time (CT) to meet the required cyst and viral inactivation requirements, in combination with EPA recommendations.

Systems that need to provide CT to comply with the Ground Water Disinfection Rule, but are also having problems with DBP or maintaining distribution system residuals, should consider using ozone as the primary disinfectant and then chloramines for distribution system protection.

Ozone has been observed to be capable of disinfecting *Cryptosporidium*, and there is significant interest in this aspect of its application. Available data indicate that a significant increase in ozone dose and CT may be required as compared with past practices. Therefore, these needs should be considered in planning.

Iron and Manganese Removal

The standard oxidation-reduction potential and reaction rate of ozone is such that it can readily oxidize iron and manganese in groundwater and in water with low organic content. Groundwater systems that have iron levels above 0.1 milligrams per liter (mg/L) may have iron complaints if ozonation or chlorination is added.

Excessive doses of ozone will lead to the formation of permanganate, which gives water a pinkish color. This soluble form of manganese (Mn) corresponds to a theoretical stoichiometry of 2.20 mg O_3/mg Mn. Stoichiometry is the determination of the proportions in which chemical elements combine or are produced and the weight relation in a chemical reaction.

Color Abatement

Because humic substances are the primary cause of color in natural waters, it is useful to review the reactions of ozone with humic and fulvic acids. According to different authors, ozone doses of 1 to 3 mg O_3/mg C lead to almost complete color removal. The ozone dosages to be applied in order to reach treatment goals for color can be very high. It is interesting to note that when the ozone dosage is sufficient, the organic structure is modified such that the final chlorine demand can decrease.

Control of Taste and Odor

The National Secondary Drinking Water Regulations recommend that the threshold odors number (TON) be 3 or less in finished water. It has been shown that ozone can be effective in treating water for taste and odor problems, especially when the water is relatively free from radical scavengers.

It has also been observed that ozone, in combination with other downstream treatment processes, especially granular activated carbon (GAC) filtration, can greatly increase taste and odor treatment efficiency and reliability. Again, the cause of taste and odor compounds, as well as the source water to be treated, need to be carefully considered prior to designing a treatment system. Analysis and possibly pilot-scale experimentation may be required to determine the optimum choice of ozone and downstream treatment.

Elimination of Synthetic Organic Chemicals

Ozone or advanced ozonation processes can remove many synthetic organic chemicals (SOC). This removal leads to the chemical transformation of these molecules into toxic or nontoxic byproducts. Such transformation can theoretically lead to complete oxidation into carbon dioxide (CO_2); however, this is rarely the case in water treatment. Any observable reduction in total organic carbon (TOC) is due either to a small degree of CO_2 formation (for example, decarboxylation of amino acids) or the formation and loss of volatile compounds through stripping.

Effects on Coagulation

It is important to understand that the coagulating effects of ozone go beyond any direct oxidative effects on organic macro-pollutants. For this reason, one must be wary of studies claiming improved removal of organic matter when the data are based solely on color removal or ultraviolet (UV) absorbtion. Also, when studying the removal of DBP (for example, trihalomethanes), one must be careful to incorporate controls permitting the separate evaluation of ozone's direct effects. Finally, the coagulating effects of ozone may not be observed with all water. Whenever considering the use of ozone as a coagulant aid, the pre-ozonation effects should be critically evaluated in pilot studies incorporating the proper controls.

Algae Removal

Ozone, like any other oxidant, such as chlorine or chlorine dioxide, has a lethal effect on some algae or limits its growth. Ozone is also capable of inactivating certain zooplankton, e.g., mobile organisms, *Notholca caudata*. Such organisms must first be inactivated before they are removed by flocculation and filtration.

Byproducts

The alternative use of ozonation has generated much interest because of its ability to avoid the formation of halogenated organics inherent in the practice of chlorine treatment. However, raw water quality significantly affects ozonation results and could lead to the formation of other undesirable byproducts. Brominated byproducts are a major concern in source waters containing bromide. Ozonation produces its own byproducts, such as aldehydes, ketones, and carboxylic acids.Assuming equivalent disinfection, benefit is achieved as long as the health concerns for the new products are less than those for the chlorine byproducts.

Personnel Requirements

Personnel time requirements for system cleaning may be fairly substantial. However, recent advancements in ozonation technology include use of high purity oxygen feed systems, rather than ambient air-feed systems. Ozonation treatment is therefore said to run cleaner and require less cleaning-related maintenance than had the earlier versions of this technology.

No Residual

Ozone will not provide a disinfecting residual that protects finished water in the distribution system. Therefore, the role of chlorine as a disinfecting agent is not entirely replaced, and its use in either the free chlorine or chloramine form will be required for this purpose in many locations.

Process and Equipment

The basic elements of an ozone system include ozone generation, feed gas preparation, ozone contacting, and ozone off-gas destruction components. While many of these components can involve a high degree of sophistication in large facilities, less complex alternatives are available for smaller systems. Figure 1 (see below) shows the five basic components of an ozonation system. To insure effectiveness and safety simultaneously, all components must be taken into account when designing/installing an ozone system. Central to the ozonation system is the ozone generator itself, which in turn is connected to an appropriate power supply. Instrumentation and controls for ensuring the effective and safe operation of the total system may be added to the five-component system shown in (Fig. 1).

Feed Gas Preparation

The feed gas preparation component is critical, as a high-quality gas stream is required for the generator to

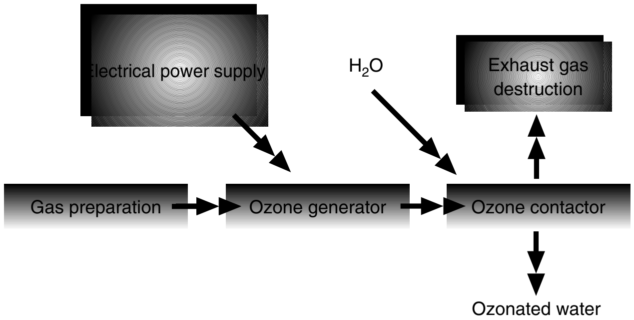

Figure 1. Basic components of an ozonation system. *Source*: "Ozone Treatment of Small Water Systems" 1999.

perform properly. This requires a gas stream that is low in moisture and particles. In older air-feed systems, the feed gas preparation systems for small systems tended to rely on high-pressure compressors that produce a pressurized feed stream, which is easier to dry and can accom- modate simpler, less maintenance-intensive drying devices than were typically applied in larger systems where lower-pressure compressors are typically used.

Alternatives for application of oxygen-rich feed gas streams have also emerged for small system applications in recent years. These include purchasing liquid oxygen and using small package oxygen-generation systems that are based on pressure swing adsorption. The use of these oxygen-enriched feed streams allows improved electrical efficiency in ozone generation and yields a product stream with a higher ozone content.

Ozone Contactors

Since ozone is only partially soluble in water, once it has been generated it must contact water to be treated. Many types of ozone contactors have been developed for this purpose.

Ozone contacting for disinfection has typically been accomplished in deep, multistage contactors that employ fine bubble diffusers. Newer alternatives have emerged that provide an option for small systems through the use of side-stream injection technologies that eliminate the need for fine bubble injection. Package units are available that include a gas separator that fuses and eliminates excess gas that results from ozone addition and a venturi jet that is used to inject and blend the ozone with a solution feed stream. These systems allow the alternative of injecting ozone into an enclosed vessel or a pipe. Note that materials need to be compatible with ozone. One possibility in this regard is the use of stainless steel. Several other contacting configurations, including turbine mixers, have been developed and may provide benefits as well.

Exhaust Gas Destruction

Ozone off-gas destruction is the final major component in the ozonation process. This system is required to remove ozone from spent off-gas streams, which are collected and treated prior to discharge into the atmosphere. Both catalytic and thermal destruction devices are used for this purpose or by passage through GAC.

How Safe is Ozone?

EPA notes that ozonation technology requires careful monitoring for ozone leaks, which pose a hazard in the work place. As with any other chemical, the Occupational Health and Safety Administration (OSHA) has established maximum contaminant inhalation guidelines for ozone in the work place. Ozone concentration of 0.1 part per million inhaled during an eight hour work period in a work area is the maximum limit set by OSHA regulations.

WHERE CAN I FIND MORE INFORMATION?

(1) American Water Works Association. 1993. *Controlling Disinfection By-Products*. Denver: American Water Works Association.

(2) Budd, G.C., G.S. Logdson, and B.W. Long. 1999. "Overview of Chlorine Dioxide, Ozone and Ultraviolet Irradiation." J.A. Cotruvo, G.F. Craun, and N. Hearne, eds. *Providing Safe Drinking Water in Small Systems: Technology, Operations, and Economics.* Boca Raton: CRC Press LLC.

(3) Collins, M.R. 1998. *Small Systems Water Treatment Technologies: State-of-the-Art Workshop.* Denver: American Water Works Association.

(4) International Ozone Association. 1999. Regional Conference on Ozonation and Advanced Oxidation Processes (AOPs) in Water Treatment. *Applications and Research in Poitiers, France. Stamford: International Ozone Association.*

(5) Langlais, B., D.A. Reckhow, and D.R. Brink. 1991. *Ozone in Water Treatment: Application and Engineering*. Denver: AWWA Research Foundation and Lewis Publishers.

(6) Rice, R.G., P.K. Overbeck, and K. Larson. 1999. "Ozone Treatment of Small Water Systems." J. A. Cotruvo, G. F. Craun, and N. Hearne, eds. *Providing Safe Drinking Water in Small Systems: Technology, Operations, and Economics*. Boca Raton: CRC Press LLC.

(7) Vigneswaran, S. and C.Visvanathan. 1995. *Water Treatment Processes: Simple Options*. Boca Raton: CRC Press, Inc.

(8) U.S. Environmental Protection Agency. 1998. *Small System Treatment Technologies for Surface Water and Total Coliform Rules.* Washington, DC: EPA Office of Ground Water and Drinking Water.

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OZONE WITH ACTIVATED CARBON FOR DRINKING WATER TREATMENT

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The removal of organic compounds by adsorption on activated carbon is very important in water purification. Removal of organic compounds from the drinking water supply results in reduction in taste and odor and in DBP precursors and removal of volatile organic compounds (VOCs) and synthetic organic compounds (SOCs). Activated carbon supports a higher rate of biodegradation than sand or nonactivated carbon. The advantages of activated carbon include (1) enrichment of oxygen by sorption, (2) enrichment of the substrate in a biofilm, and (3) extended adsorption resulting from bioregeneration and development of a biofilm that can degrade less biodegradable but adsorbable organics.

In recent years, there has been a lot of emphasis on finding alternative disinfectants to free chlorine because of the carcinogenic nature of the halogenated disinfection byproducts (DBPs). Ozone has come up as an alternative disinfectant because of its distinct beneficial effects in water purification. However, ozonation raises two design issues. First, ozone produces byproducts that may eventually be regulated by environmental agencies; these include aldehydes, organic acids, and peroxides. Second, ozone increases the biodegradability of natural organic matter (NOM), which can lead to bacterial regrowth in distribution systems. The engineering solution to both problems has been to recommend that ozonation precede filtration. In this way, the filter can be used to promote biodegradation of NOM and ozonation byproducts; the process has been referred to as biological filtration. The filter could be either an adsorbing medium, the most common of which is granular-activated carbon (GAC), or a nonadsorbing medium, typically a combination of anthracite and sand. If activated carbon is used, the interaction between adsorption and biodegradation becomes important. Activated carbon removes contaminants by adsorption, whereas a microbial population removes biodegradable components. It is observed frequently that adsorbability is affected negatively by ozonation but positively by biodegradation.

Activated carbon coupled with an ozone pretreatment can be used in a treatment process either in a filter–adsorber or postfilter–adsorber configuration. Filter-adsorbers basically integrate filtration and adsorption processes into a single process. In other words, a filter–adsorber is a dual medium filter in which the top layer is GAC and the bottom layer is sand. Postfilter-adsorbers are simply granular-activated carbon columns that are employed after a conventional filtration process. Both filter–adsorbers and postfilter–adsorbers become biologically active when ozone precedes the treatment process. An ozone-activated carbon filtration system (e.g., a filter-adsorber) will enable removal of turbidity, organics, pesticides, and organic micropollutants. It will be biologically stable and can help in preventing bacterial regrowth in distribution systems. Postfilter–adsorbers normally do not remove turbidity because they are designed for organics removal.

OZONE–BROMIDE INTERACTIONS

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As utilities consider changing their primary disinfection practices from free chlorine to ozone to provide pathogen control while minimizing chlorinated disinfection by-product (DBP) formation, the potential for producing ozonation DBPs like bromate ion must be addressed. This article focuses on the interactions, not only of molecular ozone and bromide ion, but also of radical species with bromide ion. The data evaluations include discussions of reaction products, potential for bromate ion formation, reaction kinetics, and the effect of various water quality parameters and treatment conditions on bromate ion formation. Based on evaluation of existing data, areas requiring new or intensified research efforts are identified.

An additional aspect of this article is a presentation of most available data on the minimization of bromate ion formation during ozonation. A summary of bromate ion removal processes after ozonation has been incorporated.

SOURCES AND OCCURRENCE OF BROMIDE ION

Bromide ion (Br^-) in drinking water supplies has no direct public health ramifications; however, its presence during water-treatment disinfection can lead to the formation of DBPs such as bromate ion (BrO_3^-). Hence, bromide ion is a precursor to the formation of bromate ion and other brominated oxidation/disinfection by-products. An understanding of the sources and levels of bromide ion in different source waters is crucial for an understanding of the bromate ion formation potential in drinking waters. If bromide ion is present in source waters, it is difficult to remove it economically during drinking water treatment.

Bromide ion can enter water sources from dissolution of geologic sources, from saltwater intrusion into surface water and aquifers, and from human activities. Methyl bromide and ethylene dibromide are used to fumigate crops and soil and as additives to leaded gasoline. Once in soil, they break down into inorganic forms that subsequently are leached by agricultural runoff into ground waters; bromide ion concentrations may attain 0.01–6 mg/L (1). Bromide ion is also associated with salt-spreading on roads during the winter, and some fertilizers are known to contain iodate and bromate ions. Other bromide ion containing compounds can enter water through sewage and industrial effluents (2). Electrolytic chlorine obtained from salt contains bromine estimated at a level of 2 mg/L (3).

Amy et al. (4) conducted a nationwide survey of bromide ion in source waters throughout the United States, and found an average concentration of almost 100 μg/L. In a study of more than 35 water treatment facilities that were selected to provide a broad range of source water qualities and treatment processes, influent bromide ion levels ranged from 10–3000 μg/L (5). Legube et al. (6) found bromide ion concentrations in the influents of 23 different European utilities ranging from 12–210 μg/L, and Kruithof et al. (7) found bromide ion concentrations in Dutch waters ranging from 10–240 μg/L. Considering that the average bromide ion concentration in U.S. waters is approximately 100 μg/L, it is expected that detectable bromate ion can form in a majority of waters that are subjected to ozonation. A Cl^-/Br^- ratio of about 300:1 is indicative of seawater influence.

MEASUREMENT OF BROMATE ION

Ion chromatography is the predominant analytical technique for bromate ion measurement at such low concentrations. Several techniques have been described to reach the required level of sensitivity for measuring bromate ion (8–11).

Siddiqui et al. (11), Legube et al. (6), and Kuo et al. (9) measured bromate ion with detection limits of 2 μg/L, 2 μg/L, and 5 μg/L, respectively, using a conductivity detector without preconcentration and employing a borate eluent (100–150 μL sample loop). They also employed Ag cartridges to remove chloride prior to injection. Legube et al. (6) followed a sequence of steps to measure bromate ion. Each sample was first filtered using membrane filters to remove suspended solids, then filtered through Ag filters to remove Cl^-, and finally was acidified and stripped of bicarbonate as carbon dioxide by helium to avoid interference from the bicarbonate peak.

Gordon et al. (12) developed a non-ion chromatographic method using chlorpromazine to determine bromate ion in ozone-treated waters. In the presence of bromate ion, chlorpromazine oxidizes forming a relatively stable colored product that can be monitored at 530 nm. Chemical masks are described to minimize potential interference from nitrite and chloride ions.

BROMATE ION FORMATION: PATHWAYS AND MECHANISMS

During the oxidation and/or chemical disinfection of natural waters containing bromide ion with ozone, bromate ion can be formed at concentrations ranging from 0 to 150 μg/L under normal water treatment conditions. During ozonation, bromide ion is first oxidized by dissolved ozone to hypobromite ion (OBr^-) which is then further oxidized to bromate ion. The reaction is pH-dependent because OBr^- is in equilibrium with hypobromous acid (HOBr). OBr^- builds up rapidly during ozonation and becomes the main reservoir for bromate. Hypobromite reacts further with ozone to form bromide ion (77%) and bromate ion (23%) in pure aqueous solutions.

The molecular ozone mechanism does not account for OH radicals formed as secondary oxidants from decomposed ozone during water treatment. Richardson et al. (13) and Yates and Stenstrom (14) indicate that there is a radical pathway which is influenced by both pH and alkalinity. The OH· radical and, to a lesser degree, the carbonate radical pathway ($CO_3\cdot^-$) may be more important than the molecular ozone pathway. Oxidants such as OH and CO_3^- radicals may interact with intermediate bromine species leading to the formation of BrO radicals which eventually undergo disproportionation to form hypobromite and bromite (BrO_2^-). Bromate ion is then formed through oxidation of bromite by ozone. The radical mechanism for the formation of bromate ion includes two decisive reaction steps still involving molecular ozone: the formation of hypobromite and oxidation of bromite (15). In contrast, Yates and Stenstrom (14) suggest that BrO· is formed primarily by the direct reaction of ozone with Br·, which is formed by the oxidation of Br^- by OH·. Siddiqui et al. (16) assumed that rate constants obtained by Haag and Hoigne (17) through molecular ozone pathways may intrinsically take into account bromate ion formation through both molecular ozone and radical pathways.

Bromate ion formed through reactions with molecular ozone contributes in the range of 30–80% to overall bromate ion formation in natural organic matter (NOM)-containing waters. Ozekin et al. (18) report up to 65% and 100% bromate formation through a radical pathway in NOM-free and NOM-contaning waters, respectively. Differences in NOM-containing waters can be attributed to differences in the characteristics of NOM. A change in mechanism as a function of pH and the competitive roles of the free radical (one-electron transfer) mechanism above pH 7 versus oxygen-atom (two-electron transfer) mechanisms help explain both the large variations in bromate ion yield and the sensitivity to reactor design, concentration of NOM, and ozone/bromide ion concentrations (19). In summary, bromate ion formation can occur through both radical and molecular ozone pathways depending on NOM concentration in source waters. This is an important finding that will have strong implications for bromate ion control strategies.

BROMATE FORMATION: EFFECT OF WATER QUALITY PARAMETERS AND TREATMENT CONDITIONS

Several studies have demonstrated that several water quality and ozonation parameters affect the formation of bromate ion. A better mechanistic understanding relating these parameters to bromate ion formation is critical to control its formation during ozonation.

Bromide Ion Concentration

An important difference from the chlorine system exists in that Br^-, unlike Cl^-, reacts with ozone at a significant rate and this reaction is independent of pH because Br^- is not protonated in water. At low pH (≤ 6), the bromine formed is relatively inert to ozonation ($k < 10^{-3}$ M^{-1} s^{-1}), and nearly all of the Br^- is present as HOBr. In the absence of NOM (or other substances that react rapidly with HOBr), all of the Br^- can eventually be recovered as bromate ion when ozonated. The ranges of bromate ion levels found by different investigators for various bromide ion-containing waters are summarized in Table 1.

Siddiqui and Amy (21) have shown that there is a threshold bromide ion concentration below which no detectable (<2 μg/L) bromate ion formation occurs. This threshold level is dependent on pH, ozone dose, DOC, and alkalinity of the water being ozonated and hence will vary from source to source. Siddiqui and Amy (21) have shown a bromide ion threshold concentration of 0.25 mg/L for an O_3/DOC ratio of 1.5:1 at pH 7.5 for groundwater with a DOC of approximately 4 mg/L. Krasner et al. (23) indicated that bromide ion levels of $\geq$0.18 mg/L yield measurable levels of bromate ion when a target ozone residual for disinfection is met.

Ozone Dose

The ozone dose plays a critical role in the formation of bromate ion. Increasing ozone dose increases the formation of bromate ion until all bromide ion is converted to bromate ion (21). If sufficient ozone is added to meet the ozone demand of a water, bromate ion will be produced if there is sufficient bromide ion ($\geq$100 μg/L). However, according to Krasner et al. (23) and Siddiqui et al. (21), appropriate staging of ozone through two or three chambers can minimize ozone residual and bromate ion formation in full-scale ozone contactors. Siddiqui and Amy (24) and Kruitof et al. (7) have shown that there is an ozone threshold concentration below which no bromate ion formation occurs. For pretreated Meuse River water with a DOC content of 2.4 mg/L, the lowest ozone dose at which bromate ion could be detected was 1.0 mg/L over a pH range of 6.8–7.8 (7, Table 2.4). Optimization of ozone dose for preoxidation or disinfection should take into account the formation potential of bromate ion.

Alkalinity

An important factor controlling the half-life of ozone in natural waters is alkalinity. Addition of alkalinity increases the formation of bromate ion (16). Their research has shown that the contribution to bromate ion formation due to carbonate radicals at pH 8.5 was much more predominant than at pH 6.5 (30% vs. 5%). This is presumably due to a shift toward HCO_3^- ions from CO_3^{2-} ions and higher production of OH radicals. CO_3^{2-} ions react about 30 times faster with OH radicals than HCO_3^- ions and therefore have a larger scavenging effect.

In summary, during ozonation, part of the ozone added reacts directly with bromide ion, and a part of it decomposes to radicals which further react with carbonate alkalinity to produce carbonate radicals. The higher the pH, the faster the decomposition rate of ozone (initiated by OH^-), and the faster the formation of bromate ion. Additionally, it is accelerated by a chain reaction for which the bromine species radicals formed act as carriers. Because of this chain reaction, dissolved ozone decay depends on bromate ion yielding radical intermediates which additionally catalyze the decomposition of ozone and alkalinity which scavenge the OH radicals. Alkalinity quenches the chain reaction resulting in an increase in ozone half-life.

Natural Organic Matter

The reaction of ozone with NOM can occur by direct reaction or by radical processes. The ozone decomposition and OH radical yield from NOM is influenced by the type and concentration of NOM in natural waters. Direct consumption of ozone is greater when the UV absorbance

Table 1. Summary of Bromate Ion Formation Potential in Different Source Waters

No. Samples	Br^-, μg/L	O_3, mg/L	pH	Alkalinity, mg/L	DOC, mg/L	BrO_3^-, μg/L	Reference
18	10–800	1–9.3	5.6–9.4	20–132	2.2–8.2	<5–60	(20)
4	60–340	3–12	6.5–8.5	90–230	3–7	<5–40	(21)
28	10–100	2–4	6.8–8.8	20–120	0.3–11	<5–100	(22)
4	12–37	0–3.97	7.8	N/A	N/A	<7–35	(8)
1	500	2.3–9.5	7.2–8.3	N/A	N/A	13–293	(14)
23	12–207	0.3–4.3	5.7–8.2	14–246	0.5–6.8	<2–16	(6)
8	107–237	1–5	6.8–8.0	N/A	2–5	<5–50	(7)

(due to electrophilic and nucleophilic sites) of the source water is significant, resulting in decreased bromate ion. The radical process is initiated by active sites present in humic substances or formed during ozonation of nucleophilic sites and by hydroxide ions. Amy et al. (22) have shown that bromate ion formation, with all factors equal except NOM, varies from source to source. Amy et al. (22) studied more than seven different source waters containing a wide range of NOM characteristics. Krasner et al. (23) suggest that at fixed CT (Concentration of Disinfectant × Time of Contact) values, BrO_3^- increases with NOM.

In summary, the presence of NOM may accelerate ozone consumption and can reduce bromate ion formation potential. Besides pH, NOM concentration, measured as dissolved organic carbon (DOC), is influential; a higher Br^-/DOC ratio enhances bromate ion over organo-Br formation. The formation of bromate ion in NOM-containing waters is predominantly through a radical pathway rather than by the molecular ozone pathway.

Temperature

The effects of temperature are several: (1) dissolved ozone (DO_3) is more stable at lower temperatures, (2) increasing temperature increases the reaction rate constant, and (3) the pK_a of the $HOBr/OBr^-$ system is temperature dependent. Siddiqui and Amy (21), Amy et al. (22), and Kruithof et al. (7) have observed an increase in bromate ion concentration as temperature increases. Kruitof et al. (7) studied bromate ion formation at two different temperatures (5 and 20 °C) in Meuse River water in bench-scale experiments and found a significant increase in bromate ion formation potential upon increasing the temperature from 5 to 20 °C. Siddiqui and Amy (21) indicated that increasing either ozonation temperature or incubation temperature had a positive effect on the formation of bromate ion. An increase in ozonation temperature produced more bromate ion than a corresponding increase in incubation temperature. This may be partially attributable to bromate ion formation occurring in less than 10 minutes.

In summary, increasing temperature generally increases the formation of bromate ion during drinking water treatment. Hence, more bromate ion formation may be expected in summer months than in winter months for the same applied ozone dose.

Reaction Time

Perhaps more than any other factor, reaction time is most important. Amy et al. (22) and Yamada (25) have shown that most bromate ion formation occurs within about 5 minutes, although its formation can continue over 30 minutes, suggesting that bromate ion forms mainly through the radical pathway. Control strategies to minimize bromate ion formation must take into account its kinetic time frame. Reaction rate increases upon the addition of H_2O_2 and at elevated pH levels, strengthening the argument that radicals are responsible for bromate ion formation. Bromate ion formation occurs only in the presence of DO_3, so maintaining an appropriate amount of DO_3 is critical to minimizing bromate ion formation. A small increase in DO_3 can result in a severalfold increase in bromate ion formation.

BROMATE ION MINIMIZATION STRATEGIES

Given preliminary health information and the potential of a low MCL for bromate ion, control options require careful optimization to achieve low concentrations in ozonated waters containing significant levels of bromide ion. A better understanding of the mechanisms of bromate ion minimization strategies is required to control its formation during ozonation. Bromate ion can be minimized by chemical factors (chemical addition) or physical/hydrodynamic factors (contactor design).

pH Depression

Bromate ion concentration increases as pH increases. Reducing the pH of water before ozonation impacts bromate formation minimization in a number of ways. At $pH < 7$, oxidized bromide ion is primarily in the form of HOBr, thus minimizing bromate ion formation, and at $pH > 8.0$, the efficiency of OH radical generation from ozone decomposition increases. Siddiqui et al. (21) showed that decreasing the pH from 8 to 6 lowered the ozone dose required for disinfection by 33% for a source water containing 3.5 mg/L DOC. In addition, because ozone residuals are more stable at lower pH levels, a lower ozone dose is required to achieve the same CT value at a reduced pH, compared to ozonation at ambient pH.

Draft drinking water regulations in the United States will tentatively specify a best available treatment (BAT) of pH adjustment for bromate ion minimization. The major constraint to this BAT is the acid cost for high alkalinity waters, and the subsequent need to adjust pH after treatment for corrosion control. As an example, Krasner et al. (23) indicated that treating State Project Water (CA) at an average flow of 520 mgd could potentially reduce the ozone dose for minimum disinfection from 1.7 to 1.0 mg/L, resulting in an ozone cost savings of approximately $0.8 million per year. The estimated chemical costs, however, would be approximately $4 million and $2 million per year, respectively, for the acid to reduce the pH from 8 to 6 and the caustic to raise the pH back to 8.0 prior to distribution.

Ammonia Addition

Ammonia addition theoretically can tie up bromine ($HOBr/OBr^-$) as bromamine and can exert a free radical demand; however, the complexity of bromamine chemistry has yielded mixed BrO_3^- formation results in lab and pilot studies. Ammonia addition may result in a time-lag minimization of BrO_3^- formation in low DOC waters because of additional reactions with ammonia (reaction of ammonia with bromine proceeds faster than oxidation of bromamine and bromide ion by ozone). Glaze et al. (26) and Siddiqui and Amy (21) observed up to a 30% decrease in bromate ion formation upon the addition of ammonia at pH levels near 7.0. Siddiqui et al. (27) indicated that the effect of ammonia addition on bromate ion formation is more predominant in low

DOC groundwaters. They attribute this to a majority of bromate ion formation in NOM-containing waters proceeding through the radical pathway.

Hydrogen Peroxide

At low pH levels ($pH < 7$), production of OH radicals and subsequent consumption of H_2O_2 by OH radicals is slower, thereby decreasing the rate of decomposition of ozone and enhancing the rate of bromate ion formation. At high pH values ($pH > 9$), the degree of dissociation of H_2O_2 to HO_2^- becomes apparent, and the decomposition of H_2O_2 by the reaction of O_3 with HO_2^- proceeds fast. The amount of bromate ion formed increases as long as the synergistic effect of OH radicals and molecular ozone is maintained. If the H_2O_2 concentration is too high, the half-life for ozone is too small for the formation of bromine species and eventually bromate ion.

Siddiqui and Amy (21) and Krasner et al. (23) have observed an increase in bromate ion formation, whereas Daniel et al. (28) and Kruitof et al. (7) have observed a decrease in bromate ion formation upon the addition of H_2O_2.

The differences in H_2O_2 effects on bromate ion formation may be attributed to differences in ozonation pH, H_2O_2 concentration maintained during ozonation, and the DOC content of the source waters. Excess H_2O_2 decreases the DO_3 concentration (less CT value) resulting in reduced bromate ion formation. On the other hand, if an optimal amount of H_2O_2 with respect to O_3 is present, bromate ion formation increases. In some full-scale plants, the addition of ozone is automated based on ozone residual at the outlet of the ozone contactors. Maintaining a constant residual with and without the addition of peroxide implies an increase in applied ozone which leads to an increase in bromate ion concentration.

Contactor Hydrodynamic Factors

Gas–liquid contactor hydrodynamics plays a critical role in bromate ion formation; it influences mass transfer rates, peak ozone residuals, spatial-temporal concentration gradients, and liquid backmixing phenomena. A number of conditions may be imposed on the operation of a full-scale contactor to minimize bromate ion formation. These contactor operating conditions may include contactor operation at low residual ozone concentrations and minimal backmixing.

Krasner et al. (23) and Siddiqui et al. (24) demonstrated that staging ozone application within a full-scale contactor or splitting ozone application in a pilot-scale ozone contactor can optimize ozone residual throughout the contactor as well as result in less bromate ion formation. This strategy minimizes bromate ion formation but may require larger ozone doses to ensure the same disinfection.

The ozone-content of the carrier gas and ozonation contact time affect the formation of bromate ion in laboratory-scale reactors (24). In full-scale experiments, Gramith et al. (29) observed higher bromate ion formation in an eductor system (6% ozone) than in an air-fed system (1.5% ozone). These differences in bromate ion production by the two different configurations indicate the sensitivity of bromate ion formation to ozone contactors and differences in mass transfer of ozone.

BROMATE ION REMOVAL

Several different options to remove bromate after its formation, applicable to surface water treatment plants contemplating the use of ozone at various points of application, have been evaluated by Siddiqui et al. (11): ferrous iron reduction, granular activated carbon (GAC) surface reduction, ultraviolet irradiation (UV) and high energy electron beam irradiation. In all processes, chemical analysis of the treated water showed the formation of bromide ion, indicating that chemical reduction of bromate to bromide ion is the significant mechanism. Bromate removal by activated carbon has been shown to be carbon specific, and not all the carbons have shown the ability to reduce bromate to bromide. The use of ferrous iron appears more promising because it also acts as a coagulant for removing disinfectant by-product precursors.

SUMMARY

Bromate ion formation occurs through both a molecular ozone and a free radical pathway. Most authors have shown that pH, bromide ion concentration, temperature, and alkalinity favor bromate ion formation whereas DOC has been shown to decrease bromate ion formation. pH depression reduces the formation of bromate ion, but this technique may not be cost-effective for high alkalinity source waters and may favor organobromine compounds. Different types of NOM can exert different ozone demands and associated different bromate ion formation potentials. Addition of ammonia has produced mixed results. Clearly, optimization of pH to minimize bromate ion formation by ammonia addition requires further study because the stability of different bromamine species depends on the pH of the water. Bromate ion can be minimized by manipulating ozone contactor design and operation. Appropriate staging of ozone through two or more chambers and optimizing the hydrodynamics of the ozone contactor can minimize ozone residual and bromate formation.

BIBLIOGRAPHY

1. Wegman, R.C. and Greve, P.A. (1981). Methyl bromide ion and bromide ion in drainage water after leaching of glassware soils. *Water Air Soil Pollut.* **16**(3): 3–11.
2. Luong, T.V., Peters, C.J., and Perry, R. (1981). Influence of bromide ion upon THM formation during water chlorination. *Water Ind., 81, Int. Water Conf.*, Brighton, U.K.
3. Vogt (1980).
4. Amy, G., Siddiqui, M., Zhai, W., and Debroux, J. (1993). National survey of Br^- in drinking waters. *1993 AWWA Annu. Conf. Proc.*, San Antonio, TX.
5. Krasner, S.W., et al. (1989). The occurence of disinfection by-products in US drinking water. *JAWWA* **81**(8): 41.

6. Legube, B., Bourbigot, M., Bruchet, A., Deguin, A., Montiel, A., and Matia, L. (1998). Bromide ion/bromate ion survey on different European water utilities. *Proc. Int. IWSA Workshop*, Paris.
7. Kruithof (1993).
8. Hautman, D.P. and Bolyard, M. (1993). Using ion chromatography to analyze inorganic disinfection by-products. *JAWWA* **85**(10): 88–93.
9. Kuo, C., Krasner, S.W., Stalker, G.A., and Weinberg, H.S. (1990). Analysis of inorganic disinfection by-products in ozonation drinking water by ion chromatography. *AWWA WQTC Proc.*, San Diego, CA.
10. Jagt vander der, H., Noij, Th.H.M., and Ooms, P.C.A. (1993). Analysis and identification of bromate ion in water by ion chromatography and multiple detection at the low-ppb level. *IWSA Workshop*, Paris, pp. 25–32.
11. Siddiqui, M., Amy, G., Ozekin, K., Zhai, W., and Westerhoff, P. (1994). Alternative strategies for bromate ion removal from drinking water. *JAWWA* **86**(10): 81.
12. Gordon, G., Bubnis, B., and Kuo, C. (1994). A flow injection, non-ion chromatographic method for measuring low level bromate ion in ozone treated waters. *Ozone: Sci. Eng.* February.
13. Richardson, L.B., Burton, D.T., Helz, G.R., and Rhoderick, J.C. (1981). Residual oxidant decay and bromate formation in chlorinated and ozonated sea-water. *Water Res.* **15**: 1067–1074.
14. Yates, R.S. and Stenstrom, M.K. (1993). Bromate production in ozone contactors. *AWWA Annu. Proc.*, San Antonio, TX.
15. von Gunten, U., Hoigne, J., and Bruchet, A. (1993). Bromate formation during ozonation of bromide ion containing waters. *IWSA Workshop*, Paris, pp. 51–56.
16. Siddiqui, M.S., Amy, G.L., and Rice, R.G. (1995). Bromate ion formation: A critical review. *JAWWA* **87**(10): 58.
17. Haag, W.R. and Hoigne, J. (1983). Ozonation of bromide-contaning waters: Kinetics of formation of hypobromous acid and bromate ion. *Environ. Sci. Tech.* **17**: 261.
18. Ozekin, K., Siddiqui, M., Amy, G., and Haag, W. (1994). Pathways for bromate formation in NOM-Free water. *AWWA Annu. Conf.*, New York.
19. Gordon, G. (1993). The chemical aspects of bromate control in ozonated drinking water containing bromide ion. *IWSA Workshop*, Paris, pp. 41–49.
20. Krasner, S.W., Glaze, W.H., Weinberg, H.S., Daniel, P.A., and Najm, I. (1993). Formation and control of bromate during ozonation of waters containing bromide ion. *JAWWA* **85**(1), 73–81.
21. Siddiqui, M. and Amy, G. (1993). DBPs formed during ozone-bromide reactions in drinking water treatment. *JAWWA* **85**: 63–72.
22. Amy, G., Siddiqui, M., Ozekin, K., and Westerhoff, P. (**1993**). Threshold levels for bromate ion formation in drinking water. *Proc. IWSA Workshop*, Paris, pp. 169–180.
23. Krasner, S.W., Gramith, J.T., Coffey, B.M., and Yates, R.S. (**1993**). Impact of water quality and operational parameters on the formation and control of bromate during ozonation. *IWSA Workshop*, Paris, pp. 157–168.
24. Siddiqui, M., Amy, G., Ozekin, K., Miller, K., and Westerhoff, P. (1993). The role of relating pilot-scale tracer data with bench-scale data for bromate prediction. *11th Ozone World Congr.*, San Francisco, CA.
25. Yamada, H. (1993). By-products of ozonation of low bromide waters and reduction of the by-products by activated carbon. *11th IOA Proc.*, San Francisco, CA.
26. Glaze, W.H., Weinberg, H.S., and Cavanagh, J.E. (1993). Evaluating the formation of brominated DBPs during ozonation. *JAWWA* **85**(1): 96–103.
27. Siddiqui, M. and Amy, G. (1994). Removal of bromate using UV irradiation. *IOA Reg. Conf.*, Zurich, Switzerland.
28. Daniel, P.A., Zafer, M.A., and Meyerhofer, P.F. (1993). Bromate control: Water quality, engineering and operational considerations. *IWSA Workshop*, Paris, pp. 181–188.
29. Gramith, J.T., Coffey, B.M., Krasner, S.W., Kuo, C., Means, E.G. (1993). Demonstration-scale evaluation of bromate formation and control strategies. *AWWA Annu. Conf.*, San Antonio, TX.

MUNICIPAL WATER SUPPLY: OZONATION

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OZONE IN WATER TREATMENT

Since the first full-scale application of ozone for water treatment in late 1800s, ozone has been widely used in municipal water supplies in many countries. The primary goal of the ozonation process in water treatment is often disinfection, but ozonation is also used in many other applications, including taste and odor control, color removal, oxidation of manganese and iron, flocculation enhancement, oxidation of natural organic matter (NOM) and accompanying promotion of its biodegradability, and control of chlorination byproducts (1). Recently, the application of ozone as a disinfectant has been receiving more attention because of its effectiveness in treating pathogens, such as oocysts of the protozoan parasite *Cryptosporidium parvum*, which have shown strong resistance to chlorine-based disinfectants (2,3).

In water treatment, ozone can be applied either at the early stage of treatment (i.e., preozonation) or after other treatment processes, including conventional processes such as coagulation/flocculation and sedimentation. Ozone is sometimes used with hydrogen peroxide or UV to promote the formation of hydroxyl radicals in advanced oxidation processes (AOPs). Due to the increased biodegradability of organic matter after ozonation, ozonation is typically followed by biological filtration to remove biodegradable organic matter and to minimize microbial regrowth in the distribution system. Ozone decomposes relatively fast, so secondary disinfectants such as free chlorine and monochloramine are often applied after ozonation to provide residual disinfectant in the distribution system.

OZONE CHEMISTRY

Ozone is a strong oxidant with a standard redox potential of 2.07 V in aqueous solution (4). Ozone has four resonance structures thus allowing it to act as both an electrophile and as a nucleophile (5). Because ozone is a highly selective oxidant, its use in water treatment allows it to inactivate pathogenic microorganisms selectively, oxidize manganese and iron, and react with organic matter that contains olefins, amines, sulfides, and phenolic functional groups. Reactions with ozone are generally categorized into electron-transfer, oxygen atom transfer, or ozone addition processes (6). Inorganic compounds such as ferrous ion (Fe^{2+}) tend to react with ozone primarily through oxygen atom transfer, but ozone addition to a saturated bond followed by rearrangement and formation of carboxylic acid is typical of ozone reactions with organic matter. The rate constants of ozone reactions with various inorganic and organic compounds in the aqueous phase can be found in the literature (6–8). The reactions of ozone with NOM are complicated and not well understood primarily due to the heterogeneity of NOM. Ozone reactions with NOM are known to reduce aromatic carbon content, selectively reduce phenolic carbon content, and can lead to the formation of smaller molecular weight carboxylic acids and aldehydes (9–11).

Ozone is not stable in water and has a half-life ranging from seconds to hours depending on the water quality. In addition to the various reactions between ozone and organic and inorganic constituents in water, aqueous phase ozone undergoes a chain-type decomposition that results in the formation of secondary oxidants such as hydroxyl radicals ($\cdot OH$), ozonide radicals ($HO_3\cdot/O_3^-\cdot$), and superoxide radicals ($HO_2\cdot/O_2^-\cdot$). The mechanism of ozone decomposition has been studied for decades. Figure 1 shows one plausible mechanism, constructed from the literature, of ozone decomposition in the absence of organic matter (12–18). The rate of ozone decomposition in the aqueous phase depends strongly on pH because ozone decomposition is initiated by hydroxide ion. In the presence of alkalinity, carbonate radicals are formed (19–22), as shown in Fig. 1. In natural waters, ozone and secondary oxidants react with naturally occurring organic and inorganic matter. Such reactions may result in consumption of ozone and secondary oxidants as well as formation of other secondary oxidants such as hydrogen peroxide, ozonide, and superoxide radicals (23,24), therefore adding considerable complexity to the decomposition mechanism shown in Fig. 1. Overall, ozone decay in natural water is a combined effect of ozone decomposition and reaction with aqueous constituents. The kinetics of ozone decay in natural waters is often characterized as an initial fast decrease in ozone concentration followed by a slower phase where ozone follows a first-order decrease in concentration (25).

The contribution of hydroxyl radical, the major secondary oxidant, to the overall oxidation potential during ozone application has often been expressed as R_{ct}, the ratio between hydroxyl radicals and ozone (26). In the case of AOPs, the intent is to form hydroxyl radicals typically to react with inorganic and organic compounds that are resistant to ozone.

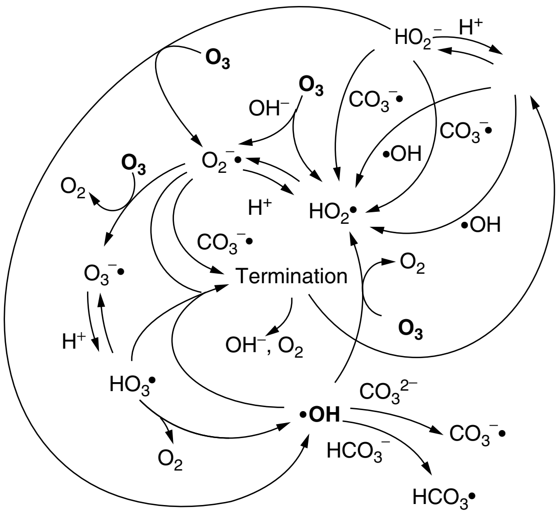

Figure 1. Mechanism of ozone decomposition in aqueous solution.

BY-PRODUCT FORMATION

A variety of organic byproducts such as aldehydes, ketones, keto aldehydes, carboxylic acids, keto acids, hydroxyl acids, alcohols, and esters are formed during ozonation of natural waters (27). In the presence of bromide, various brominated organic by-products are formed. Bromate (BrO_3^-) is one of the by-products formed during ozonation of bromide-containing waters. Bromate formation follows a complex set of reactions involving several bromine species such as $HOBr/OBr^-$, $BrO\cdot$, and BrO_2^- as intermediates (28–30). Formation of bromate during ozonation has been one of the major concerns in using ozone in drinking water treatment. Bromate is currently regulated at 10 µg/L in the United States and the European Union (31,32) due to its potential carcinogenicity (33).

OZONE CONTACTOR

Ozone is generally produced on site from air or pure oxygen by electrical discharge using ozone generators. A typical ozone concentration in the gas phase is 15 g/m^3 when air is used, but concentrations as high as 150 g/m^3 can be achieved when pure oxygen is used. The gaseous phase ozone is then transferred into water in ozone contactors that typically provide 10–20 min of contact time. Ozone is relatively insoluble in water (e.g., Henry's law constant at 20 °C is 100 atm/M), so efficient transfer of ozone to water is an important factor in designing ozone contactors. There are several different types of ozone contactors used for disinfection, depending on the methods of ozone introduction and modes of contacting with water. The most typical configuration is a multichamber bubble-diffuser contactor, though other types of contactor configurations such as rapid mixers, submerged turbines, pipeline injectors, packed towers, and deep U-tubes are also used (1). In the multichamber bubble-diffuser contactor, one or more of the upstream chambers in these units are transfer chambers in which ozone gas is introduced through a set of ceramic or stainless steel diffusers installed at the bottom of the unit. The remaining downstream chambers are used as reactive chambers for additional contact with residual dissolved ozone. A transfer chamber can be designed for operation in either countercurrent flow (water and gas flowing in opposite

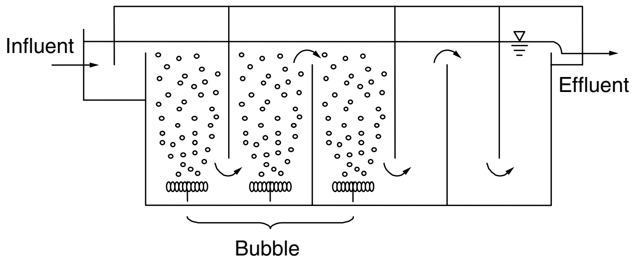

Figure 2. Schematic of full-scale ozone bubble-diffuser contactor located in Oakland, CA.

directions) or cocurrent flow (both water and gas flowing in the same direction) configuration. The transfer portion of a bubble diffuser contactor can consist of countercurrent and cocurrent flow chambers of similar size connected in series (34) or countercurrent flow chambers connected by small reactive upflow chambers (35). The residual ozone in the effluent of the contactor can be destroyed by hydrogen peroxide or activated carbon. A schematic of a typical ozone contactor is shown in Fig. 2. Off-gas from the contactor may contain residual ozone, which is subsequently treated by heat and/or catalyst for further destruction.

The design of an ozone bubble-diffuser contactor requires decisions such as selecting the number and distribution of transfer and reactive chambers, water column height, chamber cross-sectional area, number and type of diffusers, gas flow rate, and ozone gas concentration. The choice of contactor configuration and operating conditions can affect the hydrodynamics and mass transfer, which in turn can impact the ozone concentration throughout the ozone contactor. In addition, the performance of the contactor is also affected by certain water quality parameters, primarily those affecting the kinetics of ozone decomposition, such as temperature, pH, natural organic matter content, and alkalinity. Computer simulation has often been employed to model the complex phenomena involved in process design and optimization (25,36).

BIBLIOGRAPHY

1. Langlais, B., Reckhow, D.A., and Brink, D.R. (1991). *Ozone in Water Treatment Application and Engineering*. American Water Works Association Research Foundation, Denver, CO, and Lewis, Chelsea, MI.
2. Rennecker, J.L., Mariñas, B.J., Rice, E.W., and Owens, J.H. (1999). Inactivation of *Cryptosporidium parvum* oocyst with ozone. *Water Res.* **33**: 2481–2488.
3. Rennecker, J.L., Driedger, A.M., Rubin, S.A., and Mariñas, B.J. (2000). Synergy in sequential inactivation of *Cryptosporidium parvum* with ozone/free chlorine and ozone/monochloramine. *Water Res.* **34**: 4121–4130.
4. Bard, A.J., Parsons, R., and Jordan, J. (1985). *Standard Potentials in Aqueous Solution*. Marcel Dekker, New York.
5. Fessenden, R.J. and Fessenden, J.S. (1994). *Organic Chemistry*, 6th Edn. Brooks/Cole, New York.
6. Hoigné, J. (1998). Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes. *The Handbook of Environmental Chemistry*, Vol. 5, Part C. J. Hrubec (Ed.). Springer-Verlag, Berlin.
7. Neta, P., Huie, R.E., and Ross, A.B. (1988). Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **17**: 1027–1284.
8. von Gunten, U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.* **37**: 1443–1467.
9. Killops, S.D. (1986). Volatile ozonation products of aqueous humic material. *Water Res.* **20**: 153–165.
10. Schechter, D.S. and Singer, P.C. (1995). Formation of aldehydes during ozonation. *Ozone Sci. Eng.* **17**: 52–69.
11. Westerhoff, P., Debroux, J., Aiken, G., and Amy, G.L. (1999). Ozone-induced changes in natural organic matter (NOM) structures. *Ozone Sci. Eng.* **21**: 551–570.
12. Staehelin, J. and Hoigné, J. (1982). Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* **16**: 676–681.
13. Bühler, R.E., Staehelin, J., and Hoigné, J. (1984). Ozone decomposition in water studied by pulse radiolysis 1.HO_2/O_2^- and HO_3/O_3^- as intermediates. *J. Phys. Chem.* **88**: 2560–2564.
14. Staehelin, J., Bühler, R.E., and Hoigné, J. (1984). Ozone decomposition in water studied by pulse radiolysis. 2.OH and HO_4 as chain intermediates. *J. Phys. Chem.* **88**: 5999–6004.
15. Forni, L., Bahnemann, D., and Hart, E.J. (1982). Mechanism of the hydroxide ion initiated decomposition of ozone in aqueous solution. *J. Phys. Chem.* **86**: 255–259.
16. Sehested, K., Holcman, J., and Hart, E.J. (1983). Rate constants and products of the reactions of e_{aq}^-, O_2^-, and H with ozone in aqueous solution. *J. Phys. Chem.* **87**: 1951–1954.
17. Sehested, K., Holcman, J., Bjergbakke, E., and Hart, E.J. (1984). A pulse radiolytic study of the reaction $OH + O_3$ in aqueous medium. *J. Phys. Chem.* **88**(18): 4144–4147, additions and corrections (1985) **89**: 388.
18. Christensen, H., Sehested, K., and Corfitzen, H. (1982). Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *J. Phys. Chem.* **86**: 1588–1590.
19. Buxton, G.V. and Elliot, A.J. (1986). Rate constant for reactions of hydroxyl radicals with bicarbonate ions. *Radiat. Phys. Chem.* **27**: 241–243.
20. Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms, and hydroxyl radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **17**: 513–886.
21. Behar, D., Czapski, G., and Duchovny, I. (1970). Carbonate radical in flash photolysis and pulse radiolysis of aqueous carbonate solutions. *J. Phys. Chem.* **74**: 2206–2210.
22. Eriksen, T.E., Lind, J., and Merenyi, G. (1985). On the acid-base equilibrium of the carbonate radical. *Radiat. Phys. Chem.* **26**: 197–199.
23. Echigo, S. (2002). *Kinetics and Speciation of Brominated Disinfection By-Products During Ozonation*, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL.
24. Staehelin, J. and Hoigné, J. (1985). Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ. Sci. Eng.* **19**: 1206–1213.
25. Kim, J.H., Tomiak, R.B., and Mariñas, B.J. (2002). Inactivation of *Cryptosporidium* in a pilot-scale ozone bubble-diffuser contactor. Part I: Model development. *ASCE J. Environ. Eng.* **128**: 514–521.

26. Elovitz, M.S. and von Gunten, U. (1999). Hydroxyl radical/ozone ratios during ozonation processes. I. The R_{ct} concept. *Ozone Sci. Eng.* **21**: 239–260.
27. von Gunten, U. (2003). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide, or chlorine. *Water Res.* **37**: 1469–1487.
28. von Gunten, U. and Hoigné, J. (1994). Bromate formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions. *Environ. Sci. Technol.* **28**: 1234–1242.
29. von Gunten, U. and Oliveras, Y. (1998). Advanced oxidation of bromide-containing waters: Bromate formation mechanisms. *Environ. Sci. Technol.* **32**: 63–70.
30. Kim, J.H., von Gunten, U., and Mariñas, B.J. (2004). Modeling bromate formation and *Cryptosporidium parvum* inactivation in synthetic waters. *Environ. Sci. Technol.* **38**: 2232–2241.
31. *Federal Register* (1998). **63**: 241: 69389.
32. European Union. (1998). *Amtsblatt der Europäischen Gemeinschaften. Richtlinie 98/83/EG des Rates*. 3-12-1998, pp. 32–54.
33. Wilbourn, J. (1995). Toxicity of bromate and some other brominated compounds in drinking water. *Water Supply* **13**: 1–8.
34. Coffey, B.M., Graff, K.G., Mofidi, A.A., and Gramith, J.T. (1995). On-line monitoring of ozone disinfection effectiveness within an over/under baffled contactor. *Proc. 1995 Am. Water Works Assoc. Natl. Conf.*, Anaheim, CA, June 18–22, 1995, pp. 77–132.
35. Mariñas, B.J., Liang, S., and Aieta, M.E. (1993). Modeling hydrodynamics and ozone residual distribution in a pilot-scale ozone bubble-diffuser contactor. *J. Am. Water Works Assoc.* **85**: 90–99.
36. Kim, J.H. et al. (2002). Inactivation of *Cryptosporidium* in a pilot-scale ozone bubble-diffuser contactor. Part II: Model verification and application. *ASCE J. Environ. Eng.* **128**: 514–521.

REVIEW OF PARASITE FATE AND TRANSPORT IN KARSTIC AQUIFERS

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Every year in the United States cases of waterborne illness are generally characterized by gastrointestinal problems (vomiting, diarrhea, etc.). However, these same symptoms can be more serious and even fatal in certain groups, such as the young, elderly, and those with compromised immune systems. Furthermore, *viral pathogens* found in groundwater are linked to chronic diseases such as adult onset diabetes and myocarditis. Recognizing that preventing contamination of water sources is the first step in the multiple barrier approach to drinking water protection, the Interim Enhanced Surface Water Treatment Rule (IESWTR) and the Disinfectants/Disinfection Byproducts Rule (DBPR) were released in 1999. The two rules will provide additional protection of public water supplies and address microbiological contamination. The rules address the risks of the trade-offs between disinfection necessary for *microbial inactivation* and disinfection byproducts. The requirements of 40 CFR 141.72(b) are consistent 99.99% removal and/or inactivation of viruses and 99% removal of *Cryptosporidium oocysts*. The code gives public water suppliers the option to demonstrate compliance through pilot plant studies or other means that combine filtration techniques with *disinfection* as in EPA 1999 Microbial and Disinfection Byproducts Rules Simultaneous Compliance as in Guidance Manual.

Presently, only surface water systems and systems using groundwater under the direct influence of surface water are required to disinfect their water supplies. Although historically considered free of microbial contamination, most recent research has shown that aquifers can be readily contaminated by pathogens. To lessen the requirement for disinfection and to protect water resources, water suppliers have sought to use natural systems to treat *Cryptosporidium*. Thus, there is a critical need for information regarding the transport and fate of pathogens during water infiltration into subsurface systems.

Highly porous limestone aquifers are the primary water supply for about 25% of the U.S. population, including several large municipalities such as Atlanta, Austin, Miami, Nashville, San Antonio, and Tampa. After discussion with the water utilities and regulators in some of these cities, we found that there was tremendous concern about microbial contamination from parasites such as *Cryptosporidium*. Their concern was from the lack of information needed to determine the potential for *Cryptosporidium* and other pathogens to travel through their limestone aquifers from septic fields, wastewater treatment plants, and agricultural feedlots to the wells and springs from which they derive their water supplies. Through our discussion, we determined that a contaminant transport model compatible with existing models for limestone systems is needed. To produce the model, extensive laboratory tests are needed to garner transport parameters, and field tests are needed to evaluate the performance of the model. A recent report by the National Research Council on the role of science and technology in countering terrorism reached similar conclusions (1). Section 8.15 of that report states,

> research should be undertaken on water sampling schemes to determine what types and population of data points are required for a spatiotemporal network and on intelligent decision processing to be able to reliably recognize the patterns of attack indicators vs. natural hazards. Such research would require that priority attention be given to the development of simulation models that would both analyze and simulate events and serve to train operators in systematic recovery, emergency response, and evacuation.

KARSTIC LIMESTONE AQUIFERS

Karstic landscapes cover approximately 15% of the earth's land surface and are characterized by caves, sinkholes, and springs. Karstic aquifer systems occur throughout the United States and are particularly significant for groundwater resources in Texas and Florida, the second and fourth most populous states. There is significant interchange between surface and subsurface features, fluids, and waterborne materials. In many unconfined karstic aquifers, groundwater and surface water behave as a single body of water (2). The Edwards and Trinity aquifers are the only significant water sources for semiarid south central Texas, including San Antonio, the eighth largest city in the United States. The Edwards aquifer is one of the most permeable and productive carbonate aquifers in the world. It provides a public water supply to more than 2 million people, water for agriculture and industry, and discharges into major springs. These springs support recreation and business, provide flow to downstream users, and are a habitat for several threatened and endangered species. Its high porosity and permeability result in part from the development of secondary porosity and fracturing. The Trinity aquifer, by contrast, is much less permeable or productive than the Edwards. Its lithologies contain significantly more clay minerals and other siliciclastics, as well as minor evaporites. Nevertheless, it supplies water to scattered communities, ranches, and individual wells north of the Edwards in an area of rapid urbanization and growth.

Karstic limestone aquifers are characterized by three primary types of porosity: intergranular matrix porosity, fracture porosity, and the development of cavern conduits (3). A conduit is defined as any interconnected pathway for water of sufficient size to permit turbulent flow. Resistance to flow in conduits is much less than in the adjacent matrix, and, as a consequence, most regional flow is concentrated in conduits. Similarly, most local matrix flow is toward the nearest conduit. Thus, hydrodynamic gradients can vary significantly between conduit recharge and regional flow.

Contaminant dispersion would take place by a variety of methods using this model. Contaminants within conduits travel much more rapidly than those within the matrix, which follow Darcy's law and the advection–dispersion equation. However, exchange of contaminants between the two can occur under a variety of naturally occurring cycles, such as floods versus droughts. Thus the system should be modeled as a network of conduits embedded in a porous matrix (4). The complex depositional environments that produce carbonate rocks, their pronounced digenetic susceptibilities, and the fabric controls related to tectonic alteration of large carbonate units result in groundwater systems that are highly heterogeneous and poorly understood. Regional bedrock karstic limestone aquifers cannot be understood without critical information on the geologic boundary conditions.

CRYPTOSPORIDIUM

Cryptosporidiosis has been recognized as a human disease since 1976 (5). The first diagnosed waterborne outbreak of cryptosporidiosis in the world occurred in Braun Station, Texas, in 1984 (6). The first report of the disease associated with a contaminated municipal water supply was in 1987 in Carrollton, Georgia, where 13,000 became ill (7). This water system met all state and federal drinking water standards. In Milwaukee, Wisconsin, in 1993, municipal drinking water infected 400,000 people with *Cryptosporidium* and resulted in approximately 50 deaths (8,9). Subsequently, the Texas Department of Health reported a more recent water outbreak in Brushy Creek, Texas, in 1998. Overall, there have been 12 documented waterborne outbreaks of cryptosporidiosis in North America between 1985 and 1997; in two of these (Milwaukee and Las Vegas), mortality rates in the immunocompromised ranged from 52% to 68% (10).

Cryptosporidium parvum is a protozoan tissue parasite and is an agent of enterocolitis in mammals (11). *Cryptosporidium* has a complicated and extensive life cycle. The environmental stage is an oocyst, which is a metabolically dormant protective phase (12). The oocysts are nearly spherical and have a diameter of 4.5 to 5.5 μm. Their surfaces are slightly negative to neutrally charged in natural waters (13,14), and their density is close to that of water at 1.025 to 1.070 (14). The oocyst encases four sporozoites, each capable of infecting a host cell. Ingestion of as few as 10 oocysts can lead to infection; the feces of infected mammals may contain as many as 10^7 oocysts/mL (15).

Cryptosporidium can enter the environment via human and animal wastes. It has been found in marine water and bathing beaches in the vicinity of a nearby sewage outfall (16). Cryptosporidiosis has been reported in many domestic animals, especially cattle. An infected calf can excrete 10^{10} oocyts per day. In a study of farm drains, Kemp et al. (17) found 0.06 to 19.4 oocysts per liter, which can result in contamination of surface waters. Typical concentrations of *Cryptosporidium* in untreated domestic wastewaters are between 1 and 10 oocysts/mL (18) and in polluted streams, are between 0.1 to 100 oocysts/mL (19). *C. parvum* forms a hardy oocyst that can survive chlorine disinfection as commonly practiced in conventional water treatment (20,21). Furthermore, Chauret et al. (22) concluded oocysts exposed to environmental conditions are as resistant to inactivation by chlorination as freshly shed oocysts. *C. parvum* oocysts have also survived for weeks in surface waters (23).

Mawdsley et al. (24) quantitatively monitored the movement of *Cryptosporidium parvum* oocysts from livestock waste through low-permeability silt clay loam soil in laboratory column and box studies. In their box studies, livestock waste was applied to a portion of the surface of 20 cm deep by 80 cm long blocks of undisturbed low-permeability silt clay loam soil. The soil was contained within a tilted box and water was applied for 70 days. Oocysts were found in leachate in numbers ranging from 10^4 to 10^6 oocysts. Postsoil core analysis found decreasing numbers of oocyst with distance from inoculation.

Brush et al. (25) and Harter et al. (11) performed laboratory column studies of *Cryptosporidium parvum* oocyst transport and fate. Brush et al. examined oocyst transport through columns containing glass beads, well-sorted sand, and shale aggregates. In these short-duration studies, approximately 50% of the oocysts were retained in the sand and roughly 40% in the glass beads and shale. Despite the losses within the column, oocysts were eluted during the same timeframe as the conservative tracer chloride in the sand and glass beads. The velocity of *C.*

parvum oocyst through the shale aggregate was slightly faster than chloride ions. Brush et al. (13) suggest that this was due to size exclusion and not charge exclusion because of the nearly neutral surfaces of the oocysts. Brush et al. modeled the movement of oocyst with a one-dimensional convective–dispersion transport equation. Sorption was described as instantaneous equilibrium sorption where the relationship between sorbed and aqueous concentrations was linear. All loss processes, including decay, sieving, impingement, and settling, were modeled as a single (i.e., lumped) first-order rate process. The results of their modeling efforts indicated that oocysts experienced less shear and turbulence than dissolved chloride ions and that the oocysts did not adhere to the porous media.

Harter et al. (11) investigated the influence of pore-water velocity and sand grain size on the transport and fate of *Cryptosporidium parvum* oocysts. They used 10 cm long columns, groundwater of medium ionic strength (100 to 150 mg/L TDS), and bovine *Cryptosporidium parvum* oocysts. Their results indicated no trend between sand size and oocyst recovery in the three studies. They found that oocysts arrived before chloride and the elution of oocysts continued after chloride for all column studies. In a limited number of extended studies, tailing of oocyst concentration was observed until the end of the experiment (250+ pore volumes). The early breakthrough, as with Brush et al., was attributed to size exclusion. The tailing in oocyst elution was attributed to reversible deposition.

Harter et al. (11) used a more complex one-dimensional transport model to simulate their data. Filtration was modeled as a first-order irreversible process calculated from the physical properties of the soil (grain size, porosity, and bulk density), water (density, viscosity, pore velocity), and microbial colloid (density, size, diffusion coefficient). Sorption was modeled as a first-order, rate-limited reversible process. Half of the loss was attributed to irreversible filtration, but rate-limited reversible sorption could account for the early breakthrough and partially account for the extended tailing. Harter et al. called for further experimental and theoretical research to measure and explain the long-term elution behavior of *Cryptosporidium parvum* oocysts.

GIARDIA

Giardia lamblia is the cause of the most frequently identified intestinal disease in the United States (26). Humans become infected by ingesting giardia cysts, which are the environmentally resistant stage of giardia (27). Giardia cysts can survive for prolonged periods. For example, Bingham et al. (28) documented cysts surviving in distilled water for 77 days at 8 °C. In another study, cysts of *Giardia muris* (a species that infects mice but is often used as analogue for *Giardia lamblia*), survived 28 and 56 days in lake water at depths of 4.5 meter (19 °C) and 9 m (6.6 °C), respectively. In cold river water (0–2 °C), cysts survived for 56 days (28). Typical concentrations of *Giardia* are between 1 and 100 cysts/mL in untreated domestic wastewater (18) and about 1 cyst/mL in polluted streams (19).

The *Giardia* cysts, which are 8–16 μm in diameter, are somewhat resistant to typical levels of wastewater treatment methods. During primary settling, only 0–53% of cysts are removed. Secondary treatment with clarification can remove 98.6–99.7% of cysts (28). Advanced tertiary treatment can further reduce the numbers of cysts by physical filtration and precipitation.

MICROSPORIDIUM

Microsporidia are unicellular protozoan parasites that infect a wide variety of animals, from insects and fish to every class of mammal, including humans. The vehicle for transmitting these organisms is its spores, which are shed from infected individuals (animal and human) via the urine, feces, respiratory sputum, and upon death and decay. Human infections are of concern in immunodeficient patients, especially those who are HIV+, and may infect a broad range of tissues. *Enterocytozoon bieneusi* and *Encephalitozoon intestinalis* are the most common species of microsporidia isolated from patients with chronic diarrhea attributed to microsporidiosis (29,30). Exact routes of transmission for human microsporidial infection have not been confirmed, but considerable evidence supports fecal–oral, sexual, respiratory, and waterborne routes (29–31).

The potential for waterborne transmission of spores is the focus of our research. At least two published studies have detected the presence of *E. bieneusi* (32) or *E. bieneusi, E. intestinalis*, and *Vittaforma corneae* (another human pathogenic microsporidium) (33,34) in surface water using the polymerase chain reaction (PCR). Hutin et al. reported in a case-controlled risk factor analysis of HIV+ individuals in France that the greatest risk for intestinal microsporidiosis was use of a swimming pool in the prior 12 months.

At least one outbreak of microsporidiosis has been described and attributed to contaminated drinking water originating from a particular treatment plant. According to Cotte et al. (31), an outbreak of intestinal microsporidiosis in the summer of 1995 affected 200 people (all apparently HIV+), or about 1% of the HIV+ population in the study area. Additionally, 15% of the 361 patients from whom microsporidia were identified during the 3-year study had no known immunodeficiency condition. The clustering of residences of infected individuals in the town of Lyon, France, led the authors to suggest that a water treatment facility serving the area may have been a contributing factor to these cases. This plant employs flocculation, ozoflotation, and filtration but not chlorination in the treatment process and uses surface water as a water source.

A few studies have described the susceptibility of human-pathogenic microsporidial spores to drinking water treatment methods and environmental conditions. Laboratory studies by Kucerova-Posisilova et al. (35) indicate that *E. intestinales* spores retain infectivity for at least 2 weeks at temperatures up to 33 °C. However, information on the viability of spores concentrated from the environment has yet to be published to our knowledge. A very recent study by Wolk et al. (36) determined that a chlorine concentration of 2 mg/L with exposure for at least 16 minutes resulted in a 99.9% reduction in the viability of *E. intestinalis* spores. Microsporidia were detected in four recreational water samples from Arizona; one was confirmed as *E. intestinalis*. In addition to the three recreational water samples, three irrigation water samples from Mexico and two from Arizona were positive for microsporidia. One of the samples from Mexico was confirmed as *E. intestinalis. V. corneae* spores were identified from irrigation water from Costa Rica and from secondary sewage from Tucson, Arizona (37).

In summary, mounting evidence demonstrates that microsporidia are found in water, may originate from human and animal reservoirs, and need to be considered as potential waterborne pathogens. As such, more information is needed on the incidence and survival of spores in the environment and through the treatment process.

BACTERIOPHAGE

Several bacteriophage transport studies have been conducted under well-characterized conditions [see recent review by Schijven and Hassanizadeh (38)]. The bacteriophages PRD-1 and MS-2 are often employed as surrogates for viruses of concern in human health (39,40) because of the hazards and costs associated with human viruses.

CALCULATING FLOW IN KARSTIC LIMESTONE AQUIFERS

In karstic limestone aquifers, groundwater often flows through highly permeable flow paths formed by dissolution along faults, fractures, bedding plane partings, or stratigraphic features. Compared with diffuse flow through granular aquifers, groundwater velocities in karstic systems can be very high, often in the range of miles per day. Consequently, karstic aquifers require a much larger wellhead protection area than common for wells in sand and gravel.

Multiple options exist for modeling flow and transport in karstic aquifers. For simple applications requiring only global water balances in steady-state conditions, existing modeling tools such as MODFLOW have served adequately. For modeling responses to storms or contaminant movement, more advanced models involving explicit flow features (40), irregular grids, and/or multiple interacting flow systems (41) are needed. Software tools necessary for explicit modeling of karst features have recently appeared (42).

TRANSPORT MODELS

Models for microbe transport and of colloid transport in general are analogous to solute transport models nonideal sorption terms account for rate limitations in the attachment/detachment processes. The relevant physical processes include advection, dispersion, attachment/detachment, physical filtration, inactivation, and advection facilitated by sorption on other types of colloids (38). Early models of microbe transport in saturated porous media used the equilibrium sorption assumption and an empirical distribution coefficient to model microbe attachment/release (43,44). These equilibrium sorption models performed poorly in case studies (45) and fail to reproduce the results of experiments that show unretarded breakthrough and slow (nonequilibrium) release (50). Modern models of microbe transport and of colloid transport in general use kinetic models for attachment/release. Single-site kinetic models are often used (46–49). Bales et al. (50) use a two-site model with one set of sites in equilibrium and the other kinetically controlled. Bhattacharjee et al. (55) and Schivjen et al. (56) use two-site models wherein attachment to both types of sites is kinetically controlled but with different rate constants. Schivjen et al. (56) analyze several laboratory experiments and clearly demonstrate that a two-site kinetic model is necessary to reproduce the measured breakthrough curves.

Most previous studies use the first-order rate law. Second-order rate laws have been used to model sorption of inorganic colloids (49) and microbes (55). In either case, attachment rates may be empirical or determined from mechanistic models of colloid filtration (46,49). Combinations of empirical rates and mechanistic rate models have also been used (48). When mechanistic models are used to calculate the attachment rate, models for colloid filtration in packed-bed reactors (50) are the usual choice.

Transport facilitated by other colloids is another process to be considered. Schivjen and Hassanizadeh (38) note that the removal rate for viruses declines with increasing travel distance, and that this nonlinear removal may be due to partial attachment to other colloidal particles. Colloid-facilitated transport is of particular concern in karst systems that often have large amounts of suspended sediments whose attributes are favorable for facilitating transport (51,52). Two studies (48) have addressed the effect of random spatial variability of hydraulic conductivity on microbe transport. These studies clearly provide important insights into the effect of spatial variability on microbe transport but are better suited to granular aquifers, where spatial variability can be more readily represented as a simple random space function.

BIBLIOGRAPHY

1. National Research Council: Committee on Science and Technology for Countering Terrorism. (2002). *Making the Nation Safer: The Role of Science and Technology in Countering Terrorism*. National Academy Press, Washington, DC, p. 251.
2. Katz, B.G., DeHan, R.S., Hirten, J.J., and Catches, J.S. (1997). Interactions between ground water and surface water in the Suwannee River Basin, Florida. *J. Am. Water Resour. Assoc.* **33**: 1237–1254.
3. Martin, J.B. and Screaton, E.J. (2001). *Exchange of matrix and conduit water with examples from the Floridian Aquifer*. United States Geological Survey Water-Resources Investigations Report 01-4011: 38–44.
4. Loper, D. (2001). *Steps Toward Better Models of Transport in Karstic Aquifers*. United States Geological Survey Water-Resources Investigations Report 01-4011: 56–57.
5. Meisel, J., Perra, R., and Meloigro, C. (1976). Overwhelming watery diarrhea associated with cryptosporidium in an immunosuppressed patient. *Gastroenterology* **70**: 1156–1160.

7. Avery, B.K. and Lemley, A. (1996). *Cryptosporidium: A Waterborne Pathogen*. Cornell University, Ithaca, NY, under the sponsorship of the U.S. Department of Agriculture's Working Group on Water Quality.
8. MacKenzie, W. et al. (1994). A massive outbreak in Milwaukee of Cryptosporidium infection transmitted through the public water supply. *N. Engl. J. Med.* **331**: 161–167.
9. Hoxie, N.J., Davis, J.P., Vergeront, J.M., Nashold, R.D., and Blair, K.A. (1997). Cryptosporidium-associated mortality following a massive waterborne outbreak in Milwaukee, Wisconsin. *Am. J. Public Health* **87**: 2032–2035.
10. Rose, J. (1997). Environmental ecology of Cryptosporidium and public health implications. *Annu. Rev. Public Health* **18**: 135–161.
11. Harter, T.W. and Atwill, E.R. (2000). Colloid transport and filtration of Cryptosporidium parvum in sandy soils and aquifer sediments. *Environ. Sci. Technol.* **34**: 62–70.
12. Reynolds, K.A. and Pepper, I.L. (2000). Microorganisms in the environment. In: *Environmental Microbiology*. R.M. Maier, I.L. Pepper, and C.P. Gerba (Eds.). Academic Press, San Diego, CA.
13. Brush, C., Walter, M., Anguish, L., and Ghiorse, W. (1998). Influence of pretreatment and experimental conditions on electrophoretic mobility and hydrophobicity of Cryptosporidium parvum oocysts. *Appl. Environ. Microbiol.* **64**: 4439–4445.
14. Medema, G.J., Bahar, M., and Schets, F.M. (1997). Survival of Cryptosporidium parvum, Escherichia coli, faecal enterococci and Clostridium perfringens in river water: Influence of temperature and autochthonous microorganisms. *Water Sci. Technol.* **35**: 249–252.
15. Casemore, D.P., Wright, S.E., and Coop, R.L. (1997). In: *Cryptosporidium and Cryptosporidiosis*. R. Fayer (Ed.). CRC Press, Boca Raton, FL, pp. 65–92.
16. Johnson, D.C., Reynolds, K.A., Gerba, C.P., Pepper, I.L., and Rose, J.B. (1995). Detection of Giardia and Cryptosporidium in marine waters. *Water Sci. Technol.* **31**: 439–442.
17. Kemp, J.S., Wright, S.E., and Bukhari, Z. (1995). On farm detection of Cryptosporidium parvum in cattle, calves and environmental samples. In: *Protozoan Parasites and Water*. W.B. Betts, D. Casemore, C. Fricker, H. Smith, and J. Watkins (Eds.). The Royal Society of Chemistry, Cambridge, UK.
18. Metcalf, R. and Eddy, I. (1991). *Wastewater Engineering*. McGraw-Hill, New York.
19. USEPA. (1998). *Comparative Health Risk Effects Assessment of Drinking Water*. United States Environmental Protection Agency, Washington, DC.
20. Kornich, D.G. et al. (1990). Effects of ozone, chlorine dioxide, chlorine, and monochloramine on *Cryptosporidium parvum* oocyst viability. *Appl. Environ. Microbiol.* **56**: 1423–1428.
21. Venczel, L.V., Arrowood, M., Hurd, M., and Sobsey, M.D. (1997). Inactivation of Cryptosporidium parvum oocysts and Clostridium perfringens spores by a mixed-oxidant disinfectant and free chlorine. *Appl. Environ. Microbiol.* **63**: 1598–1601.
22. Chauret, C., Nolan, K., Chen, P., Springthorpe, S., and Satter, S. (1998). Aging of Cryptosporidium parvum oocysts in river water and their suspectibility to disinfection by chlorination and monochloramine. *Can J. Microbiol.* **44**: 1154–1160.
23. Johnson, D.C. et al. (1997). Survival of Giardia, Cryptosporidium, poliovirus and Salmonella in marine waters. *Water Sci. Technol.* **35**: 261–268.
24. Mawdsley, J., Brooks, A., Merry, R., and Pain, B. (1996). Use of a novel soil tilting table apparatus to demonstrate the horizontal and vertical movement of the protozoan pathogen Cryptosporidium parvum in soil. *Biology and Fertility Soils* **23**: 215–220.
25. Brush, C.G., Anguish, L.J., Parlange, J., and Grimes, H.G. (1999). Transport of Cryptosporidium parvum oocysts through saturated columns. *J. Environ. Qual.* **28**: 809–815.
26. Adams, R. (1991). The biology of giardia. *Microbiol Rev.* **55**: 706–732.
27. Rusin, P., Enriquez, C.E., Johnson, D., and Gerba, C.P. (2000). Environmentally transmitted pathogens. In: *Environmental Microbiology*. R.M. Maier, I.L. Pepper, and C.P. Gerba (Eds.). Academic Press, San Diego, CA, pp. 447–489.
28. Deregnier, D., Cole, L., Schupp, D., and Erlandsen, S. (1989). Viability of Giardia cysts suspended in lake, river and tap water. *Appl. Environ. Microbiol.* **55**: 1223–1229.
29. Hutin, Y.J.F. et al. (1998). Risk factors for intestinal microsporidiosis in patients with human immunodeficiency virus infection: A case-control study. *J. Infect. Dis.* **178**: 904–907.
30. Franzen, C. and Muller, A. (1999). Molecular techniques for detection, species differentiation, and phylogenetic analysis of microsporidia. *Clin. Microbiol. Rev.* **12**: 243–285.
31. Cotte, L. et al. (1999). Waterborne outbreak of intestinal microsporidiosis in persons with and without human immunodeficiency virus infection. *J. Infect. Dis.* **180**: 2003–2008.
32. Sparfel, J.M. et al. (1997). Detection of microsporidia and identification of *Enterocytozoon bieneusi* in surface water by filtration followed by specific PCR. *J. Eukaryotic Microbiol.* **44**: 78S.
33. Dowd, S., Gerba, C., Kamper, M., and Pepper, I. (1998). Evaluation of methodologies including immunofluorescent assay (IFA) and the polymerase chain reaction (PCR) for detection of human pathogenic microsporidia in water. *Can. J. Microbiol.* **44**: 1154–1160.
34. Dowd, S.E., Gerba, C.P., and Pepper, I.L. (1998). Confirmation of the human-pathogenic microsporidia *Enterocytozoon bieneusi*, *Encephalitozoon intestinalis*, and *Vittaforma corneae* in water. *Appl. Environ. Microbiol.* **64**: 3332–3335.
35. Kucerova-Pospisilova, Z., Carr, D., Leitch, G., Scanlon, M., and Visvesvara, G. (1999). Environmental resistance of *Encephalitozoon* spores. *J. Eukaryotic Microbiol.* **46**: 11S–13S.
36. Wolk, D.M. et al. (2000). A spore counting method and cell culture model for chlorine disinfection studies of Encephalitozoon syn. Septata intestinalis. *Appl. Environ. Microbiol.* **66**: 1266–1273.
37. Gerba, C.P. (1999). Virus survival and transport in groundwater. *J. Ind. Microbiol. Biotechnol.* **24**: 247–251.
38. Schijven, J.F. and Hassanizadeh, S.M. (2000). Removal of viruses by soil passage: Overview of modeling, processes, and parameters. *Crit. Rev. Environ. Sci. Technol.* **30**: 49–127.
39. Gerba, C.P. (1984). Applied and theoretical aspects of virus adsorption to surfaces. *Adv. Appl. Microbiol.* **30**: 133–168.
40. Sudicky, E.A. and McLaren, R.G. (1992). The Laplace transform Galerkin technique for large-scale simulation of mass transport in discretely fractured porous formations. *Water Resour. Res.* **28**(2): 499–514.
41. Teutsch, G. (1993) An extended double-porosity concept as a practical modelling approach for a karstified terrain. In: *Hydrogeological Processes in Karst Terranes*. G. Gultekin,

A.I. Johnson, and W. Back (Eds.). *IAHS Publication 207*, Wallingford, UK, pp. 281–292.

42. Diersch, H-J.G. (2002). *Interactive, Graphics-Based Finite-Element Simulation System FEFLOW for Modeling Groundwater Flow, Contaminant Mass and Heat Transport Processes*. WASY Ltd., Berlin.
43. Park, N-S., Blanford, T.N., and Huyakorn, P.S. (1991). *VIRALT: A Model for Simulating Viral Transport in Groundwater, Documentation and User's Guide*. Version 2.0. Hydrogeol., Inc., Herndon, VA.
44. Tim, U.S. and Mostaghimi, S. (1991). Model for predicting virus movement through soils. *Ground Water* **29**(2): 251–259.
45. Yates, M.V. (1995). Field evaluation of the GWDR's natural disinfection criteria. *J. Am. Water Works Assoc.* **87**: 76–85
46. Dowd, S.E., Pillai, S.D., Wang, S.Y., and Corapcioglu, M.Y. (1998). Delineating the specific influence of virus iso-electric point and size on virus adsorption and transport through sandy soils. *Appl. Environ. Microbiol.* **64**(2): 405–410.
47. Sim, Y. and Chrysikopoulos, C.V. (1996). One-dimensional virus transport in porous media with time-dependent inactivation rate coefficients. *Water Resour. Res.* **32**(8): 2607–2611.
48. Rehmann, L.L.C., Welty, C., and Harvey, R.W. (1999). Stochastic analysis of virus transport in aquifers. *Water Resour. Res.* **35**(7): 1987–2006.
49. Saiers, J.E., Hornberger, G.M., and Liang, L. (1994). First- and second-order kinetics approaches for modeling the transport of colloidal particles in porous media. *Water Resour. Res.* **30**(9): 2499–2506.
50. Yao, K.M., Habibian, M.T., and O'Melia, C.R. (1971). Water and waste water filtration: Concepts and applications. *Environ. Sci. Technol.* **5**(11): 1105–1112.
51. Mahler, B.J., Lynch, L., and Bennett, P.C. (1999). Mobile sediment in an urbanizing karst aquifer: implications for contaminant transport. *Environ. Geol.* **39**(1): 25–38.
52. Mahler, B.J., Personne, J.C., Lods, G.F., and Drogue, C. (2000). Transport of free and particulate-associated bacteria in karst. *J. Hydrol.* **238**(3–4): 179–193.
53. Gerba, C.P. and Naranjo, J.E. (2000). Microbiological water purification without the use of chemical disinfection. *Wilderness Environ. Med.* **11**: 12–16.

PARTICULATE REMOVAL

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Coagulation is used in water treatment plants as a pretreatment step to remove particulate matter (such as clay and silt particles, bacteria, viruses, and protozoan cysts) and dissolved materials, especially natural organic material (NOM). Although the removal of particulate matter continues to be an important reason for using coagulation, recent concern about carcinogenic byproducts has emphasized that a coagulation process must also optimize the removal of NOM to reduce the formation of disinfection byproducts. Coagulation is a process for enhancing the tendency of particulate matter in aqueous suspension to attach to one another and/or to attach to collector surfaces. Coagulation promotes destabilization of surface charges on colloidal particles. Destabilization and aggregation of particulate matter and precipitation or adsorption of NOM in subsequent solid–liquid separation processes are the primary functions of a coagulation process. The coagulation process involves two steps: (1) the addition of chemical coagulants to destabilize particulate matter and react with NOM and (2) physical transport of collisions among particulate matter resulting in their aggregation or floc formation. In the water treatment literature, coagulation refers to all reactions and mechanisms that result in aggregation, and the physical transport step of producing interparticle aggregation is called flocculation. In water treatment plant operation, coagulation is achieved by rapid or flash mixing of coagulants followed by flocculation.

The other example of particle alteration and particle production process technology is chemical oxidation. The main application of this process is in iron and manganese removal. Iron and manganese are relatively soluble under reducing conditions, for example, in groundwater, stagnant surface water, and certain lakes. Dissolved iron and manganese are usually removed from water by oxidizing them under engineered conditions to their insoluble forms by adding an oxidant and removing the precipitated ferric hydroxide and manganese dioxide by sedimentation and filtration. The oxidants used most often for this are oxygen, chlorine, permanganate, chlorine dioxide, and ozone.

Sedimentation is a particle separation process (Fig. 1). In conventional water treatment systems, it follows flocculation and precedes filtration. Its purpose is to enhance the filtration process by removing particulate matter. Sedimentation requires that water flow through the basin at a slow enough velocity to permit the particulate matter to settle to the bottom of the basin before the water exits the basin. The equipment required for this process includes a rectangular, square, or circular settling basin. The basin includes provisions for inlet and outlet structures and a sludge collection system. In addition, sedimentation systems are optionally equipped with tube or plate settlers to improve performance. The settling velocity of the particles or particulate matter is governed by the particle size, shape, density, and water viscosity (which varies with temperature). The surface overflow rate is the primary design parameter for sizing sedimentation basins. This rate is defined as the rate of inflow (Q) divided by the tank surface or floor area (A). Units are typically rated in gallons per day per

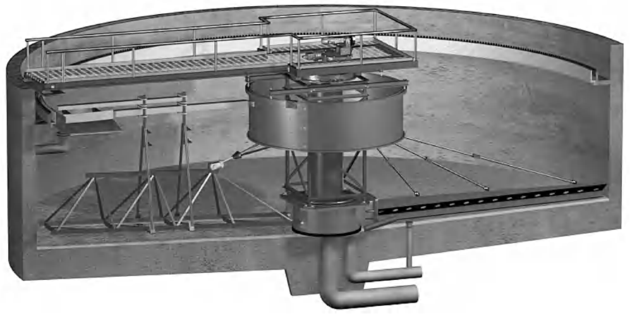

Figure 1. Circular sedimentation tank (*Source*: U.S. Filter).

square foot, gallons per minute per square foot, or cubic meters per hour per square meter. Design hydraulic overflow rates vary with the nature of the settling solids, water temperature, and hydraulic characteristics of the sedimentation basin. The settling efficiency for ideal conditions is independent of the depth and dependent on the tank plan or surface area. In reality, depth is important because it can affect flow stability if it is large and scouring if it is small.

In a conventional water treatment process train, filtration follows sedimentation. Particulate matter that is removed by this process includes microorganisms (bacteria, viruses, and protozoan cysts), clay and silt particles, colloidal and precipitated humic substances and other organic particulates from natural decay of vegetation, precipitates of aluminum or iron coagulation processes, calcium carbonate and magnesium hydroxide precipitates from lime softening, and iron and manganese precipitates. A number of different types of filters are used in water filtration, and they are described by various classification schemes. The most common filtration technologies used in water supply systems are rapid sand filtration, slow sand filtration, package plants, diatomaceous earth filtration (precoat filtration), membrane filters, and cartridge filters. High-rate granular filters or rapid sand filters are most widely used in conventional treatment and direct filtration (Fig. 2). Granular medium filtration is a water treatment process that uses a porous medium through which water passes to remove particulates or suspended solids. For granular medium filtration to be effective, source water must be pretreated. Chemical destabilization is an essential prerequisite for effective filtration. Chemicals used for particle destabilization are limited primarily to metal salts or cationic polymers as primary coagulants. Pretreatment may also include aeration or introducing an oxidant if water treatment aims to remove iron or manganese. Sometimes, a filter aid polymer is added in the influent to the filter to improve particle capture efficiency. Filtration by granular media consists of three principal mechanisms: (1) transport, (2) attachment, and (3) detachment. *Transport* mechanisms move a particle into and through a filter pore so that it comes very close to the surface of the filter medium or existing deposits where *attachment* mechanisms retain the suspended particle in contact with the medium's surface or with previously deposited solids. *Detachment* mechanisms result from the hydrodynamic forces of flow acting so that a certain portion of the previously attached particles, less strongly adhered to others, is detached from the filter medium or previous deposits and carried further, deep into or through the filter.

Flotation can be described as a particle separation process. It is a gravity separation process in which gas bubbles attach to solid particles to make the apparent density of the bubble–solid agglomerates less that of water, thereby allowing the agglomerate to float to the surface. The floated material (float) is removed from the surface, and clarified water is taken from the bottom of the flotation tank. Different methods of producing gas bubbles give rise to different types of flotation processes, which are electrolytic flotation, dispersed-air flotation, and dissolved air flotation (Fig. 3). Flotation is employed mainly for treating nutrient-rich reservoir waters that may contain heavy algal blooms and for low-turbidity, low-alkalinity waters.

In recent years, there has been considerable interest in using ultrafiltration (UF) or microfiltration (MF) membranes for particle separation in potable water treatment (Fig. 4). Similar to depth filtration, the performance of membrane filtration units is likely to be affected by the concentration and size of particles in raw water as well as the dissolved organic carbon

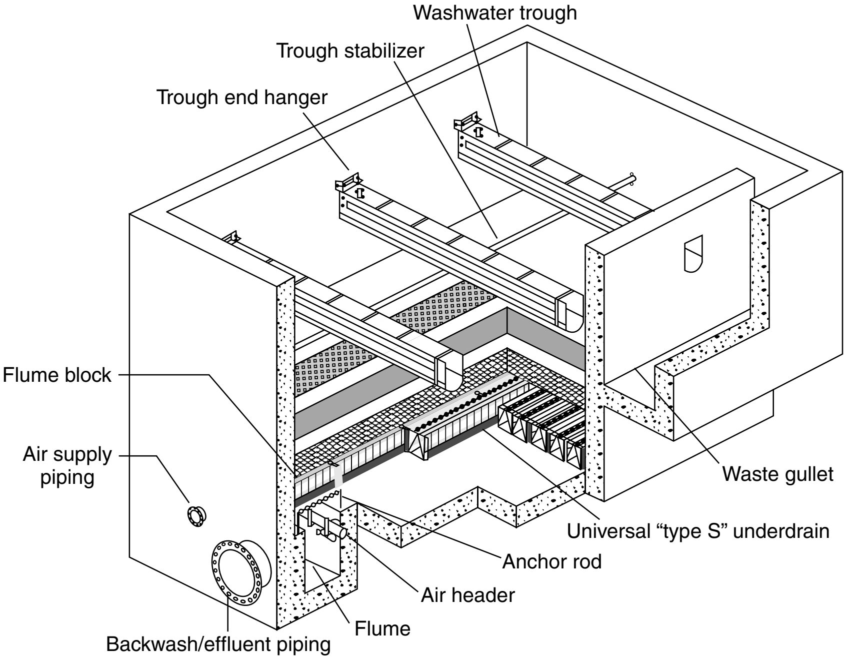

Figure 2. Rapid gravity filter box (*Source*: F.B. Leopold Co.).

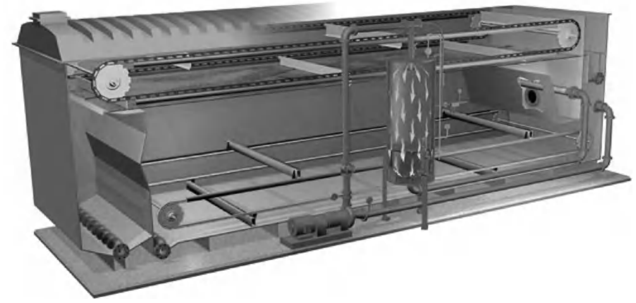

Figure 3. Dissolved air flotation (DAF) system (*Source*: U.S. Filter).

Figure 4. Membrane filtration system (*Source*: PALL).

(DOC). Particles of an effective size larger than the minimum pore size (or membrane cutoff) will be removed by the membrane. Permeate flux is closely related to the pressure drop across the membrane filter. Materials that accumulate on the membrane filter produce an additional layer of resistance to flow that is manifested as an increase in head loss or pressure drop across the membrane. A frequent backwash (every 15 min to 1 h) removes the cake formed on the membrane surface. In a conventional UF or MF process, the driving force to produce filtrate can work in two ways: Positive pressure moves fluid through the fibers; negative pressure moves fluid through fibers under vacuum pressure. The conditions under which membrane filtration processes might be preferable to granular medium filtration or conventional treatment are still largely unknown.

The selection of particulate removal technologies should be based on treatment objectives and control requirements. This process involves a number of basic data and other considerations, including effluent requirements, influent characteristics, existing system configuration, required investment, operation and maintenance (O&M), additional pretreatment and posttreatment processes, and waste management.

READING LIST

ASCE and AWWA. (1998). *Water Treatment Plant Design*. 3rd Edn. McGraw-Hill, New York.

AWWARF. (1998). *Treatment Process Selection for Particle Removal*. American Water Works Association Research Foundation, Denver, CO.

AWWA. (1999). *Water Quality and Treatment*. 5th Edn. McGraw-Hill, New York.

Hudson, H.E. (1981). *Water Clarification Processes*. Van Nostrand Reinhold Company, New York.

Kawamura, S. (2000). *Integrated Design of Water Treatment Facilities*. John Wiley & Sons, New York.

USEPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*. Office of Drinking Water, Center for Research Information, Cincinnati, OH.

PHARMACEUTICALS IN WATER SYSTEMS

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THE EMERGING PROBLEM OF PHARMACEUTICALS IN THE ENVIRONMENT

As the demographic pattern in most regions of the world changes in response to epidemiological transition, life expectancy is lengthened, and human reliance on medications to maintain the quality of life intensifies. It is now indisputable that widespread use of pharmaceutical products results in their release into the environment. This occurs primarily through the excretion of partially metabolized doses and the disposal of expired or unused medication (1–3). It is inevitable that that these fugitive releases lead to exposures of aquatic organisms and other natural ecosystem components. However, the driving force behind recent concerns is the potential for large-scale human exposures through natural drinking water recycling processes. Historically, most investigations of anthropogenic chemicals in the environment have focused on acutely toxic industrial chemicals from mining, energy, and agricultural industries. The environmental impacts of products emanating from the pharmaceutical industry have largely been excluded from scrutiny. The U. S. Geological Survey conducted the first national survey of pharmaceutical products in natural water systems in 2000. The results of that study confirmed prior suspicions about the widespread contamination of aquatic systems by these products (4).

The conclusions of several investigations of pharmaceuticals in the environment have now demonstrated an urgent need for rigorous ecological evaluation of potentially harmful prescription and over-the-counter products. These include hormones, antibiotics, analgesics, steroids, and their bioactive metabolites that are continuously introduced into the environment from the disposal of partially treated domestic wastewater. The fate of these compounds in the aquatic ecosystem depends in part on their chemical structure and physicochemical characteristics, including solubility in water and lipids, adsorption to soil particles, volatility, and potential biodegradability. These characteristics determine whether the chemicals will bioaccumulate through the foodweb, partition into sediments, mobilize through groundwater, or impact drinking water resources (5).

Information is sparse on the ecological effects of pharmaceutical products in the environment because the mode of action, dose response, and pharmacokinetic metabolism in humans are not fully understood for many medications. Therefore, it is difficult to predict with reasonable certainty, how specific pharmaceutical products will affect the myriad species that may become exposed following the release of pharmaceutical chemicals into the environment. However, there is a growing body of evidence that subtle, chronic effects from low-level exposures are occurring. These effects are occurring, in particular, from hormonal products and from chemicals that are known to induce the expression of phylogenetically conserved genes and the production of key metabolic enzymes (3).

For nontarget (e.g., aquatic) organisms whose chemical receptors are similar to those found in humans, it is possible to predict unintentional physiological effects of exposure to pharmaceutical products such as growth and reproductive hormones. In fact, estrogen receptors have been designed to monitor the occurrence and distribution of estrogenic pharmaceutical compounds in the environment. However, the sensitivity of such monitoring systems means that they can recognize chemicals from sources other than the pharmaceutical industry (6). Although understanding chemical interactions with biological receptors has been very useful for predictive modeling of the ecosystemic effects of pharmaceutical products, there is only rudimentary knowledge of potential synergistic and additive effects due to human or wildlife exposure to multiple pharmaceutical products found in many contaminated systems. In addition, unlike persistent organic pollutants from other industrial sectors, pharmaceutical contaminants do not necessarily have to be persistent to exert major physiological effects. This is due in part to the trained potency of their actions and the fact that concentrations in receiving waters are constantly replenished through the disposal of contaminated wastewater effluents (7). To initiate a thorough understanding of which pharmaceutical products are most likely to pollute water systems and which products are likely to provoke disturbances to ecosystemic and public health, either alone or in interactions with other chemicals, it is important to evaluate the societal distribution of pharmaceuticals with respect to prescription volume, doses, and disposal.

DISTRIBUTION OF PHARMACEUTICALS IN THE UNITED STATES

The pharmaceutical industry is a major contributor to the global economy; annual commercial transactions in prescription drugs in the United States approach $300 billion. In the year 2001, approximately 3.1 billion pharmaceutical prescriptions were filled for several thousand different medicinal chemicals in the United States alone (8). The top-ranked pharmaceuticals products prescribed in 2002 are presented in Table 1. The identity of popular prescriptions and their associated medical functions provides a reasonable summary of the societal burden of diseases. Attention to the quantity of drug doses multiplied by the number of each prescription is also a reasonable estimate of the quantity of potent drugs that enters the domestic sector annually. Very little attention has been paid to the question of what happens to the drugs after they leave the human body. In general, many drugs are prescribed at doses that can be supported by human metabolic capacity. Quite frequently, administered drugs and their partial metabolites leave the human body through excretion in urine and feces soon after ingestion. The period of excretion for some drugs may last for days (2,3). The list of products in Table 1 does not include those used in the agricultural industry, although they are important contributors to the distribution of pharmaceuticals into the environment, particularly antibiotics (9). Veterinary pharmaceutical products are routinely dispersed into the environment through the same pathways as human medications, but in many cases, there is no benefit of sewage treatment to reduce the concentration of influent pharmaceuticals because animal wastes can contaminate surface waters directly (2).

The top 20 pharmaceutical products found in streams during a reconnaissance project conducted by the U.S. Geological Survey between 1999 and 2000 are shown in Table 2. The data are limited by the narrow scope of chemicals investigated, compared to the main categories of prescriptions drugs presented in Table 1. Caffeine, the fourth ranked most commonly found organic chemical in surface waters, is the first in the list to be associated with pharmaceutical products, although its main source is dietary. Caffeine is an inducer of cytochrome P450 enzymatic activity in humans and in wildlife. Its presence in water systems is due to its resistance to biodegradation in many wastewater treatment processes. Therefore, caffeine has been used as a reliable tracer of wastewater effluent discharge, and it has been proposed as a monitoring sentinel for the distribution of pharmaceutical products in the environment (10,11).

FATE OF PHARMACEUTICALS IN SEWAGE TREATMENT FACILITIES

The capacity of human physiological systems to metabolize pharmaceutical products varies greatly from complete breakdown of a compound into various metabolites to excretion by the consumer in an essentially unaltered free form. The degree of metabolism is a function of chemical characteristics; the genetic, physiological, and dietary potential of the consumer; and the timing of the dose (2). Some pharmaceutical degradation products can be more bioactive than the parent compound, and the nontoxic conjugates can later be converted by microbial action to the original bioactive parent compound (4). It is also possible for microbial action to convert certain pharmaceutical products into chemicals that could resemble pollutants from other industries, thereby confusing monitoring programs and enforcement regulations. For example, (Fig. 1) shows the hypothetical pathway for the biodegradation of clofibrate, a hypolipidemic medicinal product commonly found in contaminated water systems when it enjoyed a

Table 1. Characteristics of Top Prescription Pharmaceutical Products in the United States[a]

Drug Category, 2001 Rank Order	Total Prescriptions for 2000, Millions	Leading Product	Manufacturer	Function	Prescriptions per Year (1999) (Millions)	Quantity per Dose, mg	Human Metabolite, % Excreted	Conc. in Surface Water, μg/L[b]
Codeine and combinations	124.2	Hydrocodone	Watson Laboratories	Pain reliever; antitussive and opioid analgesic	30.4	5–7.5	Codeine and morphine up to 10 μg/mL in urine	0.1–1.0 (codeine)
Cholesterol reducers	96.9	Lipitor (Atorvastatin)	Parke-Davis	Lipid-lowering	37.7	10–40	Varies	No data
Synthetic thyroid hormone	70.2	Synthroid (Levothyroxine)	Knoll	Thyroid hormone	41.1	50–200 μg	Varies	No data
Estrogen/Progesterone	79.1	Premarin (conjugated estrogens)	Wyeth-Ayerst	Reproductive hormone therapy	47.8	0.3–2.5 (tablet)	Varies	
						25 (injection)		
		Estrone						0.11
		Equilin						0.15
		17-a-Dihydroequilin				0.625/g (cream)		
		17-a-Estradiol						
		Equilenin						0.03
		17-a-Dihydroequilenin						0.14
Beta blockers	87.6	Atenolol (Tenormin)	Geneva Pharm	Antihypertensive; antianginal	12.4	50	Varies	No data
Aminopenicillins	62.3	Trimox	Apothecon	Antibiotic	24.8	125–500	Up to 0.73	No data
Diuretics	49.6	Furosemide (Lasix)		Hypertension	16.0	10	Varies	No data
		Hydrochlorothiazide	Parke-Davis					
Calcium blockers	94.1	Amlodipine (Norvasc)	Pfizer	Hypertension	27.1	5–10	Varies	No data
Steroid antibronchospasm	–	Albuterol	Warrick	Asthma	–	0.5% or 200 μg	20–70% of absorbed dose in urine	No data
		Ventolin						
Benzodiazepines	66.6	Alprazolam (Xanax)	Pharmacia/Upjohn	Anxiety disorder	1.8	0.25–2	Varies	No data
Proton pump inhibitors	60.1	Prilosec	Astra	Proton pump inhibitor (heartburn)	31.1	20–40	Varies	No data
Propoxyphene compound	–	Propoxyphene HCl		Narcotic	–	65	Varies	No data
		Aspirin		Analgesic		389		
		Caffeine		Pain relief		32.4		
Selective serotonin reuptake Inhibitor/Selective Norepinephrine reuptake inhibitors (SSRI/SNRI)	96.4	Prozac	Lilly	Antidepressant	24.7	20–80	Varies	No data
		Zoloft	Pfizer	Antidepressant	23.1	50–200		
ACE inhibitors	94.1	Zestril (Lisinopril)	Zeneca	Hypertension	20.7	2.5–40	Varies	No data
Antiarthritic	61.3	Celebrex	Searle	Rheumatoid arthritis; osteoarthritis	17.5	100–400	Varies	No data
Antihistamines	59.1	Claritin	Schering	Environmental allergies	25.4	10	Varies	No data
Seizure disorders	57.0	Lamictal	Glaxo	Epilepsy and seizures	–	12.5–200	Varies	No data
		Dilantin	Parke-Davis			30–100		

[a] Reference 8.
[b] Reference 4.

high prescription rate in the 1980s. Human metabolism of clofibrate produces clofibric acid, which is excreted in feces and disposed of into the domestic sewer system. The structure of clofibric acid suggests that heterotrophic bacteria can cleave the side chain to produce chlorobenzoate and/or chlorobenzene, which are chemicals commonly associated with the petrochemical solvent industry.

Pharmaceutical products, their synthetic precursors, and biotransformation products are continuously released into the environment through consumer excretion and through the disposal of unused or expired medications. Although sewage treatment facilities are the most obvious sinks for pharmaceutical products, municipal landfills are also important sinks for solid products that are disposed of with domestic solid waste (3). In addition, episodic leakage of sewer lines and overflow of veterinary solid waste contaminated with pharmaceuticals may lead to the release of completely untreated medicines into the environment (5). In the United States, about a million homes do not have sewage treatment systems but instead rely on direct discharge of raw sewage into streams by "straight-piping" (3). Some Canadian cities reportedly discharge 3.25 billion liters per day of essentially untreated sewage into surface waters and the ocean (3).

Sewage treatment generally processes human waste in three steps: primary (clarifying), secondary (aerobic biodegradation of organic matter), and tertiary (finishing step to reduce the concentrations of specific pollutants such as nitrates and phosphorus to acceptable standards). The liquid effluent is generally discharged by release into surface freshwater systems or the ocean. Waste from biomass and other precipitated solids are treated as sludge, which is used in many different ways. Most domestic sewage treatment facilities are not designed to process specialty chemicals such as pharmaceutical products. It is also possible that certain pharmaceutical products may be sufficiently toxic to inhibit the action of activated sludge microorganisms that are responsible for degrading organic materials in sewage. If undegraded pharmaceutical products in sewage are precipitated, they may end up in the sludge material. This is sometimes used to fertilize soils, raising the complex issues of soil contamination, groundwater infiltration, and human exposure through agricultural products. In addition, many municipalities do not process sewage completely through the tertiary stage, and the effluent is used for landscape irrigation, again raising the possibility of human and ecosystemic exposures. Finally, the process of chlorinating completely treated sewage and recycling the water for drinking is increasingly attractive as many regions experience water shortages. Chlorination of pharmaceutical products may produce highly toxic chemicals. For example, there is some evidence that the chlorination of caffeine will result in the production of chlorocaffeine, a potential mutagen (10,11).

Many pharmaceutical compounds survive biodegradation in sewage treatment plants. Some products are as persistent as more widely studied organochlorine pollutants, but only few large-scale studies have been completed. The removal efficiencies of pharmaceuticals in

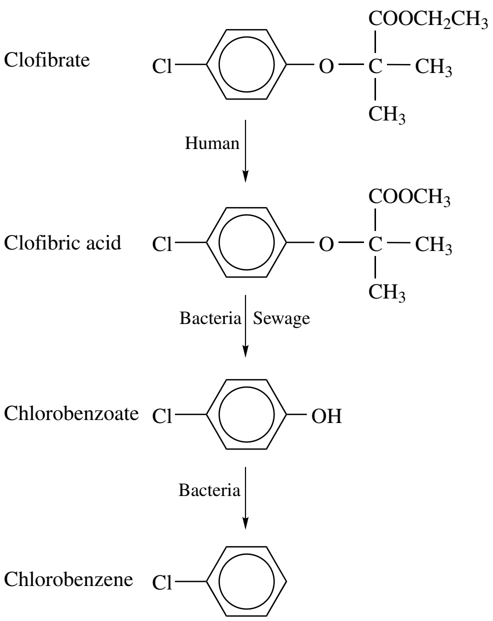

Figure 1. The production of chemical pollutants usually attributed to other industries may result from human and microbial metabolism of pharmaceutical products. The example shows the hypothetical degradation of clofibrate to chlorobenzene.

Table 2. Top 20 Organic Contaminants (Including Pharmaceuticals) Found in Streams in 39 States from 1999–2000 in the United States[a]

Rank	Chemical Compound	Source
1	Coprostanol	Fecal steroid/Hormone
2	Cholesterol	Human steroid
3	*N-N*-diethyltoluamide	Insect repellent
4	Caffeine	Dietary stimulant, pharmaceutical additive
5	Tri (2-chloroethyl) phosphate	Fire retardant
6	Triclosan	Antimicrobial disinfectant
7	4-Nonylphenol	Nonionic detergent metabolite
8	4-Nonylphenol monoethoxylate	Nonionic detergent metabolite
9	Ethanol, 2-butoxy-phosphate	Plasticizer
10	4-Octylphenol monoethoxylate	Nonionic detergent metabolite
11	Bisphenol A	Plasticizer
12	Cotinine	Tobacco cigarettes (nicotine metabolite)
13	4-Nonylphenol diethoxylate	Nonionic detergent metabolite
14	5-Methyl-1H-benzotriazole	Anticorrosive agent
15	Fluoranthene	Polyaromatic hydrocarbon oils
16	1,7-Dimethylxanthine	Caffeine metabolite
17	Pyrene	Polyaromatic hydrocarbon oils
18	Trimethoprim	Antibiotic
19	1,4-Dichlorobenzene	Deodorizer
20	Diazinon	Insecticide

[a] Reference 4.

treatment plants are still largely unknown (4). However, a study in Germany demonstrated that the removal efficiencies of pharmaceuticals by sewage treatment might be as low as 60% (2). There are many possible reasons for the low efficiency. Most pharmaceutical products are designed for metabolism at the human body temperature of 37 °C, which is not usual in sewage treatment facilities or anywhere else in nature. The identification of metabolic products is difficult because different metabolites can result under different environmental conditions and standard reference compounds are difficult to synthesize (2). The ability of treatment facilities to degrade pharmaceuticals can also change on the basis of operational state and seasons. Wet weather runoff and overflows from plant failure or overcapacity can also lead to direct release. Finally, influent concentrations of most pharmaceutical products may be so low that the microbial enzymes that degrade them are either not induced, or other more abundant substrates compete for their actions (2).

In the most comprehensive reconnaissance project that has been conducted to date, the U.S. Geological Survey investigated the occurrence of medicines, hormones, and other organic wastewater contaminants in a network of 139 streams across 39 states (4). Whereas previous research has shown that antibiotics, prescription drugs, and nonprescription drugs can be present in streams, this was the first study to examine their occurrence in a wide variety of hydrogeologic, climatic, and land-use settings across the United States. Although the data covered only a limited number of pharmaceutical compounds, it is reasonable to assume that many other compounds survive wastewater treatment and biodegradation and are ultimately released into water systems.

DETECTION OF PHARMACEUTICALS IN WATER SYSTEMS THAT RECEIVE EFFLUENT

There is a paucity of data on the distribution and fate of pharmaceuticals in natural water systems because, until recently, there have been few analytical methods that are sufficiently sensitive to detect these compounds at the expected low concentrations (4). In addition to sensitivity, analytic methods specifically developed for pharmaceutical products must also be able to discriminate among anthropogenic and natural constituents. For example, the use of artificial reproductive hormones as birth control pills and to control osteoporosis in postmenopausal women is widespread and has probably contributed significantly to the environmental distribution of these human hormones. However, it is sometimes difficult to discriminate between the artificial variety from the pharmaceutical industry and natural hormones excreted by humans, especially after partial metabolism by microbial action (2). The pending creation of mass spectral libraries for environmental pharmaceutical products and their degradation products will facilitate the development and reliability of methods in this direction. Ecotoxicological assessment of pharmaceutical products in the environment also requires developing sentinel and monitoring species that are expected to concentrate certain chemical moieties reliably or to respond to their effects at the physiological level (2).

In the USGS study, five analytical methods were used to measure concentrations of 95 organic wastewater contaminants (of which pharmaceuticals were a major part) in water samples. The methods used for measuring contaminants in the water included solid-phase extraction (SPE) with liquid chromatography/mass spectrometry positive-ion electrospray [LC/MS-ESI (+)] analysis and whole-water continuous liquid–liquid extraction (CLLE) with capillary gas chromatography/mass spectrometry (GC/MS) analysis (5). Although sampling locations were biased toward locations that were downstream of urban centers and livestock production, organic wastewater contaminants were still present in 80% of the streams that were sampled. There was a median of 7 and as many as 38 contaminants found in the water samples. Nonprescription drugs were found at the greatest frequency. Antibiotics, other prescription drugs, and reproductive hormones were found at relatively similar frequencies. It was hypothesized that the greater frequency of detection for nonprescription drugs might have been due in part to suspected greater annual use compared to other compounds. Measured concentrations rarely exceeded drinking-water guidelines, drinking-water health advisories, or aquatic-life criteria. However, most of the 95 contaminants do not have guidelines or established safe-level concentrations because not much is known about the ecotoxicological effects of the contaminants investigated (5).

ECOLOGICAL EFFECTS OF PHARMACEUTICALS IN WATER SYSTEMS

Acute toxicity is one of the many possible ecotoxicological end points of the exposure of nontarget species to pharmaceutical products synthesized strictly for human consumption. The low levels of pharmaceuticals found in polluted waters that contain many different species is not a reason for complacency in the expectation of toxicity (2). The low concentrations may not always pose acute risk, but the cumulative risks of prolonged exposure to low levels of chemicals is known to represent considerable hazard in animal studies and human epidemiology. Laboratory studies that do not simulate simultaneous exposures to multiple pharmaceutical products are likely to underestimate their ecotoxicological impacts. In most cases, there is limited information on which receptors in nontarget organisms are sensitive to chemical exposure. For these organisms, the most important threats are subtle behavioral modifications or genetic alterations that can lead to profound long-term changes in ecosystemic structure and function. Many such subtle effects have been demonstrated in wildlife as a result of chemical exposures. These include reversal of attraction, boldness, contact avoidance, feeding and mating disturbances, and confused directional sensing (2).

The environmental distribution of antidepressants and chemical regulators of obsessive–compulsive behavior can have subtle effects on nontarget organisms at chronic low doses. Serotonin reuptake inhibitors are a major component of widely prescribed antidepressants, including Prozac, Zoloft, Luvox, and Paxil. In addition to playing an important role in mammalian neurotransmission, serotonin is involved in a wide array of physiological regulatory functions in many species. In bivalves, serotonin regulates reproductive functions, including spawning, oocyte maturation, and parturition. At molar concentrations of 10^{-4} to 10^{-3}, serotonin induces spawning. Serotonin stimulates the release of neurohormones in crustaceans. Prozac and Luvox induce spawning and spawning behavior in zebra mussels at very low concentrations. In lobsters, serotonin causes behavioral reversal by stimulating subordinates to engage in fighting against dominants by reducing their propensity to retreat (2).

Kolpin and co-workers (4) detected compounds in water systems known or suspected to have weak hormonal activity and the potential to disrupt normal endocrine function. These compounds were detected in practically all streams investigated during the study. The expected low levels of exposure ($<0.001\ \mu$g/l) to specific hormonally active compounds can adversely affect the reproduction of aquatic species. Other potential ecological problems of pharmaceutical exposure include increases in the incidence of cancers and the proliferation of antibiotic-resistant bacteria.

In addition to possible ecotoxicological effects, the prospects of human health effects from ingesting subtherapeutic doses of multiple pharmaceuticals from every intake of drinking water or through inhalation of volatilized products from every bath raises substantial concern. For many pharmaceutical products, the potential effects on humans and aquatic ecosystems are not clearly understood. Many drugs currently detected in aquatic waters already have known effects on nontarget organisms. Synthetic oral contraceptives (17α-ethynylestradiol) generally occur at concentrations lower than 7 μg/liter in effluents from publicly owned waste treatment facilities. In combination with steroidal estrogens 17β-estradiol and estrone, exposures to 17α-ethynylestradiol, it is believed, causes feminization in male fish, as observed in sewage treatment lagoons in the mid-1980s (2).

The consolidation and proliferation of resistance to multiple antibiotics in pathogenic microorganisms is an increasing threat to human reliance on antibiotics for treating dangerous infectious diseases. Acquired antibiotic resistance may remain stable indefinitely, even after the sources of exposures are removed. This means that the threats posed by microbial antibiotic resistance can only grow in the future, even if strict controls are placed now on the environmental release of antibiotics. For example, bacterial isolates from wild geese that have never been treated with antibiotics were resistant to ampicillin, tetracycline, penicillin, and erythromycin (2). Sufficiently high concentrations of multiple antibiotics can also have ecotoxicological effects on microbial communities that sustain global biogeochemical cycles and many local ecosystem functions, including the detection of indicators of fecal contamination in water systems.

REGULATORY STRATEGIES FOR CONTROLLING PHARMACEUTICAL PRODUCTS IN WATER SYSTEMS

Pharmaceutical products target more than 500 distinct biochemical receptors in the human body. Many of these receptors are also found in aquatic organisms (2). However, current guidelines for approving the effectiveness and metabolic fate of pharmaceutical products do not necessarily include testing across phylogenetic branches or documenting potential bioaccumulation and biodegradation. Even among humans, unrecognized genetic polymorphisms may make certain individuals much more sensitive to the effects of certain drugs, to the extent that a “zero tolerance” guiding principle for pharmaceuticals in domestic water supplies does not appear unreasonable. However, such broad regulatory goals are deemed too expensive to be implemented effectively.

Although the risks posed by inadvertent exposures to pharmaceutical products are not specifically controversial, only a limited number of federal agencies are responsible for managing the release of pharmaceuticals into the environment. In Europe, the Organization for Economic Cooperation and Development (OECD), an intergovernmental organization that has representatives in 29 countries, regularly publishes “Test Guidelines” for assessing the hazards of chemicals, including pharmaceuticals, in various environmental contexts (2). The problems of pharmaceutical products in the environment were first recognized widely in Europe, and the leading edges of regulatory issues appear to be evolving similarly from Europe. The European Union (EU) first expressed concern for the release of veterinary pharmaceuticals and their metabolites into the environment in the early 1980s because these products, it was perceived, have a much more direct route of introduction to the environment than medications prescribed for humans. The EU established two assessment levels to determine if a veterinary drug is dangerous to the environment. The first level considers the potential for release; the second level evaluates fate in various environmental compartments and investigates effects on specific biota that are likely to be exposed. All new applications for veterinary pharmaceuticals must include an environmental impact report based on the two levels of assessments. Regulatory guidelines for human pharmaceuticals are pending ratification by the EU (2).

In the United States, the Food and Drug Administration (FDA) and the U.S. Environmental Protection Agency (EPA) have separate roles regarding the distribution and release of pharmaceutical products in the environment. The FDA is responsible for assessing the risk to the environment caused by the manufacture, use, and disposal of human and animal drugs (5,12). FDA approval for new medications requires the submission of Environmental Assessment (EA) reports under the National Environmental Policy Act of 1969. As with the European Commission, the concern for new drugs rests primarily on acute and chronic effects, as measured by traditional toxicity tests (2). Much less concern has been given for more subtle behavioral effects. The FDA uses a tiered approach, similar to that of the EU, to determine if regulatory action is required. Generally, an Environmental Assessment report is required if the expected environmental concentration of the active ingredient of the drug in the aquatic environment exceeds 1 ppb (5,12). More recently, published literature and various conferences have indicated that in addition to the EA reports, pharmaceutical chemicals might have long-term effects on various wildlife species, but firm regulation will require additional research to evaluate these effects (12).

One of the top five goals of the EPA's Strategic Plan 2000 is identifying emerging risks of previously unknown, unrecognized, unanticipated, or unsuspected chemical pollutants in the environment (2). The EPA regulates emissions and effluent discharges from pharmaceutical manufacturing facilities, which are subjected to various restrictions or schedules of compliance regarding processed or raw effluent discharges (5,6). Despite considerable progress in recognizing and regulating risks posed by pharmaceuticals in water systems, important shortcomings remain in the current approaches used to determine ecological risk. Additive, synergistic, or antagonistic impacts of similar drugs or different classes of drugs that affect the same receptors are not currently being evaluated or considered part of regulatory principles. Additionally, the FDA's expected environmental concentration limit of 1 ppb for any given drug could easily be exceeded when the cumulative concentrations of similar-mode-of-action medications are considered. This regulatory loophole may allow potentially damaging chemicals to skip through the environmental assessment process.

In conclusion, the multidisciplinary demands of understanding and regulating the design, approval, consumption, metabolism, excretion, disposal, and environmental fate of pharmaceutical products in water systems requires developing innovative strategies in academic and regulatory institutions. These strategies may be consolidated under the umbrella of a new subdiscipline entitled "pharmecology" whose ultimate mission is protecting the environment from the chemical hazards associated with the pursuit of human health.

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BIBLIOGRAPHY

1. Buser, H-R., Poiger, T., and Müller, M.D. (1999). Occurrence and environmental behavior of the pharmaceutical drug ibuprofen in surface waters and in wastewater. *Environ. Sci. Technol.* **33**: 2529–2535.
2. Daughton, C.G. and Ternes, T.A. (1999). Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Perspect.* **107**(Suppl. 6): 907–938.
3. Kummerer, K. (Ed.). (2001). *Pharmaceuticals in the Environment*. Springer, Berlin, p. 265.
4. Kolpin, D.W. et al. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. *Environ. Health Sci. Technol.* **36**(6): 1202–1211.
5. Daughton, C.G. and Jones-Lepp, T.L. (2001). *Pharmaceuticals and Personal Care Products in the Environment: Scientific and Regulatory Issues*. ACS Symposium Series 197, American Chemical Society, Washington, DC, pp. 2–53; 264–281.
6. Soto, A.M. et al. (1995). The E-SCREEN assay as a tool to identify estrogens: An update on estrogenic environmental pollutants. *Environ. Health Perspect.* **103**: 113–122.
7. Daughton, C.G. (2003). Cradle-to-cradle stewardship of drugs for minimizing their environmental disposition while promoting human health. 1. Rationale for and avenues toward a green pharmacy. *Environ. Health Perspect.* **111**(5): 757–774.
8. Rx List: The Internet Drug List. (2003). *The Top 200 Prescriptions for 2002 by Number of Prescriptions Dispensed*. ONLINE 2003. Available: http://www.rxlist.com/top200.htm.
9. Hirsch, R., Ternes, T., Haberer, K., and Kratz, K.L. (1999). Occurrence of antibiotics in the aquatic environment. *Sci. Total Environ.* **225**: 109–118.
10. Ogunseitan, O.A. (1996). Removal of caffeine in sewage by *Pseudomonas putida*: Implications for water pollution index. *World J. Microbiol. Biotechnol.* **12**: 251–256.
11. Ogunseitan, O.A. (2002). Caffeine-inducible enzyme activity in *Pseudomonas putida* ATCC 700097. *World J. Microbiol. Biotechnol.* **18**: 423–428.
12. Velagaleti, R., Burns, P.K., Gill, M., and Prothro, J. (2002). Impact of current good manufacturing practices and emission regulations and guidances on the discharge of pharmaceutical chemicals into the environment from manufacturing, use, and disposal. *Environ. Health Perspect.* **110**(3): 213–220.

POINT-OF-USE/POINT-OF-ENTRY SYSTEMS (POU/POE)

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Numerous households use point-of-use/point-of-entry (POU/POE) systems primarily to deal with aesthetic concerns, such as taste and odor. These treatment devices are installed just as their name implies—at the point where water enters a household or where it is used, such as a faucet. In certain situations, however, using POU/POE systems to provide safe drinking water to a system's customers is not an individual's choice, but that of the water system cooperating with regulatory authorities. Therefore, this "Tech Brief" only discusses POU/POE treatment options that meet Safe Drinking Water Act (SDWA) water quality requirements.

WHAT IS THE ROLE OF POU/POE SYSTEMS?

Some small water systems find complying with U.S. Environmental Protection Agency (EPA) maximum contaminant level (MCL) requirements difficult. Installing expensive treatment technologies may be the largest obstacle for these systems. In many cases, obtaining water from some other source may not be an option. In these situations, POU/POE water treatment systems may provide a low-cost alternative to centralized water systems.

Water system personnel can install POE treatment units at individual households where water lines enter the home, alleviating the expense of treating large amounts of water at a central facility. An even less expensive alternative is the POU system, as these systems only treat the water at an individual tap.

POU/POE systems are used to control a wide variety of contaminants in drinking water and often use the same technology concepts employed in centralized treatment—but at a much smaller scale. This technology is applied to reduce levels of organic contaminants, control turbidity, fluoride, iron, radium, chlorine, arsenic, nitrate, ammonia, microorganisms (including cysts) and many other contaminants. Aesthetic factors, such as taste, odor, or color, can be improved with POU/POE treatment.

In addition to treating raw water, POU/POE systems can be used to treat finished water that may have degraded during distribution or storage. They insure that susceptible consumers, such as the very young or immunocompromised, receive safe drinking water.

POU/POE can save many small communities money where individual households have private wells. The community then does not have to build a treatment plant or install and maintain water distribution mains. Many states, however, have concerns about POU/POE treatment devices, such as:

- how well the units treat drinking water,
- the potential health risk posed by not treating all the water in the house, and
- water system officials' ability to properly monitor and maintain the equipment.

WHAT REGULATIONS AFFECT POU/POE SYSTEMS?

The 1996 SDWA lists POU/POE systems as options for compliance technologies. When a water system uses this technology to comply with a National Primary Drinking Water Regulation (NPDWR) the SDWA identifies requirements that must be met. The SDWA states the public water system or a person under contract with the public water system shall own, control, and maintain the POU/POE system to ensure proper operation, maintenance, and compliance. The act also states that the treatment mechanism should be equipped with mechanical warnings that automatically notify customers of operational problems.

Other conditions in the SDWA include: "If the American National Standards Institute has issued product standards applicable to a specific type of POE/POU treatment unit, individual units of that type shall not be accepted for compliance with a MCL or treatment technique unless they are independently certified in accordance with such standards."

POU devices are listed as compliance technologies for inorganic contaminants, synthetic organic contaminants, and radionuclides. POU devices are not listed for volatile organic contaminants because they do not address all routes of exposure.

WHAT ARE THE TYPES OF POU/POE SYSTEMS?

No single type of residential water treatment system is available to remove all water quality problems. Therefore, selection of one or more technologies may be necessary to solve multiple water quality problems. The following is a short summary of different types of POU/POE available (see also Table 1). Additional information and guidance is available from manufacturers, distributors, and public health agencies to help select the appropriate treatment technologies to remove specific water contaminants from water.

FILTERS

Water passes through the filter media (usually in a cartridge in smaller units), which either adsorbs or physically screens various contaminants. Common filter media include:

Table 1. Summary of POE/POU Systems and Costs (NSF, 1999)

Technology	Some Contaminants Removed	Initial Cost	Operating Cost	Operating & Maintenance Skills
Chlorine	Microbial	**$**	**$**	**$**
UV, Ozone	Microbial	**$$**	**$**	**$$**
Cartridge	Protozoa			
Filter	Bacteria	**$**	**$ to $$**	**$**
Reverse Osmosis	Microbial, Inorganic Chemicals and Metals Radium, Minerals, Some Organic Chemicals	**$$**	**$$$**	**$$$**
Distillation	Microbial, Inorganic Chemicals and Metals, Minerals, Some organic Chemicals, Radium, Uranium	**$$**	**$$**	**$**
Activated Carbon	Organic Chemicals, Radon, Odors (solid block can filter protozoa and some bacteria)	**$$**	**$$ to $$$**	**$**
Packed Tower Aeration	Radon, Volatile Organic Chemicals, Tastes, Odors	**$$**	**$**	**$$$**
Ion Exchange	Inorganic Chemicals, Radium, Nitrate	**$$**	**$$ to $$$**	**$$**
Activated Alumina	Arsenic, Selenium, Fluoride	**$$$**	**$$$**	**$$$**
		$ Low	**$$ Moderate**	**$$$ High**

- Granular activated carbon (GAC) is used for taste and odor control and to remove radon and regulated organic compounds.
- Solid block carbon treats the same contaminants as GAC, but also to removes lead, asbestos, various bacteria, cysts, and sediment particulates.
- Ceramic or synthetic fiber microfilters treat various bacteria, cysts, and sediment particulates.
- Activated alumina treatment is most often used for fluoride, selenium, silica, and arsenic removal.

REVERSE OSMOSIS

Water passes through a synthetic, semi-permeable membrane that filters all pathogens and most organic and inorganic contaminants. Reverse osmosis units must have a means of discharging filtered matter to a drain. The discharge line should be installed with an air gap so a cross-connection between wastewater and drinking water will not occur.

DISTILLATION

Distillers heat water in one chamber and turn it into steam. The steam then passes into another chamber where it is cooled and condensed to a liquid. Distillation can effectively remove microorganisms, dissolved minerals, metals, nitrates, and some organic contaminants. Distillation units require a dependable supply of electricity and usually produce only small amounts of drinking water.

ION EXCHANGE

Ion Exchange, commonly known as water softening, is used to treat all household potable drinking water. Ions of either sodium or potassium, stored in the softener's "resin bed" are exchanged for ions of the calcium and magnesium hardness minerals. Ion exchange can be used for dealkalization and to remove iron and manganese, heavy metals, some radioactivity, nitrates, arsenic, chromium, selenium, and sulfate.

DISINFECTION AND OXIDATION

Oxidizing chemicals, such as chlorine and ozone, are added to water through a feed system that controls the concentration and allows appropriate contact time. These chemicals break down organic contaminants and destroy pathogens.

Ultraviolet light (UV) is a popular disinfection method in combination with other treatment techniques. UV uses rays of ultraviolet light to deactivate pathogens. UV light damages a pathogen's DNA and prevents it from reproducing. One of the major advantages of UV disinfection is that it disinfects without the addition of chemicals; therefore, it does not generate taste, odor, or chemical by-products.

AIR STRIPPING OR AERATION

Air stripping has been used in POE systems to remove volatile organic compounds, hydrogen sulfide, and radon from water. Air stripping is a treatment method that exposes water to air. This treatment process removes or "strips" volatile organic contaminants from groundwater as air is forced through the water, causing the compounds to evaporate. GAC alone can remove volatile organics but can only be operated for short periods before the carbon has to be replaced. For these applications, it is important to vent gases adequately to avoid creating an air pollution hazard inside the home.

POU/POE OPERATION AND MAINTENANCE

Selecting POU/POE systems does not eliminate the need for evaluating treatment efficiency before the units are installed. For systems that employ cartridges (e.g., GAC columns or activated alumina), source water pilot testing may be necessary to develop valid estimates of the unit's service life.

Effective operation, maintenance, and monitoring programs are especially significant for POU/POE systems. Many homeowners assume their systems will perform properly once installed and do not understand the level of effort required to ensure proper operation. For this reason, when POU/POE systems are installed for regulatory purposes, water utilities or regulatory agencies must provide programs for long-term operation, maintenance, and monitoring.

Proper installation is the first step in effective long-term operation and maintenance (O&M) of POU/POE systems. Experienced contractors or installers whose products conform to applicable plumbing codes should be the only personnel who install the units. Qualified installers:

- carry liability insurance for property damage during installation,
- are accessible for service calls,
- accept responsibility for minor adjustments after installation, and
- give a valid estimate of the cost of installation.

After installation, POU/POE systems should have a well-defined program of O&M for continued production of high quality drinking water. The equipment manufacturer's recommended O&M requirements can serve as the basis for the O&M program. Equipment dealers may provide maintenance for a limited time period as part of an installation warranty. A local plumbing contractor, a POU/POE service representative or equipment dealer, a water service company, the local water utility, or a circuit rider may carry out a long-term maintenance program.

Monitoring programs need to be site specific and reflect the contaminant or contaminants being removed, the equipment used, the number of POE/POU units in service, and the logistics of the service area.

Minimum sampling frequencies and types of analyses should be established in cooperation with the local health department, the state regulatory agency, and the treatment system.

Monitoring programs generally include:

- raw and treated water sample collection,
- meter reading,
- field analyses (measuring pH, dissolved oxygen concentration, and other parameters),
- shipment of samples to a laboratory, and
- recordkeeping.

The use of state-approved sampling methods and certified laboratories is a requirement for regulatory compliance.

Remote monitoring and control is becoming a more practical option for small communities and could be part of an O&M agreement developed by a POU/POE vendor. Remotely monitoring operating parameters could provide an attractive alternative to fixed sampling and O&M schedules, thus, allowing customized customer service of the POU/POE device.

A POU/POE vendor could use remote telemetry equipment to review several installations and reduce the number of unnecessary system checks and visits. Remote telemetry also may be used to better schedule routine O&M, trouble-shooting problems, and emergency situations.

SELECTING AN APPROPRIATE POU/POE SYSTEM

The selection of POU/POE treatment units should be based on how well a particular type of unit removes specific contaminants from drinking water. Therefore, the selection process involves:

- an evaluation of the quality and type of source water,
- type and extent of contamination,
- treatment requirements, and
- waste disposal requirements.

The treatment requirements are usually compared based on operation and maintenance requirements, cost, and institutional requirements.

For a guarantee that a water treatment unit will perform and remove contaminants that the manufacturer claims, look for certification or registration labels on the treatment units. Two private organizations, the National Sanitation Foundation International (NSF) and the Water Quality Association (WQA), provide product testing. However, manufacturers are not required to test their products under these programs.

NSF INTERNATIONAL LISTING PROGRAM

NSF International is a nonprofit, independent testing and research group that provides standards for drinking water treatment components and tests home and personal water treatment devices to determine their ability to improve the aesthetic quality of water and remove health-related contaminants. NSF International has a certification laboratory that can conduct a full range of physical, microbiological, radiological, inorganic, and organic analyses.

NSF uses expert committees to develop its technology standards. The committee includes representation from industry, government, and consumer groups. The committee also receives input from a council of public health consultants and a certification council that has expertise in test methods.

Once an NSF committee develops a standard, the NSF applies to have it certified by the American National Standards Institute (ANSI). An ANSI designation means that only one standard exists for that type of product in the U.S. and that the standard follows all of ANSI's guidelines.

WQA Voluntary Product Validation Program and Voluntary Certification Program WQA, a nonprofit international trade association, awards its Gold Seal to water treatment equipment that passes testing under industry standards for performance, capacity, and durability. WQA does not evaluate claims for removing health-related contaminants. However, WQA has a certification program for POU/POE devices. But remember, WQA is a trade association for POU/POE equipment manufacturers, and although the association provides educational material to the consumer, they also promote the use of treatment equipment.

WHAT ABOUT SAFETY AND TERRORISM?

Recent events confirm that bioterrorism is no longer a threat, but a reality. POU filtration systems can reduce many biological warfare agents. POU systems, rated for their ability to remove waterborne biological agents, are available in a range of sizes from individual use to those capable of delivering thousands of liters of water per hour.

WHERE CAN I FIND MORE INFORMATION?

Lykins, B. W., R. M. Clark, and J. A. Goodrich. 1992. *Point-of-Use/Point-of-Entry for Drinking Water Treatment*. Boca Raton, FL: Lewis Publishers.

National Research Council. 1997. *Safe Water From Every Tap*. Washington, DC: National Academy Press

New England Water Works Association. 1998. *Small Systems Water Treatment Technologies: State-of-the-Art Workshop*. Joint Regional Operations Conference and Exhibition Proceedings, Marlborough, MA.

NSF International, World Health Organization, and Pan American Health Organization. 1999. *Providing Safe Drinking Water in Small Systems: Technology, Operations, and Economics*. Boca Raton, FL: Lewis Publishers.

Reynolds, K. 2001. "Point-of-Use Protection Against Bioterrorism." *Water Conditioning & Purification* 43:12.

U.S. Environmental Protection Agency. 1998. "Cost Evaluation of Small System Compliance Options: Point-of-Use and Point-of-Entry Treatment Units."

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ASSESSING THE BACTERICIDAL EFFICIENCY OF POLYDEX FOR THE DISINFECTION OF DRINKING WATER IN RURAL AREAS OF SOUTH AFRICA

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INTRODUCTION

In developing countries, a large number of people lack access to adequate water supply. They, therefore, are forced to use surface water drawn from polluted rivers, irrigation canals, ponds, and lakes without prior treatment. For small rural communities, groundwater remains the main water supply source. Some communities receive their drinking water directly from uncovered or covered boreholes and wells, whereas for others, the water is drawn from the boreholes (using an engine) to a reservoir, and from the reservoir, it is then delivered to the people through a public standpipe system. In both cases, groundwater is distributed to the community without any purification. However, inadequate design, construction, operation, and maintenance of wells and boreholes can lead to quality problems related to groundwater. Poor sanitary sealing is more generally a common cause of microbiological quality deterioration (1). The failure to periodically drain and clean water supply holding tanks to remove sediments provides opportunities for heterotrophic bacterial colonization and biofilm development (2).

Polluted waters are an important vehicle for the spread of disease as they are carriers of disease-causing organisms such as pathogenic bacteria and viruses. Thousands of people in developing countries become ill each year through contact with contaminated water. The full impact of contaminated water on health is difficult to determine because of poor recording of diseases. A crucial need exists for scientifically sound answers to the problems of the contamination of water sources with potentially hazardous microbial organisms and the assessment of the risks posed by such pollution. Where public health is concerned, disinfection is the most important step in any process involving drinking water treatment.

Disinfection—by application of chlorine—is the most widely used treatment for bacteriological water quality improvement. However, its efficiency is limited to the presence of an adequate chlorine residual in potable water. Once the latter depletes, any drinking water system will experience a correlation between increase in bacterial numbers and the distance away from the point of treatment. This increase has been termed regrowth and is recognized as a major problem within many water systems (3). The identification of other disinfectants and the understanding of their modes of action should be stepped up in order to improve the microbial quality of drinking water from the point of treatment to the consumers.

Polydex is the result of extensive research and development in the search for a healthier microbial control and protection of potable water and wastewater. Polydex is a Pest Management Regulatory Agency (PCPA) registered product, which is designed for use in ponds, dugouts, and potable water tanks for the control of algae and bacteria (4). Polydex is also used in agriculture for the control of noxious gases and odors in animal waste and in slaughterhouses for reducing the risks of *E. coli* contamination, such as the one which claimed several lives in Walkerton, Ontario (5). The active ingredient in Polydex is a biologically active form of the copper ion (Cu^{2+}). Polydex contains a unique hydrotropic and colloidal mineral matrix, which effectively captures and carries copper ions (Cu^{2+}) evenly throughout water in high concentrations under a wide variety of water conditions.

The biocidal effects of copper have been used for centuries. The early Greeks and Romans made water storage and drinking vessels out of this metal. More recently, copper has been used in hospital, recreational, drinking, and industrial water systems. Unlike chlorine, copper does not result in dangerous halogenated organic byproducts, such as trihalomethane (THM), chloramines, and chloroform, and this ion is stable, making it easier to maintain an effective residual (6).

The disinfection action is attributed to the positive charge of copper ion. Positively charged copper ion has an affinity for electrons and, when introduced into the interior of a bacterial cell, they interfere with electron transport in cellular respiration systems. Metal ions will bind to the sulfhydryl, amino, and carboxyl groups of amino acids, thereby denaturing the proteins, which renders enzymes and other proteins ineffective, compromising the biochemical process they control. Cell surface proteins necessary for transport of materials across cell membranes also are inactivated as they are denatured. Finally, copper will bind with the phosphate groups that are part of the structural backbone of DNA molecules, which results in unraveling of the double helix and consequent destruction of the molecule (6,7).

It is also important to consider how copper in water can be advantageous to humans, animals, and plants. Our daily diet must provide specific trace amounts of copper for a number of reasons in order to maintain human health. The essential role of copper in maintaining normal health in both animal and humans has been recognized for many years. Normally, copper is readily available in a range of foods, and normal balanced diets should provide adequate daily amounts without the need for additional supplements. Dietary copper intake will vary considerably with the type of food consumed, the condition of the soils (e.g., copper content, pH, etc.) from which certain foods are produced, and drinking water characteristics. The average daily dietary requirement for copper in the adult human has been estimated at 2 mg and for infants and children at 0.05 mg/kg bw (8–10). The NRC (11) reported "estimated safe and adequate" daily dietary intakes of copper ranging from 0.5 to 0.7 mg/for infants 6 months of age or less and up to 2–3 mg/day for adults. In cases where individuals have a change in their everyday eating habits or decide to indulge in a limited medically controlled diet that may result in an inadequate intake of copper, water treated with Polydex may come in handy in supplying the body with needed copper.

Although several tests have shown the effectiveness of copper in killing bacteria, our preliminary experiments revealed that its effectiveness was limited in raw water with high turbidity when considering the initial dose recommended by the suppliers (1 part of polydex into 60,000 parts), which automatically showed that the quality of raw water remains one of the most important parameters in determining the efficiency of polydex. It was therefore vital to re-evaluate the bactericidal efficacy of polydex by considering various types of water sources and determining the disinfectant (polydex) demand of the water. Coliform bacteria were used as the main parameters with references to South African Water Quality Guidelines–Domestic use (12,13). Total coliforms are frequently used to assess the general hygienic quality of water and to evaluate the efficiency of drinking water treatment and the integrity of the distribution system. They should not be detectable in treated water. When found, they suggest inadequate treatment, post-treatment contamination and/or aftergrowth, and an excessive concentration of nutrients. In some instances, they may indicate the presence of pathogens responsible for the transmission of infectious diseases. The total coliform group includes bacteria of fecal origin and indicates the possible presence of bacterial pathogens such as *Salmonella spp., Shigell spp., Vibrio cholerae, Campylobacter jejuni, C. coli, Yersinia enterocolitica*, and pathogenic *Escherichia coli*, especially when detected in conjunction with other fecal coliform (13). The study aimed at generating valuable information in regard to the bactericidal efficiency of polydex for the disinfection of drinking water in rural communities.

MATERIALS AND METHODS

The experimental study was conducted on the basis of five replicates for each type of test water, and the effectiveness of polydex was evaluated every hour for the period of 7 h. Microbiological analyses were conducted in aseptic conditions under a laminar flow cabinet in the laboratory. Turbidity and pH were also considered, as both factors play a significant role in the disinfection process. All microbial and physicochemical tests were performed before and after disinfection.

Sampling Sites

Raw, filtered (water after flocculation, sedimentation, and filtration), and surface water samples were collected at the Alice water purification system (Alice, Eastern Cape), Umgeni water (Durban, Natal), Rand water, (Vereeniging, Gauteng), and in Thohoyandou water purification systems (Venda, Limpopo). Groundwater samples were also collected in Alice, Vereeniging, and Thohoyandou. Test waters were collected in clean sterile 5l polyethylene bottles.

Disinfection of Test Waters

The bactericidal effect of polydex was determined using two different initial doses:

1. Dose indicated by the manufacturer: 1 part of polydex into 60,000 parts of test water to give one part per million biologically active copper ions. Therefore, 0.083 ml polydex (approximately 3.9 mg/l copper) was used to disinfect 5l of test water with turbidities ranging between 0.59 NTU and 8 NTU.
2. 5.4 mg/l copper (corresponding to 2 × 0.083 ml) was used for the disinfection of surface water with higher turbidity (>9NTU).

Physicochemical Analyses

Turbidity and pH were measured using the microprocessor Turbidity Meter (HACH Co., Model 2100P) and pH Meter, respectively, and copper (Cu) concentrations were determined according to the spectroquant NOVA 60 manual (1998) using photometric test kits (Merck).

Microbiological Analyses

Total coliforms, presumptive *E. coli*, and *Salmonella* species were detected by the membrane filtration technique using filters with 0.45 μm pore size and 47 mm diameter (Millipore). Different volumes (10 and 100 ml) were filtered depending on the type of water used. Saline water was used as a diluent for the 10 ml volumes to spread the bacteria evenly over the filter membrane. The membrane filters were placed on Chromocult agar (Merck) plates and incubated for 24 h at 37 °C. Analyses were carried out in triplicates. Water samples were analyzed for the above micro-organisms using internationally accepted techniques (14).

RESULTS AND DISCUSSION

Characteristic of Raw Surface Water Before and After Disinfection with An Initial Dose of 3.9 mg/l Polydex

Figure 1 summarizes the counts of indicator bacteria before and after disinfection and the impact of turbidity and pH on the effectiveness of this disinfectant. There was a gradual decrease in all indicator micro-organisms after an hour of disinfection, which continued throughout the 7 h of the study period. Although presumptive *Salmonella* and presumptive *E.coli* were removed at a percentage of 100% within 1 h and 5 h, respectively, in all raw water samples, the removal of total coliforms in water samples from Venda, Rand water, and Alice ranged between 90–91% throughout the 7 h of the study period. However, complete removal of total coliforms occurred 5 h after disinfection of Umgeni water, which appeared to have lesser turbidity compared with other test waters. Although all raw water samples were disinfected with the same initial copper concentration of 3.9 mg/l, copper residual was more slowly depleted in Umgeni water than in the other raw water samples. The average copper residuals in Venda, Rand, and Alice waters after 7 h were 1.02 mg/l; 1.20 mg/l, and 1.12 mg/l, respectively, whereas samples from Umgeni water still maintained the copper residual concentration of 1.71 mg/l, which gave a clear indication that higher turbidities hinder the effectiveness of polydex as a disinfectant.

Characteristics of Filtered Surface Water Before and After Disinfection with an Initial Dose of 3.9 mg/l Polydex

The effectiveness of polydex was further proved by the dramatic decrease in numbers of all indicator micro-organisms in filtered water samples with reasonably low turbidities after disinfection (Fig. 2). Complete removal of presumptive *Salmonella,* presumptive *E. coli*, and total coliform bacteria occurred after 1 h, 2 h, and 4 h of disinfection in all the water samples, respectively. Although all filtered water samples maintained copper residuals ranging between 2.06 mg/l and 2.44 mg/l after the 7 h of the study period, the water samples from Umgeni water purification system had a higher residual (2.44 mg/l) than those from Venda, Rand, and Alice water supplies, which had residuals of 2.11 mg/l, 2.20 mg/l, and 2.06 mg/l, respectively. There was an indication of a slight decrease in pH after disinfection in all samples (raw surface water, raw groundwater, filtered surface water); however, this appeared not to have any effect on the effectiveness of polydex—or public health—as the pH values obtained were within the limits recommended for potable water, which are 5–9.5 (12).

Characteristic of Raw Groundwater Before and After Disinfection with An Initial Dose of 3.9 mg/l Polydex

Initial total coliform bacterial counts of 68 cfu/100 ml, 46 cfu/100 ml, and 82 cfu/100 ml were noted in Venda, Rand, and Alice groundwaters, respectively. These bacterial counts gradually decreased to 0 cfu/100 ml after 4 h in Venda and Rand water when the copper residuals were 2.43 mg/l and 2.96 mg/l, respectively. Although this was not the case with Alice water samples, the total coliform bacterial counts were found to be within the South African recommended limits for no risk (0–5 cfu/100 ml) (13). Although a complete removal of presumptive *E. coli* occurred 3 h after disinfection in all types of water, no presumptive *Salmonella* was recorded in Venda and Alice water samples within 1 h (Fig. 3).

Characteristic of Raw Groundwater Before and After Disinfection with An Initial Dose of 5.4 mg/l Polydex

There was a notable decrease in coliform bacterial counts when the initial dose of 5.4 mg/l polydex was used for

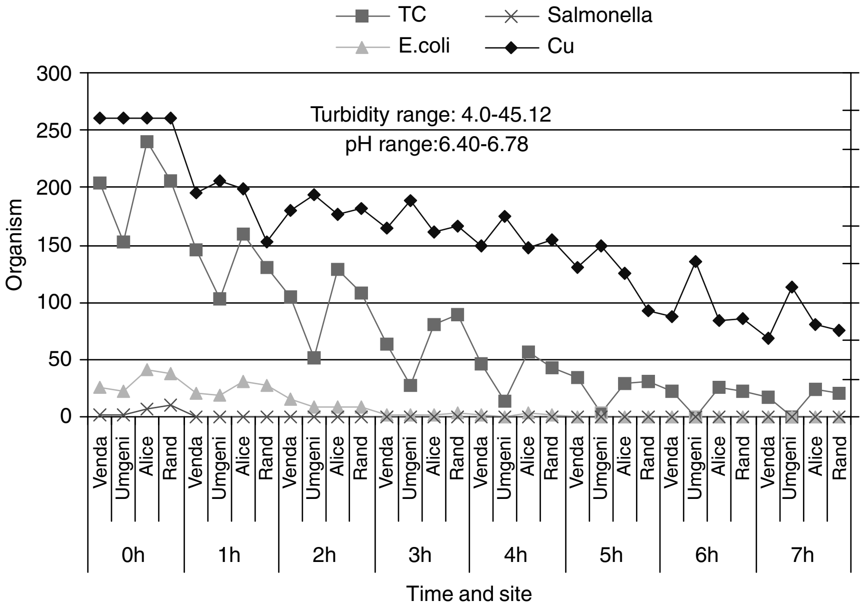

Figure 1. Average counts of indicator bacteria in raw surface water samples before and after disinfection with an initial dose of 3.9mg/l copper.

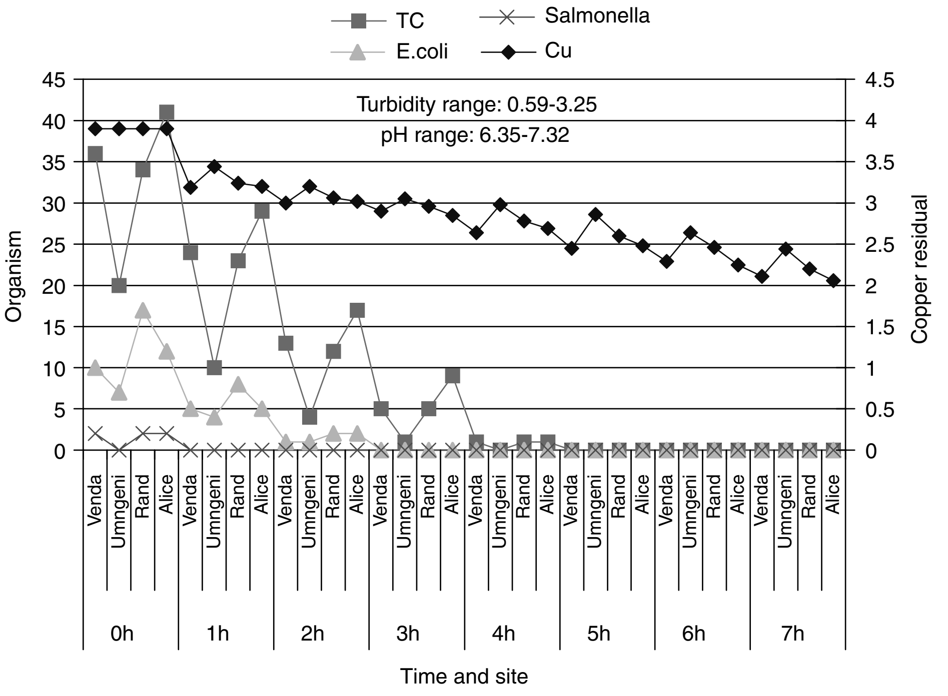

Figure 2. Average counts of indicator bacteria in filtered water samples before and after disinfection with an initial dose of 3.9 mg/l copper.

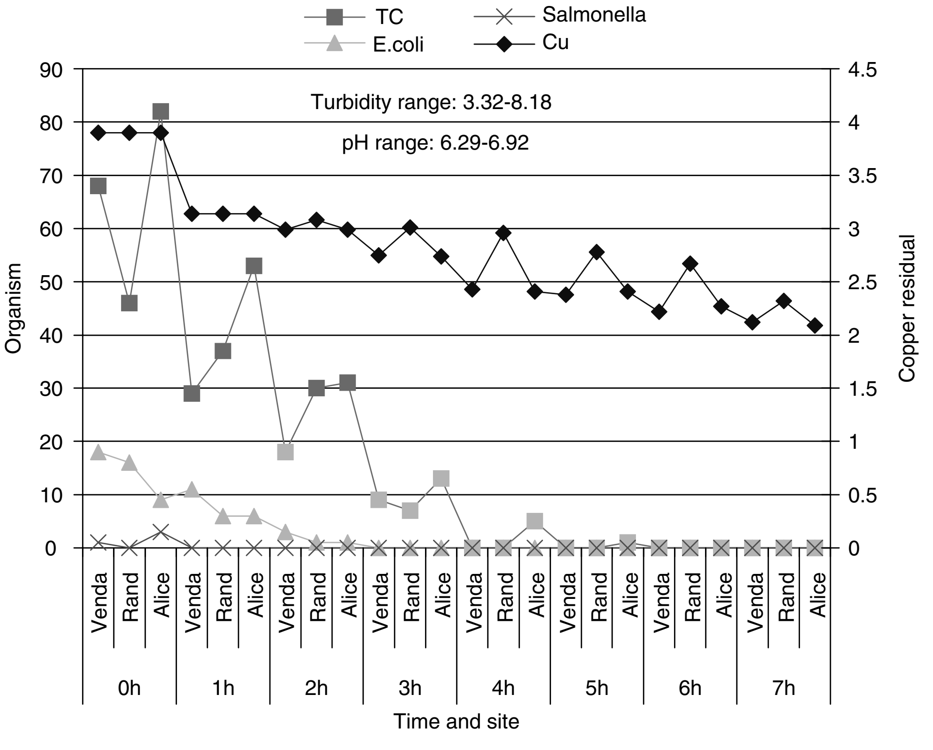

Figure 3. Average counts of indicator bacteria in groundwater samples before and after disinfection with an initial dose of 3.9mg/l copper.

the disinfection of water samples with higher turbidities. Complete removal of total coliforms occurred 6 h after disinfection of Venda and Alice water samples. Although the removal of bacteria was not complete in Rand water samples within this time, the number of total coliforms was within the limits of South African Water Quality Guidelines for no risk (0–5 cfu/100 ml) (12,13), after which the complete removal of coliforms occurred 7 h after disinfection (Fig. 4). The above observations further confirmed that polydex is highly effective in less turbid waters and, therefore, calls for an increase in dosage in highly turbid waters.

As indicated in Fig. 4, the total removal of presumptive *E. coli* in all test waters was recorded 3 h after disinfection.

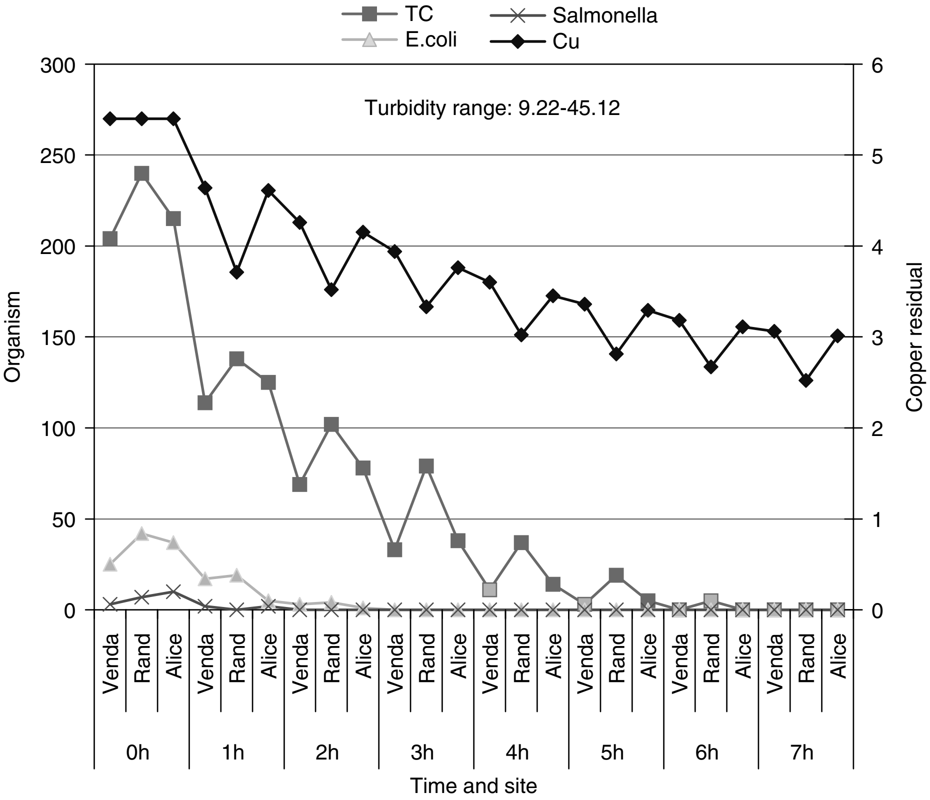

Figure 4. Average counts of indicator bacteria in water samples with high turbidity before and after disinfection with an initial copper dose of 5.4 mg/l.

In Rand water samples, the removal of presumptive S*almonella* was observed within 1 h after disinfection, and in Venda and Alice water samples, complete removal of this bacteria species occurred after 2 h.

CONCLUSIONS AND RECOMMENDATIONS

The study has revealed that polydex was effective for the removal of indicator micro-organisms. However, the turbidity of water remains one of the most important factors that can have a negative effect on its bactericidal efficiency. The dose of 3.9 mg/l appeared to be suitable for the disinfection of water samples with turbidity values ranging between 0.59 NTU and 8.18 NTU; however, this dose is not sufficient for the disinfection of highly turbid waters (>9 NTU). A dose of 5.4 mg/l is recommended for these waters as it completely removes the indicator micro-organisms thereafter leaving residuals of 2.52–3.06 mg/l after 7 h, which are within the recommended limits for potable water.

Based on the present investigations, it is important to filter highly turbid waters or increase the dose in order to increase the effectiveness of polydex. Consequently, this study suggests the followings:

- Polydex can be recommended as a disinfectant for drinking water as limits allowed by South African Water Quality guidelines are reached when this disinfectant is used: (0–5 counts/100 ml total Coliforms, 0 counts/100 ml Faecal Coliforms) (13).
- The dose of 3.9 mg/l is recommended for water with turbidity values ranging between 0.59 NTU and 8.18 NTU, and 5.4 mg/l is recommended for highly turbid waters (>9 NTU).
- The product is also recommended because the residual disinfectant ranges between limits allowed by South African Water Quality Standards (target water quality range 0–3 mg.l^{-1}).

Acknowledgment
The authors wish to express their thanks to Sibambene Trade & Services (Pty), Ltd, who sponsored this investigation. The effort of some personnel of the University of Venda, Umgeni Water, and Rand Water, especially for the collection of water samples, are immensely appreciated.

BIBLIOGRAPHY

1. Momba, M.N.B. and Notshe, T.L. (2003). The microbiological quality of groundwater-derived drinking water after long storage in household containers in a rural community of South Africa. *J. Wat. Suppl: Ers. Technol. AQUA*. **52**(1): 67–77.
2. Geldreich, E.E., Nash, D.H., Reasoner, D.J., and Taylor, R.H. (1972). The necessity of controlling bacterial populations in potable water: community water supply. *J. Am. Wat. Wks. Assoc.* **64**: 596–602.
3. Momba, M.N.B. (2000). Influence of Chloramination on Bacterial Regrowth in a chlorinated surface water laboratory scale system. *Adv. In Wat. Res.* **1**: 51–62.
4. Water Technology. (2004). *The Future of Drinking Water*. Available: http://www.watertechonline.com.

5. Mogollón, C.D. (2000). Eau Canada-Vancouver. WCP Online at: http://www.wcp.net/archive/sep00dealer.htm.
6. Meyer, W.C. (2001). Coping with resistance to copper/silver disinfection—Terms & Condition of use. *Wat Engin Manag.* **148**(11): 1–4.
7. Yayha, M., Landeen, K.L., Kutz, S.M., and Gerba, C.P. (1989). Swimming pool disinfection: an Evaluation of the efficiency of copper-silver ions. *J Environ Health*. **51**: 282–285.
8. Food Standard Committee. (1956). *Report on Copper*. Her Majesty's Stationary Office, London.
9. Browning, E. (1969). *Toxicity of Industrial Metals*. 2nd Edn. Buttersworth, London.
10. World Health Organization. (1974). *Toxicological Evaluation of some Food Additives Including Anticaking Agents, Antimicrobials, Antioxidants, Emulsifiers and Thickening Agents: Cupric sulphate*. WHO Food Additives Series No. 5.
11. NRC. (1980). *Recommended Dietary Allowances*. Food and Nutrition Board, National Research Council and National Academy of Science, Washington, DC.
12. Department of Water Affairs and Forestry, Department of Health and Water Research Commission. (1998). *Quality of Domestic Water Supplies*. Vol. 1: Assessment Guide. Water research Commission No: TT101/98. ISBN No: 1 86845 416 9.
13. Department of Water Affairs and Forestry (DWAF). (1996). *South African Water Quality Guidelines*. Vol. 1: Domestic Use, 2nd Edn. Pretoria.
14. Standard Methods for the Examination of Water and Wastewater. (1998).

PRIVATE SECTOR PARTICIPATION, MARKETING AND CORPORATE STRATEGIES IN MUNICIPAL WATER SUPPLY AND SEWERAGE

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INTRODUCTION—PRIVATE SECTOR PARTICIPATION: DEFINITION AND DRIVERS

The entry will describe how financial, commercial, and technical services are being mobilized to enable economic and social services to be provided and improved by water sector organizations in the North (the developed economies) and the South (developing economies). These needs are different because the policy contexts (politics and governance), standards, and risks experienced by entities installing and improving water services in the North and the South are different. It will be shown that the international water sector companies have evolved a diverse suite of financial and contractual arrangements often in association with international financial institutions (e.g., the World Bank). It will also be shown that the water sector is evolving as new companies shape their financial and technical competence to operate and compete internationally.

Private sector participation (PSP) refers to the formal provision of municipal water and sewerage services by the private sector. This involves providing these services commercially, where infrastructure work is funded by private capital or through a combination of finance from private investors and multilateral agencies.

There are two principal drivers for PSP. In the developed economies of North America, Western Europe, and Southeast Asia, PSP is primarily used to shift the financial burden of upgrading and extending municipal water and sewerage services from central and local government to the private sector. In developing economies, PSP is being employed to finance and manage the development and operation of the water and sewerage infrastructure on commercial lines to mobilize funding from a variety of sources.

The World Water Council's 'World Water Vision for 2025' seeks to address the current lack of access to water provision, sewerage, and sewage treatment by 2025 (1). To provide universal access to water and sewerage services, Vision 2025 calls for investment in new water and sanitation assets to rise from $30 billion in 1995 to $75 billion pa and for investment by industry and for environmental protection to increase from $10–15 billion in 1995 to $75 billion pa between 2000 and 2025 (2). Vision 2025 anticipates that national private companies will contribute 45% of this investment, against 15–21% in 1995; international finance will increase from 5–6% to 24% (3). Such a financial commitment will not take place unless adequate investment conditions exist, and these require private sector participation to manage these services (4).

HISTORY OF PSP

The first formal example of private sector participation in water provision—as opposed to municipal corporations and religious foundations—dates from 1582 when Peter Morris was granted a 500-year lease to pump water from a station underneath London Bridge (5). Early private sector water companies were concerned with providing water to individual buildings not directly served by watercourses and wells as urbanization and industrial development emerged. London's New River Water Company, incorporated in 1619 (6) was the earliest example of a corporate entity, surviving today as Thames Water, part of Germany's RWE. Typically, these companies were taken over as European municipalities developed and were given statutory obligations regarding water provision and sewerage. In the United Kingdom, a series of Acts of Parliament passed between 1867 and 1894 brought the majority of these entities under municipal control (7). Between 1850 and 1914, economic development and urbanization in Europe and the Americas brought about a new wave of water company formation (Table 1). In Europe and Latin America, these companies were usually set up to integrate water provision and distribution contracts for an entire city as opposed to localized undertakings in the United States. York Water Company, the earliest extant company in the United States was incorporated in Pennsylvania in 1816.

Economic and political considerations between 1914 and 1945 caused many European companies to be nationalized or concessions to be revoked. In the United States, the market ceased to expand, but there were a

Table 1. Early European Water Companies and Corporations (Current Owners in Brackets)[a]

Company	Country	Formed	Comments
New River Water Co (Thames Water/RWE)	U.K.	1619	Nationalized, privatized, acquired
Acque Potabili (Italgas)	Italy	1852	Private sector since foundation
Generale des Eaux (Veolia Environment)	France	1853	Private sector since foundation
Berlin Wasser Betriebe	Germany	1856	Privatized in 1999
Lyonnaise des Eaux (Suez Ondeo)	France	1880	Private sector since foundation
Aguas de Barcelona	Spain	1882	Private sector since foundation
Cia. Generale dell Acque	Italy	1884	Municipally owned since 1918
Gelsenwasser	Germany	1887	Acquired by E.ON in 2000
Aguas de Valencia	Spain	1890	Privatized in 1976

[a] Reference 8.

number of concession awards in Mexico. Except for France and Spain, where lease and concession awards were made from the 1950s, PSP continued to play a peripheral role, if at all, until the late 1980s. Between 1988 and 2002, there has been a fourfold increase in PSP and a reappraisal of its role in various economies.

FORMS OF PSP

PSP contracts can be gained outright through a bidding process, or they can evolve from contacts established through private sector consulting, construction, or engineering activities. The characteristics of the main types of water and wastewater privatization contracts are outlined in Tables 2 and 3.

These two types of contracts do not delegate full financial responsibility to the private operator, especially with regard to private capital investments. Operations and maintenance (O & M) contracts operate on a fixed fee basis and cannot address problems of municipal inefficiency.

The municipality controls the assets, and the private sector controls their operation. Risk elements start emerging because the private sector now deals directly with customers.

Table 2. Operations and Management (O & M) and Lease Contracts

Time horizon	2–5 years, up to 10	Ownership	Public
Customer	Government/ Municipality	Investment	Public
Cash flow profile	Fixed fee for service	Operation	Public
Construction risk	None	Tariff collection	Public/ Private
Regulatory risk	None		

Table 3. Lease Contract

Time horizon	10–15 years, up to 25	Ownership	Public
Customer	Retail customer	Investment	Public
Cash flow profile	Subject to market risk	Operation	Private
Construction risk	None	Tariff collection	Private
Regulatory risk	Medium		

Concessions

Concessions involve the private sector operation of assets to pay for new or upgraded facilities and upgrading work. Build-own-operate (BOO) and build-operate-transfer (BOT) contracts involve specific services to the municipality in relation to a specific program of capital improvements, whereas the full utility concession contract embraces all aspects of service provision and capital spending (Table 4). Concessions require a much more specific regulatory environment to account for the elements of risk involved. The concession company controls the service provision entity, but the municipality retains control of the asset owning entity. The latter entity is subsequently responsible for the extant assets, and new assets are vested into this entity at an agreed date. Dalton (9) discusses the political risk involved in developing concessions in developing economies.

A BOO/BOT project's cash flows are usually contractually predetermined and often have government backing. BOT/BOO projects are an effective means of rapidly organizing private capital and management toward a narrow range of services. However, some of the simpler project-oriented contracts do not affect the utility's management and operation; thus underlying problems such as leakage (and illegal interception), overstaffing, and tariff collection may not be addressed.

In full utility concessions (Table 5), existing revenues can be used immediately to service debt, thereby mitigating construction risk. During a period of time, a utility can benefit from a steady flow of revenues from a diversified customer base. A more robust balance sheet can be created, allowing for internal finance as well as the use of capital markets to sell long term debt. The operator is responsible for upgrading and operating

Table 4. BOOT/BOT/BOO Concession

Time horizon	10–30 years, up to 95	Ownership	Public
Customer	Govt./Municipal	Investment	Private
Cash flow profile	Pay on completion	Operation	Private
Construction risk	High	Tariff collection	Public
Regulatory risk	Low		

Table 5. Full Utility Concession

Time horizon	20–30 years	Ownership	Public
Customer	Retail Customer	Investment	Private
Cash flow profile	Subject to market risk	Operation	Private
Construction risk	Low	Tariff collection	Private
Regulatory risk	High if politics volatile		

Table 6. Asset Sale/Asset Ownership

Time Horizon	In Perpetuity	Ownership	Private
Customer	Retail Customer	Investment	Private
Cash flow profile	Subject to market risk	Operation	Private
Construction risk	Very low	Tariff collection	Private
Regulatory risk	Very high		

the services, while developing new assets to hand over to the municipalities in the longer term.

Asset sale is the most dramatic and politically contentious form of privatization (Table 6). To date, it has been used in the 1989 sale of the English and Welsh water and sewage companies (WASCs) and in Chile. The assets are in private hands, but the license to operate them can be subject to renewal. In the case of the U.K. WASCs, a 30-year operating license was awarded to each entity in 1989. In the United States, companies developed the assets in the first place (Table 7).

THE 'BRITISH' AND 'FRENCH' MODELS

The World Bank calls delegated water management through concession awards the 'French model.' The 'French model' is typically used to contrast it with the 'British model' of asset sales. The real 'French model' is the Affermage lease as traditionally used in private sector contracts in France.

Initial Public Offerings

Initial public offerings (IPOs) of a corporatized utility take place when all or part of the shares of a water or multiutility company are listed on the local stock exchange. Since 1976, 48 municipal entities have been privatized by this method; all but nine took place since 1989. Twelve involved outright share sales, but municipalities retain a majority holding in the other 36. In addition, seven privately held water utilities have had IPOs since 1991, along with the water activities of two larger conglomerates. Prime Utilities (Malaysia, 1994) has subsequently left the sector; Azurix was bought back by Enron, its majority holder in 2001, and its main asset, Wessex Water, was in turn acquired by YTL of Malaysia in 2002. One, Northumbrian Water of the United Kingdom was privatized in 1989, acquired by Suez in 1996, and refloated in 2003.

EXTENT OF PSP

In 1988, PSP was restricted to its 'traditional' markets in the United States (asset owning companies); England and Wales (statutory water companies); and France, Italy, and Spain (concessions and lease contracts). The World Bank noted eight PSP water and sewerage contracts in developing economies between 1984 and 1989 (10) against 97 between 1990 and 1997 (Table 8) (11).

The total number served by the private sector in 1998 is estimated at 93 million. Since 1988, it is estimated that PSP has reached a further 302 million people through privatizations; 64 million were added through service extension and population growth within contracts, along with minor contract awards, to cover a total of 460 million people, or 8% of the global population. This includes 7.2 million people in six contracts, which subsequently have been returned to municipal ownership (Table 9).

Table 10 is based on 97 water and sewerage privatization awards identified by the World Bank during the first 8 years of the 1990s involving a total investment of $24.95 billion (12) from banks and multilateral agencies.

O&M contracts do not mobilize new sources of private sector investment. Greenfield operations are typically site specific, involving the construction of a water or sewage treatment facility, as seen in the Scottish sewage treatment construction in the United Kingdom. In recent years, a number of greenfield contracts have been awarded in areas earmarked to become new housing or industrial zones. This approach has had some popularity in the Philippines. Divestitures have been seen in Chile. The concession approach, allied with the splitting of water and sewerage entities into operating and asset holding companies has become the favored approach toward water privatization in many countries (Table 11).

CORPORATE STRATEGIES

A variety of relationships have developed between companies and within companies with regard to global

Table 7. Examples of PSP Contracts by Size and Type

	O&M	BOT	Full Concession	Asset Ownership
Local/site	USA	France	Scottish PFI	USA
Town	Kazakhstan	Germany	Germany	Czech Republic
City	Mexico City	Budapest	Manila	Chile
Region	Greater Amman	Czech Regions	Argentina	UK WASCs
Country	Chad (Phase 1)	Ghana (urban)	Chad (Phase 2)	—

Table 8. Water or Wastewater Services Privatized Each Year, 1988–2002 (Million People)

Year	Running Total	Major Awards	Organic Growth	Minor Gains	Contract Losses	Year End Total	Y-O-Y Increase
1988	93	0.6	1	0	0	95	2
1989	95	45.6	1	1	0	142	48
1990	142	4.6	1	0	0	148	6
1991	148	0.0	1	0	0	149	1
1992	149	0.8	1	0	0	151	2
1993	151	32.3	2	1	0	186	35
1994	186	3.6	2	0	0	192	6
1995	192	16.4	3	1	0	212	20
1996	212	22.6	3	1	0	239	27
1997	239	42.1	3	2	0	286	47
1998	286	16.0	3	2	−1.5	305	20
1999	305	36.1	4	6	−3.6	348	43
2000	348	35.3	5	3	−0.6	390	43
2001	390	32.6	5	4	0	432	42
2002	432	22.3	5	3	−1.5	460	30
Total		310.9	40.0	24.0	−7.2		369

Table 9. People Served Through Private Sector Participation (Start of 2003)

	PSP	Population[a]	% PSP
Western Europe	161.5	388	42
C&E Europe	14.1	341	4
ME & Africa	37.6	1,041	4
Central & South Asia	1.6	1,407	0
South East Asia & Oceania	95.7	2,049	5
North America	65.2	310	21
Latin America	84.0	519	16
World total	459.7	6,055	8

[a] Million people.

Table 10. Private Participation in Water and Sewerage in Developing Countries by Contract Type, 1990–1997

% of Total	Projects	Total Investment
Concessions	50%	80%
Divestiture	6%	4%
Greenfield projects	31%	16%
Operations and management and leases	13%	0%

water and sewerage contracts. None of the water company linkages existed before 1992; only Veolia (then called Generale des Eaux) and Suez (then called Lyonnaise des Eaux) were operating as private sector multiutility companies at that time

Power and Gas Utilities Entering the Sector

The attraction of the water market for these companies is that it represents an extension of their abilities in client management, asset maintenance, and development and in dealing with regulation and politics. Many of these companies have been publicly owned until relatively recently. Power companies across Europe have entered the sector either by acquiring companies in their home markets or internationally.

Table 11. Investment in Water and Sanitation with PSP in Developing Economies ($million)[a]

Region	1990–1994	1995–1999
East Asia & Pacific	4,023	8,631
Europe & Central Asia	16	1,539
Latin America & Caribbean	4,732	8,965
Middle East & North Africa	0	4,106
South Asia	0	0
Sub-Saharan Africa	23	1,054

[a] Reference 13.

Municipal Multiutilities

To date, one German and six Italian municipal multiutilities have been partially floated. In these cases, the water activities account for a minority of group turnover, which tends to be dominated by power activities.

Multiutilities active in seeking water contracts or investments include United Utilities (UK: North West Water/NORWEB), VE (France: Veolia Water/Cofreth & Esys Montenay), Suez (France: Ondeo/Tractabel & Elyo), RWE (Germany: Thames Water/RWE), ACEA (Italy: Acqua Italia/ACEA), and Amga (Italy: Acque Genova/Amga).

From $4.8 billion in investment in 1990–2004 against $24.3 billion in 1995–1999, it is evident that the pace of investment increased in the latter half of the decade, although only $5.1 billion was invested in 1998–1999, as a result of economic problems in Asia during those 2 years. Typically, equity investment provided by the companies involved in operating concessions is equivalent to 30% of the total investment, indicating that the private sector invested $12.2 billion during the period 1990–1999, a total investment of $41.3 billion.

CONSTRUCTION AND WATER

Constructing water and wastewater facilities and their operation have always been closely interlinked. In Vivendi Environment and Suez, the water companies have branched into construction, as has been more erratically seen in the English and Welsh water companies during the past 13 years. Usually, the construction company is attracted to the services concessions, having built the facilities. Bouygues, one of the leading French construction companies, acquired Société d'Aménagement Urbain et Rural (SAUR, founded in 1933) in 1984. FCC (originally Focsa) was founded as a construction company in 1900 and gained the Barcelona sewerage contract in 1911. Dragados, a Spanish construction company, has extensive experience in water supply and sewerage projects. Dycagua, Urbaser's water tendering arm, was set up in October 1994 and has won a number of concessions. Ferrovial has adopted a similar approach through its Ferroser subsidiary.

JOINT VENTURES

Joint ventures for international water/sewerage contracts typically include a company that has experience in the water sector and has a significant presence in the target market(s). Examples include International Water (Edison/Bechtel/United Utilities—all non-U.S. markets), Sino-French Holdings (Suez/New World Developments - China, HK & Macao), VE/Hyundai (South Korea), and Proactiva (VE/FCC-Latin America) (Table 12).

It is evident that the two pioneering companies, Suez and Veolia Environment, continue to lead this market. That dominance is now being challenged, especially by Germany's RWE and a number of British companies.

BIBLIOGRAPHY

Except where a citation has been employed, data and their interpretation are based on the author's private databases and information published by the companies cited.

Table 12. The Leading International Players (by People Served)

Company (Home Country)	Home	International	Total	% Home
Suez—Ondeo (France)	17,000,000	114,100,000	131,100,000	13
Veolia Environment (France)	26,000,000	87,800,000	113,800,000	23
RWE (U.K. & Germany)	27,600,000	41,500,000	69,100,000	40
Bouygues (France)	6,000,000	24,500,000	30,500,000	20
SABESP (Brazil)	19,100,000	0	19,100,000	100
United Utilities (U.K.)	10,300,000	10,200,000	20,500,000	50
Awg (U.K.)	5,800,000	10,600,000	16,200,000	36
Severn Trent (U.K.)	8,300,000	6,300,000	14,600,000	57
FCC (Spain)	6,100,000	5,900,000	12,000,000	51
Bechtel (U.S.)	0	10,200,000	10,200,000	0

1. Cosgrove, W.J. and Rijsberman, F.R. (2000). *World Water Vision*. Earthscan, London, p. 53.
2. Cosgrove, W.J. and Rijsberman, F.R. (2000). *World Water Vision*. Earthscan, London, p. 60.
3. Cosgrove, W.J. and Rijsberman, F.R. (2000). *World Water Vision*. Earthscan, London, p. 64.
4. Cosgrove, W.J. and Rijsberman, F.R. (2000). *World Water Vision*. Earthscan, London, p. 61.
5. Barty-King, H. (1992). *Water, The Book*. Quiller Press, London, pp. 45–46.
6. Barty-King, H. (1992). *Water, The Book*. Quiller Press, London, p. 51.
7. Barty-King, H. (1992). *Water, The Book*. Quiller Press, London, p. 138.
8. Owen, D.A.L. (1998). The European Water Industry, A country-by-country analysis. *Financial Times Energy*. London, p. 46.
9. Dalton, G. (2001). *Private Sector Finance for Water Sector Infrastructure: What Does Cochabamba Tell Us about Using this Instrument?* Occasional Paper No 37, Water Issues Study Group, School of Oriental and African Studies (SOAS), University of London.
10. Silva, G., Tynan, N., and Yilmaz, Y. (1998). *Private Participation in the Water and Sewerage Sector—Recent Trends*. Public policy for the private sector note 147, World Bank, Washington, DC, p. 1.
11. Silva, G., Tynan, N., and Yilmaz, Y. (1998). *Private Participation in the Water and Sewerage Sector—Recent Trends*. Public policy for the private sector note 147, World Bank, Washington, DC, p. 2.
12. Silva, G., Tynan, N., and Yilmaz, Y. (1998). *Private Participation in the Water and Sewerage Sector—Recent Trends*. Public policy for the private sector note 147, World Bank, Washington, DC, p. 5.
13. World Bank. (2001). *World Development Indicators 2001*. The World Bank, Washington, DC, p. 272.

PUMPS

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From start to finish, pumps play an important role in all water distribution systems. They are used to transfer raw water to the treatment plant; they supply water to sections of a distribution system where it is not possible to supply it by gravity; they add appropriate chemical doses during treatment; and they transfer sludge from settling chambers for further treatment and disposal. Pumps will provide long-term efficient service if they are properly operated and maintained

PUMPS IN WATER DISTRIBUTION SYSTEMS

Pumps are an important part of any water distribution system. At the source, they help deliver raw water to the treatment plant. In the plant, pumps add chemical solutions at desired dosages for treatment processes, and other pumps remove sludge from sedimentation facilities for further treatment and disposal. Within distribution systems, pumps discharge water under pressure to the pipe network and lift water where it cannot go by gravity, especially to water towers.

PUMP APPLICATIONS

Different types of applications require different types of pumps. Pumps are selected based on system requirements, discharge pressure required, flow capacity required, and availability of space. The two most common pumps in the water industry are: centrifugal pumps, used most often in water distribution, and positive-displacement pumps, most commonly used in treatment plants for chemical dosing.

TYPES OF PUMPS USED IN WATER SUPPLY

Three kinds of pumps are most often found in water distribution systems: the aforementioned centrifugal pumps, used to move water, vertical turbine pumps, used at the intake, and submersible pumps, used in wells.

Centrifugal Pumps

Centrifugal pumps are the most common type used in water distribution. Centrifugal pumps have a circular “fan/turbine-shaped” structure called an impeller that is mounted on a centrally supporting structure called the shaft. The motor rotates the shaft and can be powered by electricity or diesel fuel. Water enters at an opening in the center called the suction. The rotating impeller imparts a high velocity to the water, and it is circulated and thrown outward (See Fig. 1). A circular-shaped covering called casing surrounds the impeller. The casing is shaped like a spiral so that the water slows down, and the velocity head is converted to pressure head as it flows out of the casing. At the junction of the casing and shaft, a seal or packing rings are provided to prevent leakage. A packing gland presses against the rings to maintain a tight seal.

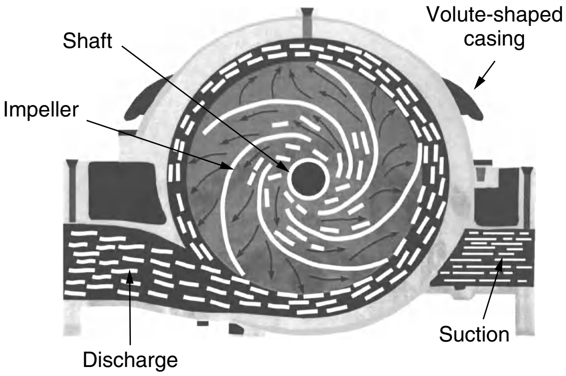

Figure 1. Volute centrifugal pump schematic. Adapted from AWWA *Water Transmission and Distribution: Principles and Practices of Water Supply Operations,* 2nd Edition.

GLOSSARY OF PUMP TERMS

Head—(1) A measure of the energy possessed by water at a given location in the water system expressed in feet; (2) a measure of the pressure or force exerted by water expressed in feet.

Velocity Head— A measurement of the amount of energy in water due to its velocity or motion.

Pressure Head—A measurement of the amount of energy in water due to water pressure.

Impeller—The moving element in a pump that drives the fluid.

Efficiency—A ratio of total energy output to the total energy input expressed as a percent.

Priming—The action of starting the flow in a pump or siphon. With a centrifugal pump, this involves filling the pump casing and suction pipe with water.

Source: American Water Works Association. 1996. *Water Transmission and Distribution: Principles and Practices of Water Supply Operations*, 2nd Edition. Denver, CO: AWWA.

Different flow rates and outlet pressures can be generated by this type of pump, depending on the size of the pump and the space between the casing and the impeller. Impellers can also have varying shapes. These pumps can be used either as a single unit or can be coupled with another similar pump in series to generate more output pressure. When more than one pump is used, it becomes a multistage pump. The pressure desired in the distribution system determines the number of stages required. If a single stage pump is not enough to supply water at adequate pressure, multiple stages are used. Centrifugal pumps can achieve an output pressure of up to 250 feet for each stage. Centrifugal pumps are used to supply large volumes of water at a constant output pressure. The pressure generated by a centrifugal pump is less compared to other types of pumps, such as a reciprocating (positive-displacement) pump.

According to the American Water Works Association’s *Water Transmission and Distribution: Principles and Practices of Water Supply Operations*, some of the advantages of centrifugal pumps are:

- wide range of capacities that range from a few gallons per minute [gpm] to 50,000 gpm. Heads of five to 700 feet are generally available;
- uniform flow at constant speed and head;
- simple construction (small amounts of suspended matter in the water will not jam the pump);
- low to moderate initial cost for a given size;
- ability to adapt to several drive types—motor, engine, or turbine;
- moderate to high efficiency at optimal operation;
- no need for internal lubrication;
- little space required for a given capacity;
- relatively low noise level; and
- ability to operate against a closed discharge valve for short periods without damage.

Some of the disadvantages are:

- an efficiency that is limited to a narrow range of discharge flows and heads;
- low capacity that is greatly dependent on discharge pressure;
- generally no self-priming ability;
- potential for running backward if stopped with the discharge valve open; and
- potential for impeller to be damaged by abrasive matter in water, or clogged by large quantities of particulate matter.

During startup, centrifugal pumps require a procedure called "priming" in which the pump is filled with water before turning the switch on. This insures that when the impeller starts rotating it starts pumping water, and energy imparted to the impeller is not lost. If a centrifugal pump is not primed, it does not operate efficiently (i.e., it does not pump water even when it is turned on). Generally, pumps have an adjacent chamber, called the priming chamber, that sucks in water when the pump is turned on and keeps the impeller submerged.

Vertical Turbine Pumps

In vertical turbine pumps, the water flows vertically through a channel of uniform cross-sectional area. The impeller is positioned in the center along the axis in the channel. The blades of the impeller are shaped so that the water flows in a radial direction (See Fig. 2). The casing has diffuser vanes, shaped so that they guide water and make it flow either into the discharge or through diffuser bowls into inlets of succeeding stages. Vertical turbine pumps are used most often at raw water intakes and at booster stations in the distribution system to augment the pressure required for service. Vertical turbine pumps are relatively more expensive than centrifugal pumps for the same capacity and require more maintenance.

According to the American Water Works Association's *Water Transmission and Distribution: Principles and Practices of Water Supply Operations,* some of the advantages of vertical turbine pumps are:

- uniform flow at constant speed and head;
- simple construction;
- individual stages capable of being connected in series, thereby increasing the head capacity of the pump;
- adaptability to several drive types—motor, engine, or turbine;
- moderate to high efficiency under the proper head conditions;
- little space occupied for a given capacity; and
- low noise level.

The main disadvantages are:

- high initial cost;
- high repair costs;
- the need to lubricate support bearings located within the casing;
- inability to pump water containing any suspended matter; and
- an efficiency that is limited to a very narrow range of discharge flow and head conditions.

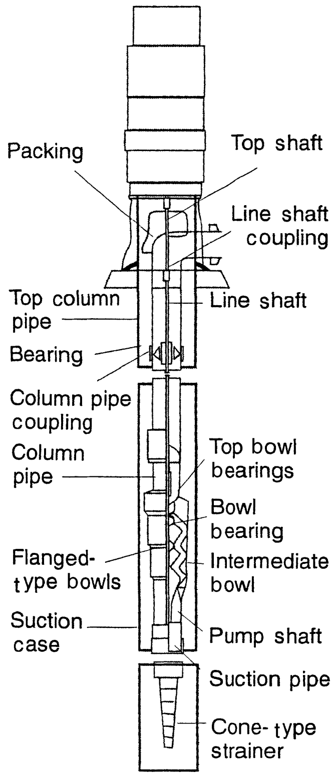

Figure 2. Verticle turbine pump. Adapted from AWWA *Water Transmission and Distribution: Principles and Practices of Water Supply Operations,* 2nd Edition.

Submersible Pumps

Submersible pumps, as the name implies, are placed below the water level (See Fig. 3). They are used mostly for pumping groundwater from wells. The pump is basically a multi-stage centrifugal pump. The impellers of the pump are mounted on a vertical shaft. Each impeller passes water to the next stage through a diffuser shaped so that the water flows vertically to the next diffuser. Each impeller and diffuser is called a stage. The desired output pressure determines the number of stages.

The pump is driven by an electric motor placed adjacent to the pump and is constructed for submerged operation. The wiring of the electric motor is such that it is waterproof. The motors are manufactured to ensure water does not cause it to fail by grounding or shorting out. However, most failures of submersible pumps are due to electrical problems with the motors.

Positive-Displacement Pumps. Positive-displacement pumps are used in water supply operations for feeding chemicals at various stages of the treatment process. They displace a certain volume of water in each stroke

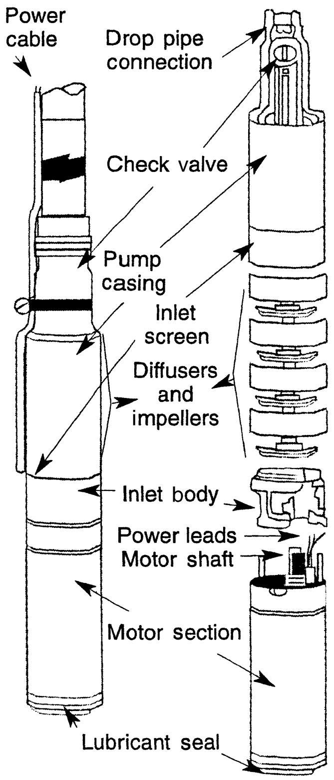

Figure 3. Submersible pumps. Adapted from AWWA *Water Transmission and Distribution: Principles and Practices of Water Supply Operations,* 2nd Edition.

as they operate. These pumps are not suitable for pumping large volumes of water, they are more suited for high pressure and low flow service. There are two types of positive-displacement pumps: reciprocating pumps and rotary pumps.

Reciprocating Pumps

Reciprocating pumps have a piston that moves back and forth in an enclosing cylinder. The arrangement of rotating shaft, connecting rod, and joint pushes the volume of the fluid in the cylinder through an outlet valve. The liquid enters and leaves the cylinder through check valves. Reciprocating pumps are suitable for applications where very high pressures are required, or where abrasive fluids, such as acids or viscous liquids, have to be pumped.

Rotary Pumps

In rotary pumps, the impeller rotates within an enclosing structure and imparts energy to the water. The impeller can be in the shape of a gear, screw, or lobes. For rotary pumps, the output is continuous and smoother compared to reciprocating pumps. Rotary pumps are better suited for lower pressures than reciprocating pumps because of slippage at higher pressures. Rotary pumps can jam if any solids enter the small clearance spaces between the impeller and casing. Rotary pumps are suitable for handling fluids of varying viscosities and are used in water treatment for chemical dosing.

OPERATION OF CENTRIFUGAL PUMPS

Because centrifugal pumps are so widely used in water distribution and because so many brands are available, the individual procedures for proper operation vary. Most manufacturers supply instructions, guidelines, or manuals with a new pump. Users must follow these instructions while operating pumps.

Pump Starting and Stopping

During pump startup, check the lubrication of the motor bearings and prime the pump. After priming, the pump must be started with the discharge valve fully closed. The discharge valve must then be opened slowly to allow any air in the system to escape. The pump discharge valve must be opened and closed slowly to prevent water hammer in the system. (For more information about water hammer, see the *Tech Brief* in the Winter 2003 *On Tap*.)

During power failure (when the motor stops running), the discharge valve can remain open. This might be a problem because the water can actually flow backward. On large pumps, emergency power operated valves are provided to prevent the impellers from running in reverse. On smaller pumps, check valves are provided.

If the pump will be shut down for longer periods, additional steps should be taken. In cold weather, for example, all water must be drained out from the pump to prevent freezing. The pump packing or seal must be removed if the pump is to be stored idle for longer periods.

Centrifugal Pump Maintenance

Centrifugal pumps require regular inspection and maintenance. Bearings on the motor may become worn and must be checked and kept well lubricated. The packing or seal can wear out due to friction resulting in leakage from the pump. These should be checked regularly. Bearing and motor temperatures must be monitored. If a surface is substantially hotter than normal, the unit should be shut down and the cause of excessive heat investigated. In case of any unusual noises or vibrations from the pump, it must be stopped and the cause investigated.

WHAT ABOUT SAFETY?

Safety instructions provided by the manufacturer must be followed. Pumps should always be switched off before any maintenance. All liquids must be drained out before servicing. People must stand away from any moving parts. Safety precautions must be taken regarding electrical motors. Maintenance personnel must wear rubber gloves and use insulated tools while servicing electrical motors. A record of all maintenance work must be maintained.

Concern that the water supply could be vulnerable to terrorist attacks has understandably been heightened by recent world events. Knowledge, planning, and preparedness helps relieve this concern. It is crucial now to regularly inspect the location, accessibility, and operation of all the pumps in the distribution system. A large-scale disruption in water supply for a large water system can happen because of pump failure at a key location. After gathering complete and accurate information on all the pumps in the system, the utility manager can run through "what if" scenarios to determine where a contaminant is likely to move. Workers can also learn how water movement can be controlled by running or shutting down pumps or other utility operations.

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WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1996. *Water Transmission and Distribution: Principles and Practices of Water Supply Operations,* 2nd Edition. Denver, CO: AWWA.

American Water Works Association. 1999. *Design and Construction of Water Systems: An AWWA Small System Resource Book*, 2nd Edition. Denver, CO: AWWA.

Dickenson, T.C. 1995. Pumping Manual. Oxford, UK: Elsevier Advanced Technology.

HDR Engineering, Inc. 2001. *Handbook of Public Water Systems*. New York: John Wiley and Sons, Inc.

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RADIONUCLIDES

National Drinking Water
Clearinghouse

Radionuclide contamination of drinking water is a significant, emerging issue. Until now, manmade radioactivity in drinking water has not been a major problem. Natural sources have been the primary cause of contamination. However, the potential for contamination exists throughout the country as releases from medical facilities or nuclear power plants may wind up in drinking water. Because of their potential health effects and widespread occurrence, natural radionuclides—including radon, radium, and uranium—cause much concern.

WHERE DO RADIONUCLIDES OCCUR, AND WHAT ARE THE PUBLIC HEALTH RISKS?

Radionuclides occur naturally as trace elements in rocks and soils as a consequence of the "radioactive decay" of uranium-238 (U-238) and thorium-232 (Th-232). This decay happens because radioactive atoms have too much energy. When radioactive atoms release or transfer their extra energy, it is called decay. The energy they release is called ionizing radiation, which may be alpha particles, beta particles, or gamma rays. This energy is transmitted through space or another medium in waves (e.g., x-rays or gamma rays) or particles (e.g., electrons or neutrons) and is capable of either directly or indirectly removing electrons from atoms, thereby creating ions, which are electrically charged atoms.

Radon-222, radium-226, radium-228, uranium-238, and uranium-234 are ions of the U-238 and Th-232 decay series. They are the most common radionuclides found in groundwater. Other naturally occurring radionuclides tend to be environmentally immobile or have short half-lives, meaning they are far less likely to be found in significant amounts in groundwater.

When ionizing radiation strikes a living organism's cells, it may injure the organism's cells. If radiation affects a significant number of cells, the organism may eventually develop cancer. Or at extremely high doses, it may even die.

Radon. Radon is a naturally occurring radioactive gas that emits ionizing radiation. National and international scientific organizations have concluded that radon causes lung cancer in humans. Ingesting drinking water that contains radon also presents a risk of internal organ cancers, primarily stomach cancer. The U.S. Environmental Protection Agency (EPA) and the U.S. Surgeon General recommend testing indoor air for radon in all homes and apartments located below the third floor. If you smoke and your home has high indoor radon levels, your risk of lung cancer is especially high.

Tap water only emits approximately 1 to 2 percent of the radon found in indoor air. However, breathing radon from this source increases the risk of lung cancer over the course of a lifetime.

Radium. Radium-226 and radium-228 are natural groundwater contaminants that usually occur at trace levels. At high exposure levels, radium-226 and radium-228 can cause bone cancer in humans and are believed to cause stomach, lung, and other cancers as well.

Uranium. Uranium is a naturally occurring radioactive contaminant that is found in both groundwater and surface water. At high exposure levels, uranium is believed to cause bone cancer and other cancers in humans. EPA also believes that uranium can be toxic to the kidneys.

Table 1. What Regulations Govern Radionuclides?

Radionuclide National Primary Drinking Water Regulations						
			EPA Standards			
Contaminants	Drinking Water Health Effects	Proposed Maximum Contaminant Level Goal MCLG	Proposed Maximum Contaminant Level (MCL)	Current MCL	Sources	Best Available Technology (BAT)[2]
Radium-226	Cancer	Zero	20 pCi/L	5 pCi/L combined with radium-228	Naturally occurring	Ion Exchange (IE); Lime Softening (LS); Reverse Osmosis (R0)
Radium-228	Cancer	Zero	20 pCi/L	5 pCi/L combined with radium-226	Naturally occurring	IE; LS; RO
Radon-222	Cancer	Zero	300 pCi/L	–	Naturally occurring	Aeration
Uranium	Kidney toxicity, Cancer	Zero	20 ug/L[3]	–	Naturally occurring	Coagulation/ Filtration; Anion exchange; LS; RO[4]
Adjusted gross alpha emitters	Cancer	Zero	15 pCi/L	15 pCi/L	Naturally occurring and manmade	RO
Gross beta and photon emitters	Cancer	Zero	4 mrem ede/yr	4 mrem ede/yr any organ or whole body	Naturally occurring	IE; RO

1. *PicoCuries per liter* (pCi/L) is an activity measurement of radioactive decay (1 pCi/L = 2.2 disintegrations per minute); *micrograms per liter* (μg/L) is a mass measurement; *mrem* is measurement of effective radiation dose to organs.
2. Except as noted, BAT for the purpose of issuing variances is the same as BAT for compliance.
3. 20 μg/L is based on kidney toxicity. 20 μg/L is the equivalent of 30 pCi/L.
4. *Coagulation/Filtration* and *Lime Softening* are not BAT for small systems (those with fewer than 500 connections) for the purpose of granting variances.

Note: EPA recognizes that most radionuclides emit more than one type of radiation as they decay. The lists of compounds labeled “alpha” or “beta” emitters identify the predominant decay mode.
Note: In this document the unit mrem ede/yr refers to the dose ingested over 50 years at the rate of 2 liters of drinking water per day.
Source: U.S. Environmental Protection Agency, 1991.

Gross Alpha. Alpha emitters naturally occur as radioactive contaminants, but several come from manmade sources. They may occur in either groundwater or surface water. At high exposure levels, alpha emitters are believed to cause cancer in humans.

Beta and Photon Emitters. Beta and photon emitters are primarily manmade radioactive contaminants associated with operating nuclear power plants, facilities that use radioactive material for research or manufacturing, or facilities that dispose of radioactive material. Some beta emitters occur naturally. Beta and photon emitters primarily occur in surface water. At high exposure levels, beta and photon emitters are believed to cause cancer in humans.

WHAT ARE THE TREATMENT TECHNOLOGIES FOR RADIONUCLIDES?

Whether or not a particular treatment technology effectively removes radionuclides from drinking water depends on the contaminant’s chemical and physical characteristics as well as the water system’s characteristics (e.g., source water quality and water system size). Other considerations include cost, service life, and co-treatment compatibility.

Table 2. Technologies for Radionuclides

Unit Technology	Limitations (See Footnotes)	Operator Skill Level Required[1]	Raw Water Quality Range and Considerations[1]
1. Ion Exchange (IO)	(a)	Intermediate	All groundwater
2. Point of Use (POU) IO	(b)	Basic	All groundwater
3. Reverse Osmosis (RO)	(c)	Advanced	Surface water usually requires prefiltration
4. POU RO	(b)	Basic	Surface water usually requires prefiltration
5. Lime Softening	(d)	Advanced	All water
6. Green Sand Filtration	(e)	Basic	
7. Co-precipitation with Barium Sulfate	(f)	Intermediate to Advanced	Groundwater with suitable water quality
8. Electrodialysis/Electrodialysis Reversal		Basic to Intermediate	All groundwater
9. Pre-formed Hydrous Manganese Oxide Filtration	(g)	Intermediate	All groundwater

[1] National Research Council (NRC). "Safe Water from Every Tap: Improving Water Service to Small Communities." National Academy Press. Washington, DC. 1997.

Limitations Footnotes

a. The regeneration solution contains high concentrations of the contaminant ions. Disposal options should be carefully considered before choosing this technology.

b. When POU devices are used for compliance, programs for long-term operation, maintenance, and monitoring must be provided by the water utility to ensure proper performance.

c. Reject water disposal options should be carefully considered before choosing this technology.

d. The combination of variable source water quality and the complexity of the chemistry involved in lime softening may make this technology too complex for small surface water systems.

e. Removal efficiencies can vary depending on water quality.

f. This technology may be very limited in application to small systems. Since the process requires static mixing, detention basins, and filtration; it is most applicable to systems with sufficiently high sulfate levels that already have a suitable filtration treatment train in place.

g. This technology is most applicable to small systems that already have filtration in place.

Source: Environmental Protection Agency, 1998.

EVALUATION OF TECHNOLOGIES

The following treatment technologies were evaluated for their ability to remove radionuclides from water:

- ion exchange (IE);
- point-of-use (POU) IE;
- point-of-entry (POE) IE;
- reverse osmosis (RO);
- POU RO; POE RO;
- lime softening (LS);
- greensand filtration;
- co-precipitation with barium sulfate;
- selective sorbents;
- electrodialysis/electrodialysis reversal (ED/EDR); and
- preformed hydrous manganese oxides (HMOs).

Ion Exchange. Small systems may readily use IE treatment, which removes approximately 90 percent of radionuclides. The effluent must be regularly monitored and the resin must be frequently regenerated to ensure that breakthrough does not occur. Ion exchange units may be controlled automatically, requiring less of the operator's time. However, it is necessary to employ a skilled operator to determine when regeneration is needed and to troubleshoot. Also, disposal of concentrated radionuclides can be expensive.

Ion exchange treatment generates wastes that include rinse and backwash water, and the resin. The rinse and backwash liquid waste includes brine, radium, and any other contaminants that the process removes.

Cation Exchange. A cation is a positively charged ion. Cation exchange resins exchange like-charged ions equally with protons—sodium ions (Na+), or in sodium-restriction cases, potassium ions (K+)—to remove undesirable cations from water. Cation exchange is often used to remove calcium and magnesium cations, and to treat hard water.

The amount of waste (rinse and backwash) that cation exchange typically generates ranges between 2 and 10 percent of the treated water.

Lime Softening. Lime softening can be used to remove radium from drinking water with 80 to 95 percent efficiency. Also, adding lime or lime-soda ash to water increases the pH of the water and induces calcium carbonate and magnesium hydroxide precipitation. Lime softening also is used to treat hard water.

Lime softening generates wastes that include lime sludge, filter backwash liquid and sludge, and sludge supernatant.

Reverse Osmosis (RO). Reverse osmosis effectively removes many inorganic contaminants, including heavy metals and radionuclides, such as radium and uranium. RO can remove 87 to 98 percent of radium from drinking water. Similar elimination can be achieved for alpha particle activity and total beta and photon emitter activity.

When using an RO system to remove radionuclides, performance depends on a number of factors, including pH, turbidity, iron/manganese content of the raw water, and membrane type. The pretreatment design depends on the quality and quantity of the source water. Existing treatment plants may already provide much of the required pretreatment—for example, coagulation/filtration of highly turbid surface water or iron removal for well waters. RO can be cost effective for small systems.

TECHNOLOGIES FOR RADIONUCLIDE REMOVAL NOT PROPOSED AS BAT IN 1991

Greensand Filtration for Radium Removal

Greensand filtration technology consists of a conventional filter box with manganese greensand replacing the traditional filtration medium. Studies indicate that greensand filtration removes up to 56 percent of radium.

This process generates wastes that include sludge and supernatant from the filter backwash, and eventually the greensand media must be disposed of.

PREFORMED HYDROUS MANGANESE OXIDE (HMO) FILTRATION

Costs for HMO treatment can be quite low, if filtration is already in place.

HMO filtration is similar to oxidation/filtration in its complexity and the operator skill it requires. Proper dosages must be determined, and if water quality varies, the dosage must be recalibrated. Once the proper dose is determined, dosing is relatively easy. HMO filtration requires simple equipment and is fairly inexpensive. Filters must be backwashed, which may require intermediate operator skill. Radium containing wastes include HMO sludge, filter backwash, and sludge supernatant.

CO-PRECIPITATION OF RADIUM WITH BARIUM SULFATE

Adding a soluble barium salt—such as barium chloride—to radium and sulfate contaminated water causes co-precipitation of a highly insoluble radium-containing barium sulfate sludge. This process has primarily been used for wastewater treatment. Mine wastewater treatment data indicates that this process removes up to 95 percent of radium.

This process generates wastes that include the barium sulfate precipitate sludge, filter backwash, and sludge supernatant.

OTHER TECHNOLOGIES

Some other technologies also are available that may remove radionuclides from drinking water. However, these technologies have not been fully tested for drinking water treatment or have only been used in industrial or experimental situations. Examples of processes that remove radium include selective sorbents (e.g., acrylic fibers or resins impregnated with manganese dioxide) and non-sodium cation exchangers (e.g., hydrogen ions and calcium ions).

WHERE CAN I FIND MORE INFORMATION?

(1) American Water Works Association & American Society of Civil Engineers. 1998. *Water Treatment Plant Design*; 3rd ed. The McGraw-Hill Companies, Inc.

(2) U. S. Environmental Protection Agency. September 1998. *Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996*. EPA 815-R-98-002.

(3) U. S. Environmental Protection Agency. August 1998. *Federal Register/Notices*. Vol.63, No. 151.

(4) U. S. Environmental Protection Agency. October 1999. Office of Groundwater and Drinking Water. *Proposed Radon in Drinking Water Rule: Technical Fact Sheet* EPA 815-F-99-006. www.epa.gov/safewater/radon/fact.html

(5) U. S. Environmental Protection Agency. June 1991. Office of Ground Water and Drinking Water. *Radionuclides in Drinking Water - Fact Sheet* EPA 570/9-91-700.

(6) U. S. Environmental Protection Agency. July 1991. "National Primary Drinking Water Regulations; Radionuclides; Proposed Rule" *Federal Register*, Vol.56, No. 138.

(7) U. S. Environmental Protection Agency. March 1997. *Federal Register*, Vol.62, No. 43.

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USE OF REDOX POTENTIALS IN WASTEWATER TREATMENT

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INTRODUCTION

Effective process control requires an understanding of where the process is with respect to reaction potential and completion. Online measurements allow for greater monitoring of the state of the process from flowrates to chlorine residuals. A measure of dissolved oxygen in the system is useful until anoxic and anaerobic conditions are encountered. Once those environmental conditions are achieved, as is the case with biological nutrient removal (BNR), the ability to measure a wider range of conditions may be achieved with oxidation–reduction potential (ORP).

BASICS OF OXIDATION–REDUCTION REACTIONS

Oxidation–reduction reactions also referred to as redox or oxido reduction involves the transfer of electrons and provides microorganisms with their free energy during transformations. The energy exchange is usually in the form of ATP (adenosine triphosphate), where the energy is in the bonds between the phosphoryl groups. Both aerobic and anaerobic metabolism produce ATP, but the anaerobic rate of production is much lower than that of the aerobic process.

The redox reaction typically transfers electrons from an electron donor (ED) to an electron acceptor (EA), where two half-reactions (or redox couples) can be derived to show the movement of the electron (Fig. 1). By taking the electron, the EA gains a net negative charge, while the ED loses an electron and gains a net positive charge.

THE NERNST EQUATION

The redox potential (ΔE) can be viewed as the electron pressure or the degree of tendency for electrons to be transferred and is defined by the Nernst equation (Fig. 2). The standard redox potential, ΔE°, is defined as the difference between the reduction potentials of the electron acceptor and donor when all components are in their standard state ($\Delta E^\circ = E^\circ_{\mathrm{EA}} - E^\circ_{\mathrm{ED}}$). This reduction potential is measured with respect to the hydrogen half-reaction.

Biochemical standard state (E° at pH 7) for the hydrogen half-reaction is −427 mV (negative 427 millivolts).

$$\mathrm{EA} + e^- \rightleftharpoons \mathrm{EA}^{(-)} \quad \text{reduction}$$

$$\mathrm{ED} \rightleftharpoons \mathrm{ED}^{(+)} + e^- \quad \text{oxidation}$$

Figure 1. Generic reduction and oxidation half-reactions (1).

$$\Delta\varepsilon = \Delta\varepsilon^\circ - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[\mathrm{ED}^{(+)}][\mathrm{EA}^{(-)}]}{[\mathrm{ED}][\mathrm{EA}]}\right)$$

where
R = universal gas constant,
T = temperature,
n = 1 mole of electrons, and
$\mathscr{F}$ = faraday, the charge of 1 mole of ?

Figure 2. The Nernst equation for redox potential (1).

The more positive the half-reaction, the greater the tendency for the oxidized form to be reduced and therefore the electron acceptor is defined (1).

TYPICAL RANGES FOR REDOX POTENTIAL IN BIOLOGICAL SYSTEMS

The wastewater treatment process involves a multitude of environmental conditions in order to achieve complete treatment of influent constituents. Each of these general environmental conditions may be defined by several ranges of redox potentials (Fig. 3). As a general rule of thumb, readings taken with an ORP electrode that are less than −200 mV are indicative of anaerobic or reducing conditions. ORP readings between approximately −200 and +200 mV are for anoxic conditions. Aerobic or oxidative conditions are present above +200 mV.

The typical wastewater processes for the anaerobic range include sulfate reduction, occurring primarily in the collection system, and methanogenesis and fermentation, which are more typical of the anaerobic digestion process. This range is defined by sulfate as the primary terminal electron acceptor. The anoxic range is useful for biological nutrient removal, where nitrate serves as the dominant terminal electron acceptor. The aerobic range involves the activated sludge process and disinfection, where oxygen or the disinfectant serves as the terminal electron acceptor (2,3).

NUTRIENT REMOVAL

For biological nutrient removal (BNR), there is a need to switch between anaerobic/anoxic conditions and aerobic

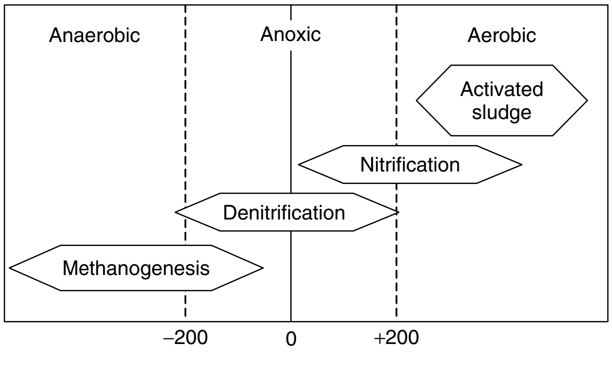

Figure 3. Redox potential ranges (mV) for typical wastewater processes. (Modified from References 2 and 3).

conditions to achieve complete removal of nitrogen and phosphorus compounds from the water. For phosphorus removal, anaerobic conditions result in a release of orthophosphate to gain energy by using up ATP. The higher energetics of aerobic metabolism then causes phosphorus uptake, so that the microorganisms can store the energy. Similarly, anoxic/anaerobic conditions allow for the conversion of nitrate and nitrite to nitrogen gas, while aerobic conditions allow for the oxidation of ammonia to nitrite and nitrate. Controlling these two processes, denitrification and nitrification, respectively, requires the ability to switch and establish the proper environmental conditions. ORP readings afford the operator greater control over these conditions (4–6).

OTHER POTENTIAL APPLICATIONS

Other applications for ORP monitoring and control are currently being researched and implemented. Waste-activated sludge hydrolysis may be enhanced to increase its bioavailability during sludge handling (7–9). Dosing may be controlled in the disinfection process (10). Aeration may be controlled and thus the organism growth influenced in the activated sludge process (11).

CONCLUSION

With increasingly better electrode technology and online monitoring and data storage capability, process control using ORP has a future in reducing operational cost and improving operational efficiency.

BIBLIOGRAPHY

1. Voet, D. and Voet, J. (1995). *Biochemistry*, 2nd Edn. Wiley, Hoboken, NJ, pp. 428–437.
2. Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd Edn. Wiley, Hoboken, NJ, p. 477.
3. Byl, T.D. and Williams, S.D. (2000). *Biodegradation of Chlorinated Ethenes at a Karst Site in Middle Tennessee*. U.S. Geological Survey, Nashville, TN, Water Resources Investigations Report 99–4285, p. 4.
4. Hidaka, T., Tsuno, H., and Kishimoto, N. (2003). Advanced treatment of sewage by precoagulation and biological filtration process. *Water Res.* **37**: 42559–4269.
5. Lee, D.S., Jeon, C.O., and Park, J.M. (2001). Biological nitrogen removal with enhanced phosphate uptake in a sequencing batch reactor using single sludge system. *Water Res.* **35**(16): 3968–3976.
6. Metcalf & Eddy, Inc. (2003). *Wastewater Engineering: Treatment and Resuse*, 4th Edn. McGraw-Hill, Boston, pp. 611–629.
7. Chang, C.-N., Ma, Y.-S., and Lo, C.-W. (2002). Application of oxidation–reduction potential as a controlling parameter in waste activated sludge hydrolysis. *Chem. Eng. J.* **90**: 273–281.
8. Chen, G.-H. et al. (2003). Possible cause of excess sludge reduction in an oxic-settling-anaerobic activated sludge process (OSA process). *Water Res.* **37**: 3855–3866.
9. Filani-Meknassi, Y., Tyagi, R.D., and Narasiah, K.S. (2000). Simultaneous sewage sludge digestion and metal leaching: effect of aeration. *Proc. Biochem.* **36**: 263–273.
10. Yu, R.-F. (2004). Feed-forward dose control of wastewater chlorination using on-line pH and ORP titration. *Chemosphere* **56**: 973–980.
11. Chen, G.-H., Yip, W.-K., Mo, H.-K., and Liu, Y. (2001). Effect of sludge fasting/feasting on growth of activated sludge cultures. *Water Res.* **35**(4): 1029–1037.

REPAIRING DISTRIBUTION LINE BREAKS

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Occasionally, water systems encounter situations where they must repair distribution system pipes. Corrosion and tuberculation (i.e., buildup of sediment, dirt, or rust) may have caused small leaks in the lines, or worse, a major line break may occur, creating an emergency situation. This Tech Brief discusses ways to manage these situations and outlines steps a utility may take to repair the distribution system.

WHAT CAUSES PIPES TO BREAK?

Distribution lines can break for a variety of reasons. Excessive weight, such as increased traffic continuously running over a buried pipe, can trigger a line break. Also, extremely cold temperatures can cause breaks because when water freezes, it expands. But environmental conditions are not the only reason a line may break.

Sometimes utility workers may unknowingly install pipes that have defects from the manufacturing process, and they are not strong enough to handle high-pressure surges. Consequently, the pipes may split or crack. Other times pipes may not have been properly installed into the trench, creating a situation where it's only a matter of time before a line bursts.

Corrosion and tuberculation are two more reasons that pipe can rupture. Corrosion may cause breaks or leaks because acidic conditions can cause pitting or holes in a metallic pipe. In addition, tuberculation can cause high-pressure pockets in some areas of pipe, because water that's under pressure may not be able to easily move beyond the area of buildup.

WHEN ARE REPAIRS NEEDED?

Over time, even small leaks can waste a substantial amount of water, which is expensive. When water system personnel detect a leak, they should repair it immediately—no matter how small it is.

When water comes out of the ground, it is obvious a leak exists nearby and its location is fairly easy to determine. However, scheduling periodic leak detection exercises helps water systems determine where and when they should make repairs in situations that aren't so obvious.

Because most leaks are not visible, all a utility worker may know is that the system is losing water. Someone then has to find the leak. This involves using listening devices, such as Geophones® or other electronic equipment. (For more information about leak detection, see the *Tech Brief* in the Spring 2001 *On Tap*, and the article, "On the Trail of the Elusive Water Leak" in the Summer 2003 *On Tap*.)

One of the best ways to trace water loss is to conduct a water audit. A water audit helps systems keep unaccounted for water loss to the recommended 15 percent or less of the total water a system produces. Conducting a water audit and following up on the results can help the utility control its water losses. (For more information about water audits, see the Fall 2002 *On Tap* article, "The Economics of Water Loss: What is unaccounted for water?").

To conduct a water audit, utility workers will need to take flow measurements over a 24-hour period. This task will require pressure gauges. Utility workers also should make sure to check meters on main lines first to see if they are accurate and calibrated. As water flows from main lines into smaller lines, utility workers take flow measurements at a number of points in the smaller lines. Large, unaccounted for nighttime flows indicate a leak.

EMERGENCY REPAIRS

Sometimes leaks aren't small. Sometimes they gush. If a main breaks, utility workers must repair it immediately. To avoid too much stress, utilities need to have a plan of action ready that details the necessary equipment, personnel, and procedures. This plan is usually referred to as an emergency response plan (ERP) and should involve law enforcement, fire protection, and city officials because utility personnel must first figure out if the leak poses a hazard to life or property.

As soon as a major break is detected, utility workers should notify customers that their water will be turned off while workers make repairs. Valves must first be shut off in the area to isolate the break and to prevent further water loss.

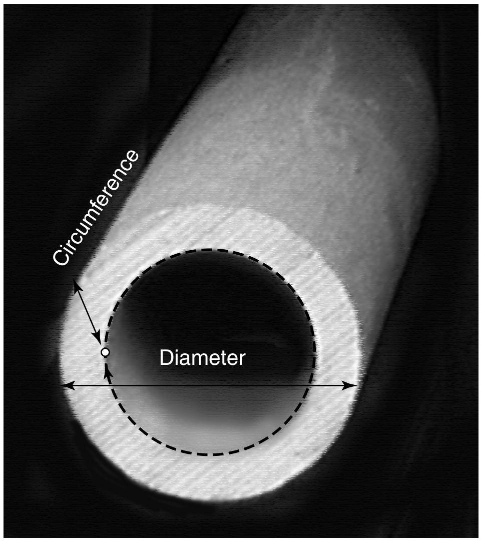
More often than not, valves can become hard to close or may even break if they are not used on a regular basis. Systems should have regular valve-exercising and hydrant-flushing programs to alleviate this problem. (For tips about developing a valve-exercising program, see the article, "Why bother with a valve-exercising program?" in the Winter 2004 *On Tap*. For more information about hydrant flushing, see "Fire Hydrant Operation and Maintenance," in the Fall 2002 *On Tap*).

If possible, repair the leak without shutting off the entire water supply. Figure 1 shows a section of a distribution system with an arrangement of four valves. The leak is near a corner before valve 2. Water flow is from left to right through the loop. When making repairs, close valve 4, valve 3, and valve 2, keeping valve 1 open till the very last minute (Fig. 3). Valve 1 is then closed slowly. Utility workers then make repairs on the leak and turn the water back on immediately. Closing the valve nearest the leak at the last minute allows the line to remain under pressure, preventing back siphoning and back pressure that can cause contaminants to get sucked in through the leak.

If, however, the valves cannot be opened and, consequently, the water cannot be turned off, one practice is to open several fire hydrants in the area. While this method will not stop the water, it will lower the water pressure enough that utility workers can repair the leak. Once the repairs have been completed, workers then slowly turn the water back on. Turning the water back on slowly ensures that water hammer will not become a problem.

Water hammer is a hydraulic shock that happens when a sudden change in velocity occurs, such as quickly closing a valve. Shock waves occur within the pipes, which travel back and forth and cause a "bang" within the pipe. This bang is the hammer that can cause pipes to burst. (See the *Tech Brief* about water hammer in the Winter 2003 *On Tap*.)

When a line is under pressure, less probability exists for contaminants to get in through the break. But if contamination does occur, the utility should take the appropriate actions to inform the public through local radio, TV, or other new service. Notification should outline



This diagram shows how to measure the diameter for a clamp.

$$\text{Circumference} = 3.14 \times \text{Diameter}$$

$$\text{Diameter} = \frac{\text{Circumference}}{3.14}$$

Figure 1. Calculating diameter from circumference. *Source*: *Water Transmission and Distribution*, AWWA, 2nd Edition.

steps customers can take to be sure their water is safe. In case of an emergency, utilities should refer to their ERP that should specifically outline what they need to do. For example, they also may need to notify state primacy agencies, depending upon what level of action they need to take.

DIGGING UP THE PIPE

Once utility workers detect the leak, they have to dig up the pipe. The trench must be parallel to the pipe on both sides and be deep enough that a person can work around the pipe to repair it. Workers must calculate the trench's depth and width based on pipe size. Water will collect in the pit and will have to be pumped out.

Utility workers also should remember that it's an Occupational Safety and Health Administration (OSHA) rule to shore the trench if it's five feet or deeper—or less than five feet if the conditions warrant it, such as extremely sandy or muddy soil.

REPAIR METHOD

If the break in the pipe is very large, that portion of the pipe will have to be cut off and a new section put in place. Cutting a pipe requires saws, pipe cutters, welding equipment (if the pipes are made of steel), pipe wrenches, couplings, and other hand tools.

If the break in the pipe is small, such as a rupture across the pipe, utility workers can wrap a flexible clamp or sleeve on it, which acts like a bandage for the pipe. Wrapping a coupling around the pipe, which is a device that holds two separate pieces of the pipe together in a "covering" device, is another way to repair a small break (see Fig. 2).

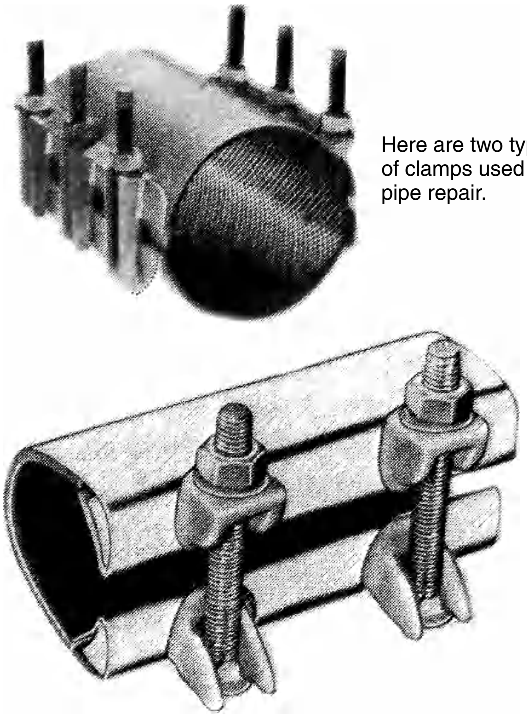
A clamp installed on the pipe has a gasket (usually made of rubber) that covers the ruptured section and helps to maintain a secure fitting. There is an arrangement of screws (preferably stainless steel) that are tightened around the clamp. Utility workers will need to clean and scrape corrosion and dirt from the pipe surface and then disinfect it with bleach.

In addition, they should measure the outside circumference of the pipe to determine the exact diameter of a coupling. (The diameter is equal to the circumference divided by 3.14159.)

After the pipe is repaired, workers should turn on the water slowly to check if there are any remaining leaks. The trench is typically covered with filling material, such as sand, crushed stone, or processed material, and compacted. The workers should ask system customers to turn on their taps and allow the water to run for some time because the water may or may not have sediment in it.

BEING PREPARED

A water utility should have an emergency vehicle, such as a pickup truck, stocked with essential tools, including pipe cutters, wrenches, shovels, traffic control equipment, barricades, flashers, cones, and flashlights. This preparation will save time in an emergency. They should keep the truck's gas tank full and not loan out tools or equipment. Qualified individuals should be on call for emergency response at all times, including scheduled holidays.



Here are two types of clamps used in pipe repair.

Figure 2. Types of clamps. *Source*: *Water Transmission and Distribution*, AWWA, 2nd Edition.

LAYING NEW PIPES

In some situations, a utility may have to replace an entire pipeline. New pipes may have to be hauled in and installed. Care must be taken to prevent pipes from breaking during shipping or storage, and the pipes must be installed correctly. Approvals or permits from the relevant state or local agency must be obtained before starting a new project.

Pipes should be placed where they will be installed before digging out the trench. One end of a pipe is shaped like a bell, and the other end is straight. Pipes are joined together straight end into bell end and secured with a gasket. Pipes should have their bell-shaped ends placed in the direction in which the installation of the pipe will proceed.

Excavating the earth to install pipes is the most expensive part of many replacement projects. Before beginning the repair project, other utility installations, such as sewer and gas lines, must be located. In addition, utility workers must notify nearby property owners and the general public.

Once the project is underway, utility workers must:

- determine the trench's width according to the pipe size required,

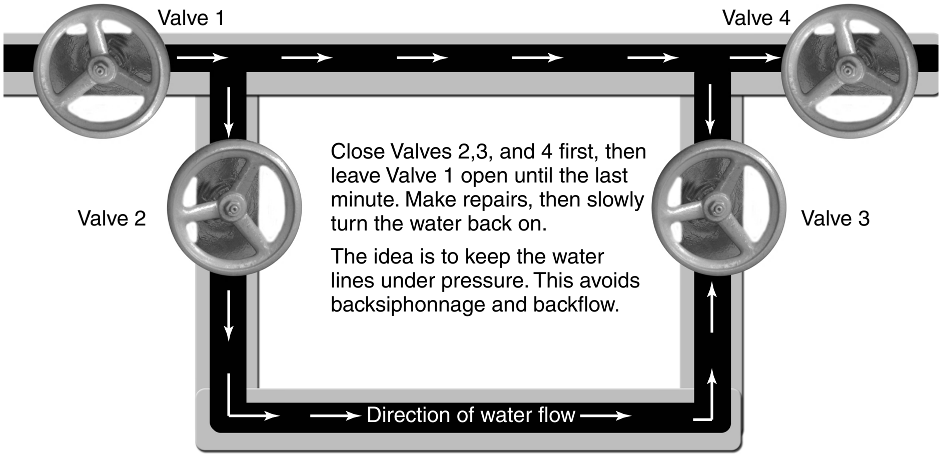


Figure 3. Overhead view of a distribution system. *Source*: *Operator Basics* CD, Montana Water Center.

- lower pipes carefully into the trench using ropes,
- dig out additional soil at the bell ends so that the pipe is supported along its entire length, and
- add some backfill material or bedding to the trench to support the pipe.

Pipes have gaskets on the bell-shaped ends. When laying new pipelines:

- the gasket must be clean, and
- pipes must be pushed all the way into the bell of an adjoining pipe to make a tight fit.

COMPLETING REPAIRS

Once workers have completed repairs, they should turn the water back on and check for leaks before backfilling the trench. The new lines should be disinfected and thoroughly flushed to remove all sediment and dirt.

According to the American Water Works Association's standards, water samples should be taken every 1,200 feet following a new installation. Samples must be bacteria free before the line can be put back into service. Workers should be sure to keep a record of where the repair needed to be made and its cause.

WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1996. *Water Transmission and Distribution*, Second Edition. Denver, Colorado: AWWA.

American Water Works Association. 1999. *Water Distribution Operator Training Handbook*, Second Edition. Denver, Colorado: AWWA.

Male, James T., Walski, Thomas M. 1991. *Water Distribution Systems, A Troubleshooting Manual*, Second Edition. Chelsea, MI: Lewis Publishers, Inc.

OSHA Rules and Regulations, CFR 1926.652 (a) at www.osha.gov/doc/outreachtraining/htmlfiles/exacavate.html

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ROLE OF SMALL WATER RESERVOIRS IN ENVIRONMENT

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> Motto:
> 'Water . . . you are the greatest treasure ever existing in all the world'.
>
> (Antoine Saint-Exupery)

The earth's fresh water supplies are diminishing at a terrifying rate. The loss of fresh-water supply per capita has reached 40% since 1970.

The annual gross supply of water in the world per person is 10,000 m^3, 1500 m^3 in Poland, 2400 m^3 in Germany, and 2800 m^3 in France. These data converted into the water availability index in cubic meters daily per capita in some European countries are presented in Fig. 1 (1,2).

Melioration works (land improvement) completed in the past 50 years in many countries in Europe, Asia, or America have focused mainly on enlarging areas of farmland (increasing food production). They were intended to drain off water rapidly and dry and reclaim land. As a result, many natural watercourses have been replaced by drainpipes (ditches) and simple canals. Other water features have also disappeared, for example, small natural lakes and other small waterbodies, natural flood waters, midfield trees, and coppices. In Poland, 80% of small ponds and water mill dams have also been liquidated (3). Natural water retention potential has been distorted. As a result of declining available freshwater supplies in many areas of the world, interest is increasing in expanding the use of small water reservoirs.

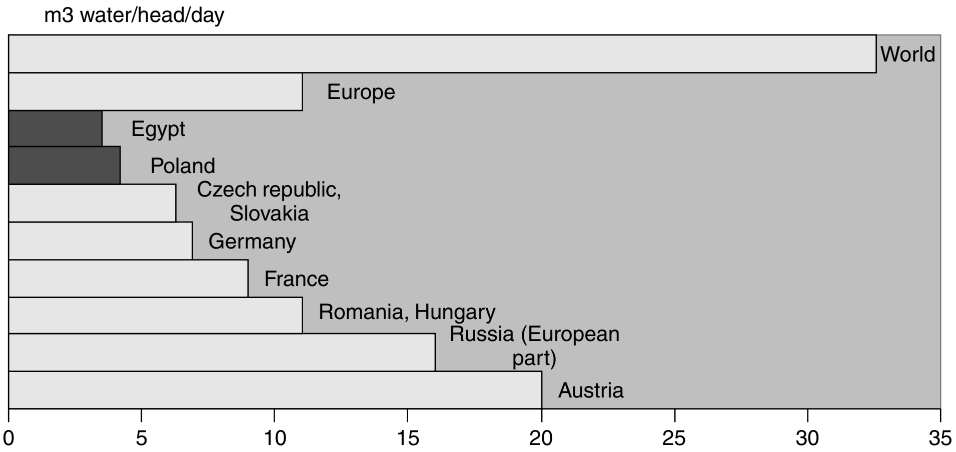

Figure 1. Water availability index in different European countries in cubic meters water per person daily (1).

The present situation calls for urgent action to reclaim lost properties in the natural environment. Natural landscape reclamation can be attained in two ways:

- *Natural Measures (Proecological, Nontechnical)*: by preserving small water reservoirs and cave-in lakes, natural wetlands and floodplains, village ponds and alike, as well as by planting forests, trees, and shelter belts in degraded areas.
- *Technical Measures*: by water retention, especially so-called small retention objects.

Natural retention means

- increased potential for water self-purification, accompanied by enriched landscape values.
- enhanced landscape attractiveness, which stimulates the development of ecotourism and also encourages the local population to enjoy living in more comfortable surroundings.

Of about 28 types of small natural inland water reservoirs and water ecosystems (4,5), wetlands known as marshes (swamps, bogs, wetlands, fens, mires) play a key role in the environment and water management. They are structural and functional waterlogged ecosystems that are transitional forms between typical land and typical water ecosystems. Features common to all marshy ecosystems are permanent or temporary waterlogging of the substrate, the presence of hydrophilous plants (hydrophytes), and specific soils. Such ecosystems are inhabited by rare plant and animal species and function as important flight paths for seasonally migrating birds as well as water plant habitats for nomadic species (6). They are also nesting and breeding areas for some rare species, frequently those on the verge of extinction (including endemic species). Owing to their specific soils and flora, marshes are often nicknamed 'kidneys of the landscape' or small wastewater purification plants (7).

The sanitary impact of wetlands on the environment is gaining in importance due to considerable contamination of surface and underground waters. A waterlogged area can function as a trap, source, or transformer of matter reaching it from the outside; each role depends on the type, age, and use of the ecosystem. Wetlands become traps mainly in spring and early summer. They are a source of phosphorus (P) when the vegetative season is ended (disappearing assimilation). Depending on the hydrologic type of supply, waterlogged areas are divided into four types (7):

- *Ombrogenic*: present in watershed zones, at the highest points, represented by high and transitional moors;
- *Topogenic*: present on lowlands and near lake areas as low, oligotrophic moors;
- *Soligenic*: marshy grounds in valleys near terraced parts of river valleys;
- *Fluviogenic*: riparian marshes, subject to the erosive impact of rivers, heavily bogged, with highly trophic (fertile) river sediments.

These types of wetlands have an exceptionally beneficial influence on the hydrologic regime of the terrain. In particular, they help retain water in the catchment, improve its water balance, and retain water in the countryside, which involves preventing water outflow from the catchment and rational time distribution of water (2,8). Wetlands also have an indirect positive effect on agricultural production (plant production) and pond fish culture (9).

In some countries, marshes and bogs cover large areas. In Poland, for example, natural and transformed marshes cover 13.1% of the country's total area (more than 4.3 million ha), of which 10.2% belongs to open (not forested) marshes, preserved in a nearly natural state.

More than 56% of Poland's natural and transformed marshes are contained in the European system ECONET Poland (European Ecological Network), where they constitute 16.7% of the total network area. The ECONET-PL network is composed of international and national core areas (that have a wealth of habitats and species) and ecological corridors. The latter are situated mainly in river valleys, providing links between core areas (7).

The most effective and currently desirable is the type of water retention that involves retaining the largest

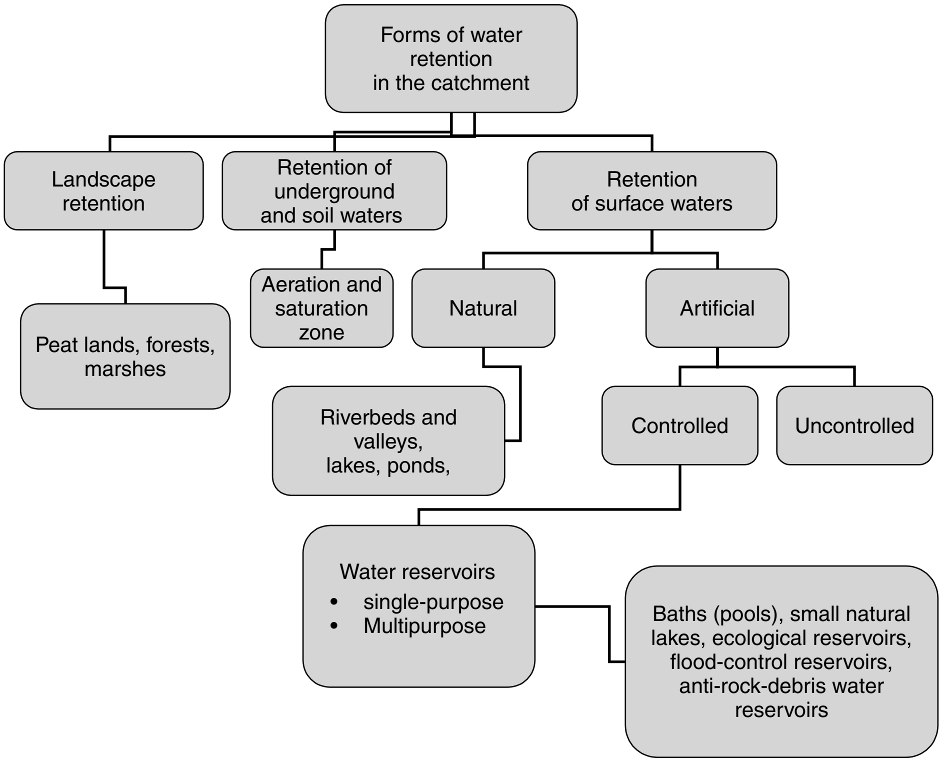

Figure 2. Basic forms of small retention in a catchment (10).

amounts of water possible in surface and near-surface water circulation systems using different measures. In short, the objective is to prevent unproductive water flow to the sea.

The total retention capacity of a catchment is the sum of individual elements that comprise many constituent forms of the catchment (Fig. 2). Economically, retention can be divided into natural and artificial forms (10). The major forms of natural retention include

–retention by river beds and valleys,
–retention by peatlands, marshes, and wetlands,
–retention by soil, underground, and surface waters,
–retention by stagnant waters—especially forest and soil retention.

Forest and soil retention are difficult to quantify. Estimates suggest that an increase in soil retention by 20 mm across 50% of the agricultural lands in Poland amounts to an additional 2 billion m^3 of water (11,12).

Artificial water retention consists mainly of retaining water in artificial reservoirs (e.g., dammed reservoirs in lowlands and mountains) and less often of lake retention obtained by artificial water lifting in natural lakes. Two types of retention are distinguished—uncontrolled and controlled. The latter is represented by artificial reservoirs of constant water lifting equipped with regulation devices, which enable water circulation control (10).

Small water retention relies mainly on waterbodies of different types. Waterbodies improve the water balance of a catchment; depress the level of flood waves, high water (after torrential rains), and thaw waves (in spring); increase low flows (summer drought seasons); and increase air humidity and soil moisture, thus improving the microclimate and conditions for arable crops.

Water reservoirs are objects that can be described by using measurable and nonmeasurable parameters. The following are most often used to compare waterbodies: size of retention (ha, m^3), runoff compensation ratio, type of regulation and discharge facilities, and hydraulic and economic functions (Table 1).

Development of water retention is an important element of integrated water management, particularly in terms of maintaining quality of water supplies and producing a positive effect on the outflow and levels of water from its surface, which in turn has some influence on the formation and shape of flood tides.

In addition, retention objects perform a variety of other tasks and functions, of which the most important are

- industrial water supply (e.g., water intake),
- fire protection
- relaxation, sports, and recreation,
- fisheries (professional and amateur),
- landscape and environmental management.

Surface water retention is attained through the following activities:

- construction and reconstruction of water reservoirs,
- construction of water lifting installations in rivers,
- filling fish ponds (especially larger pond complexes),
- water retention in amelioration installations and systems,

Table 1. Classification of Storage Reservoirs[a]

Classification Criteria	Size and Type of Reservoirs			
Retention size	**Small**		Medium	Large
Height of a dam (m)	From **5**		5 to 15	Over 15
Water capacity (m^3)	to **100,000**		to 500,000	Over 500,000
Runoff compensation (below the reservoir)	Long-term	Seasonal	Annual	Daily
Number of functions	Single-purpose[b]		Multipurpose[c]	
Hydraulic devices (discharge)	Uncontrolled : dry		Controlled: of a defined (set) water lifting level	

[a] References 10 and 13.

[b] Retention function (general).

[c] Potable water retention, flood control, irrigation of arable crops, recreational and water sport reservoirs, land melioration, electric power, sailing reservoirs, etc.

- water lifting in natural waterbodies (lakes),
- protection and management of small water reservoirs and cave-in lakes,
- flooding of valley depressions (bogs and marshes, cutoff meander lakes, old riverbeds).

The following water retention methods seem best for the natural environment:

Higher Water Retention on Areas Previously Ameliorated or Planned To Be Ameliorated

The primary objective is reconstruction of weirs on drainage ditches, which brings large contributions to water supplies [in Poland, about 500 million m^3: (11)]. The second stage comprises construction of small retention reservoirs at the end points of amelioration systems, that is, before water outflow to a river or sea. Some experts on hydrology and hydraulic engineering, however, claim that large retention reservoirs should not be built as long as 'all possibilities of constructing small retention reservoirs have not been exhausted.' It is also important to abandon amelioration of peat bogs or waterlogged meadows and pastures, which further improves water retention potential.

The most superior natural values are attributed to nonregulated rivers in undeveloped valleys. Such valleys contain a mosaic of different water ecosystems: cutoff meander lakes (old riverbeds), peat bogs, dry and moist meadows, and the so-called alder carrs (8,9). Flood control involves several methods that help preserve these unique natural water ecosystems. Of the two possible flood protection strategies—increasing water flow capacity of river valleys (hydraulic installations) or increasing water retention in the whole watershed—most specialists opt for the latter solution as more favorable for the natural environment (12,14,15). Of all methods for increasing water retention, the following seem recommendable from the viewpoint of preserving the natural environment:

Maintaining and Increasing Water Retention on Lands Used for Agricultural Production

The most important activities include doing without heavy agricultural machinery (which compacts arable layers of soil), plowing across the slope, creating terraces, not burning grass and stubble, and re-creating midfield water ponds.

Increasing Water Retention in Forested Areas

There is an array of activities available, including afforestation of lands with forest polycultures (monocultures have inferior water retaining capacity), safe transportation of felled trees (soil erosion risk), use of cable trains for transporting felled trees in mountainous areas, biological consolidation of streams, and no planning or building of main roads near streams and rivers. Despite numerous controversies, forests in river valleys are largely categorized as water protecting forests and therefore subject to less intense forest management practices.

Maintaining and Increasing Water Retention in River Valleys

It should be remembered that nonregulated rivers that have undeveloped valleys provide the highest natural values. Water retention measures undertaken in river valleys should be integrated with flood control. A partial solution that could reconcile flood control requirements with natural protection is the construction of so-called polders, waterlogged and nonreclaimable depressions. There are two types of polders: overflow polders that are flooded each time the water level rises (more favorable for protecting nature), and control polders (better for flood protection). Such solutions are used, for example, in Germany in the Rhine river valley near the water step in *Iffezheim* (16). Of all types of dammed reservoirs, dry reservoirs, which cause minimal changes in the hydrologic regime, are responsible for the smallest losses in river valley ecosystems. As far as wet reservoirs are concerned, small retention reservoirs are least damaging. According to Lewis and Williams (17), the least damage to the environment is caused by those wet reservoirs that are located in a river valley and are connected to the river by an inflow and an output canal.

To preserve ecosystems below a large reservoir, it is necessary to cause artificial floods (lasting a few days) that discharge large amounts of water in the spring. Natural and hydrologic effects of an artificial flood on the Colorado River in the United States (1996) are now a subject of wide research, so far yielding positive and promising results (18).

The water retention effects of the aforementioned measures are quite varied and, apart from typical retention reservoirs, rather limited. Their capacity for storing water (known as retention capacity) is usually measured in hundreds of thousands cubic meters of water (less frequently in millions of m^3). In Poland, objects whose capacity is less than 5 million m^3 are referred to as small retention objects (3,19).

Fish ponds—An Undervalued Element of Small Retention

Ponds are shallow artificial retention reservoirs, built in less fertile areas, usually waterlogged and agriculturally useless. Fish ponds make aquaculture possible, and they also facilitate ecological use of water and systematic water alimentation (permeation, leakage), more intense alimentation occurs when water is discharged in spring and summer and during the autumn fish catch. Pond objects are localized in the upper parts of a catchment and are supplied with water from small streams and by precipitation. Ponds significantly delay water outflow and make water flow more uniform in the whole watercourse (9,20) (Fig. 3).

Large fish pond objects and ponds of higher capacity (more than 1–2 thousand ha) located in lower parts of a catchment make it possible to store water and summer flood tides (so-called St John's floods—rains in midsummer), thus successfully alleviating the course of floods. In Europe, such pond complexes are found in the region of Milicz near Wrocław (5 thousand ha), and near Čs. Budějovic (22 thousand ha) in the south of the Czech Republic. The largest ponds in those complexes (regions) cover 100 to 700 ha (2,4,5,21,22).

The water retention potential of such pond, lies in the fact that they store water in those periods when it would otherwise flow away fruitlessly. Ponds are filled with water when the water level in rivers is the highest, meaning that it does not collide with the water uptake by other users (consumers). On the contrary, it has a positive effect on the whole water management in the catchment (23), and, particularly, on flood control. A clear example of the beneficial influence and protection against floods is the Czech pond Rožemberk (711 ha), built at the end of the sixteenth century and used for fish farming until today. In 1889 (and more recently in August 2002), it protected the town of Třeboň from a devastating flood and complete damage by spilling its waters over an area of 2,000 ha and storing more than 50 million m^3 water (3).

Figure 3. Small retention—fish ponds in Ostróda, Poland.

In Poland, for instance, there are about 71 thousand ha of fish ponds, including small ponds at farmsteads, which store about 900–950 million m^3 water, one-third of the country's total water retention (2). Regardless of these figures, many countries of central Europe pay little attention to the role of ponds and possible inclusion of fish ponds in water and amelioration systems when planning water management, and local water retention projects, in particular (4). Such notorious underestimation of the nonproductive value of fish ponds results from an erroneous assumption that fish ponds are exclusively fish production reservoirs. The truth is that, apart from their fish breeding function, they have more than 50 positive characteristics in terms of water management, agriculture, environmental protection, landscape values, water sports, angling, and professional or economic stimulation of the local population (5,22,24–27). Therefore, such merits can often exceed the primary fish breeding value of ponds in their economic assessment (28).

In general, dammed retention reservoirs significantly alter the river valley landscape, although they can also create suitable nesting and feeding areas for fish and birds, once islets and shallow shores are formed. This effect can partly compensate for the losses in the natural environment caused by construction of dammed reservoirs.

It should be added that the European Union has accepted the 'Habitat Directive' to preserve, nearly unchanged, valleys of large rivers and adjacent small reservoirs and floodplains with their wealth of ecosystems. The high diversity of species in such areas is further protected by the Convention on Biodiversity Protection, signed in 1992 by many European countries, including Poland (7,15).

BIBLIOGRAPHY

1. Szczerbowski, J.A. (1998). *Fishing and Angling Encyclopedia*. (In Polish). IRS, Olsztyn.
2. Guziur, J., Białowas, H., and Milczarzewicz, W. (2003). *Pond Aquaculture*. (In Polish). Oficyna Wyd, Hoża, Warszawa.
3. Guziur, J. (1991). *Fisheries in Small Inland Reservoirs*. (In Polish). PWRiL, Warszawa.
4. Guziur, J. (1988). Characteristics of small water reservoirs and their potential use for aquaculture Part, I-VI. (In Polish). *Acta Acad. Agric. Tech. Olst.* **16**: 15–66.
5. Guziur, J. (2000). Significance of non-productive (external) value of small inland waterbodies. *Zesz. Nauk. Tow. Inżyn. Ekolog.Polit., Rzeszów*. **1**: 62–73.
6. Kabisch, K. and Hemmerling, J. (1981). *Tümpel. Teiche und Weiher Oasen in Unsere Landschaft*. Edition Leipzig.

7. Raport SGGW Warszawa. (2002). *Use and Management of a Catchment Area—Part. 6. Small Waters Retention*. (In Polish). Available: http://levis.sggw.waw.pl/ ozw1/zintegrowgospwod/ZintegrowanagospwodREW20/U.
8. Starmach, K., Wróbel, S., and Pasternak, K. (1976). *Hydrobiology. Limnology*. (In Polish). PWN, Warszawa.
9. Hynes, H.B. (1970). *The Ecology of Running Waters*. Liverpool University Press.
10. Radczuk, L. and Olearczyk, D. (2002). Small storage reservoirs as an element of water balance improvement in the agricultural catchment. (In Polish). *Zesz. Nauk. AR w Krakowie* **393**(23): 139–149.
11. Mioduszewski, W. (1994). Water Supply Conservation and Shaping in Small Agricultural River Catchments. (In Polish). *Mater. Inform*. 25, Falenty IMUZ.
12. Mioduszewski, W. (2002). Recreation of the retention of small river catchment as an element of flood and drought control. (In Polish). *Gospod. wodna, Warszawa* **11**: 12–16.
13. Dziewoński, Z. (1972). *Storage reservoirs of agriculture*. (In Polish). PWN, Warszawa.
14. Ryszkowski, I. and Kçdziora, A. (1996). Small water retention in the rural landscape. (In Polish). *Zesz. Nauk. AR Wrocław*. **289**: 217–225.
15. Jankowski, W. (2002). Ecologic flood control methods. (In Polish). Available: http://www.tnz.most.org.pl/pow/ios_2.htm.
16. Nieznański, P. (1999). The upper course of the Rhine river as an example of possible combination of flood control and nature conservation. (In Polish). *Polder*. **15**: 16–21.
17. Lewis, G. and Williams, G. (1984). *Rivers and Wildlife Handbook: A Guide to Practices Which Further the Conservation of Wildlife on Rivers*. RSPB.
18. Collier, M.P., Webb, R.H., and Andrews, E.D. (1997). Experimental flood in the Grand Canyon, Colorado, the USA. (In Polish). *Świat Nauki*. **3**(967): 62–69.
19. Hochman, L. (1988). Limnological charakteristics of irrigation reservoirs in southwestern Slovakia (Czech Rep.). *Prace Ustavu Ryb. Hydrob. Bratislava* **6**: 139–180.
20. Manson, P.W. and Schwartz, G.W. (1968). Some aspects of the hydrology of ponds and small lakes. *Agricul. Exper. Station—Univ. of Minnesota, Tech. Bull.* **25**(7): 88.
21. Lavický, K. (1978). Function of fish ponds in a creation of life environment. In: *Current State and Perspectives of Czech Aquaculture*. CSAZ Praha, pp. 43–50.
22. Guziur, J. and Stafiniak, J. (2000). Polish experience with culture of common carp in single ponds and small water reservoirs. *Bull. VÚRH-Ju Vodňany*. **4**: 174–179.
23. Boyd, C.E. (1985). Pond evaporation. *Trans. Am. Fish. Soc.* **144**(2): 299–305.
24. Welsh, G. and Neils, K. (1978). Fish farming on the home front. *Fish Farm Aquacult. News*. **4**(6): 19–23.
25. Gergel, J. and Kratochvill, A. (1984). Teiche dienen nicht nur der Fischproduktion. *Z.Binnenfisch. DDR*. **3**(5): 178–182.
26. Szumiec, M.A. (1990). Role of ponds in landscape. (In Polish). *Biul. Inform. IRS Żabieniec*. **16**: 1–7.
27. Rożański, S. (1996). The additional benefits of fish farming in small water bodies. *Acta Acad. Agric. Ac Tech. Olst. Protectio Aquar. et Piscat.* **22**: 83–94.
28. Turkowski, K. and Guziur, J. (1999). *Small water reservoirs as an element of rural area management (case study of region of Warmia and Mazury, North. Poland)*. (In Polish). Mater. XII Sympoz. Nauk., Instrumentalizm rozwoju obszarów wiejskich. AGH, Kraków, pp. 48–56.

RESERVOIRS, TOWERS, AND TANKS DRINKING WATER STORAGE FACILITIES

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After water leaves the treatment plant but before it reaches the customer, it must be adequately and safely stored. This Tech Brief explores the various aspects of water storage.

A water distribution system transports water from the treatment facility to the user. The distribution system should supply water, without impairing its quality, in adequate quantities and at sufficient pressures to meet system requirements.

The facilities that make up the distribution system include finished water storage; pumping, transmission and distribution piping supply mains; and valves.

Storage facilities—such as reservoirs, towers, and tanks—provide storage for treated water before it is distributed. The water distribution system should have storage so that it is capable for basic domestic purposes, commercial and industrial uses, and to accommodate the flows necessary for emergencies such as fire fighting.

STORAGE RESERVOIR FUNCTIONS

Service reservoirs provide the following functions:

- provide a reserve of treated water that will minimize interruptions of supply due to failures of mains, pumps, or other plant equipment;
- help maintain uniform pressure;
- provide a reserve of water for fire fighting and other emergencies;
- act as a relief valve on a system of mains supplied by pumping;
- permit a reduction in the size of distribution mains below that which would be required in the absence of a reservoir; and
- allow pumping at the average rather than peak flow rate.

CLASSIFICATION OF STORAGE REQUIREMENTS

Storage volume requirements are classified by function: operating, equalizing, fire and/or emergency, and dead-storage volumes. Engineers must consider these individual volume components in combination to determine the total volume of storage capacity that is required for any system. The total storage required is typically the sum of all these functions.

Rather than requiring both fire and emergency storage, some local fire and state agencies allow systems to use the larger of either fire or emergency storage volumes.

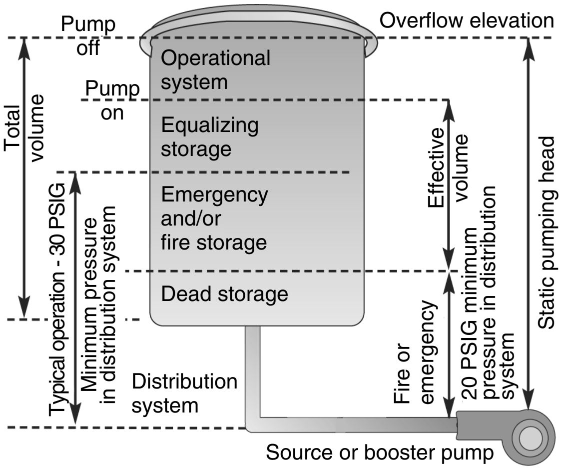

Figure 1. Storage volume classification. Source or booster pump.

These local agency requirements need to be determined on a case-by-case basis before designing a storage reservoir. Figure 1 illustrates the different components of the total storage volume.

Operating Storage—This is the difference in volume between the “pump on” and “pump off” levels when the tank is normally being used and the sources of supply pumps to the storage tank are off.

Equalizing Storage—This storage component is used when the source pump capacity is less than the peak system demands. The storage is needed so that water production facilities can operate at a relatively constant rate. Daily peak rates determine the volume, compared to the average daily demand and source capacity.

Fire Storage—The volume of water stored within the water system for fighting fires is known as “fire storage.” The storage volume required varies with the size of city and with the size, type, and classification of construction within the service area. Storage volume requirements for fire fighting should be determined based upon state and local fire districts and municipalities. Fire authorities often refer to the latest edition of the *Guide for Determination of Required Fire Flow*, published by the Insurance Services Office to determine local fire flow requirements.

The typical minimum municipal fire flow requirement is 500 to 1,000 gallons per minute (gpm) for two hours for single family residential areas. Commercial and industrial areas fire flows can be as high as 8,000 gpm or more for many hours. Typical fire storage requirements are shown in Table 1. Engineers should base the actual capacity needs upon local fire flow requirements.

Emergency Storage—This storage is used to provide water to the system during other unusual or emergency conditions. Emergency storage volume depends upon the likelihood of supply interruption and the time required to make repairs or arrange for an alternative water supply.

Dead Storage—Storage in tanks or reservoirs that cannot be drawn out or used beneficially because of piping elevations or low pressures is known as dead storage. Dead storage is typically most significant in tall standpipe-type tanks where water in the bottom of the tank cannot be used because of low system pressure.

Table 1. Typical Range of Storage Requirements for Fire Protection

Type of Development	Storage Volume, Gallons	Storage Volume, ML
Low-density residential, 2 hr at 500 gpm	60,000	0.23
Built-up residential, 2 hr at 1,000 gpm	120,000	0.45
Light commercial, 4 hr at 2,000 gpm	480,000	1.8
Commercial, 4 hr at 4,000 gpm	960,000	3.6

Storage Volume Dedicated to Contact Time—Finished water stored in clearwells at water treatment plants is sometimes used to meet the disinfection contact time. In these cases, the amount of fixed volume used to meet the disinfection requirement should also be considered in the total volume and operational limits of the reservoir.

DAILY STORAGE VOLUME USE VARIES

Water use is greater during daylight hours—typically peaking in the mid-morning and early-evening hours. Stored water is withdrawn during these peak demand hours of the day and is replenished during minimum-demand times in the late-night and early-morning hours.

Figure 2 illustrates the hourly variation in daily water use (diurnal variation) that might occur in a typical residential community on the day of maximum water use for the year.

The shape of the diurnal curve of water demand will vary significantly between different cities because of differences in climates and local economies. Local design data should be obtained for each water system to determine storage needs. However, with an adequate source of supply capacity, equalizing storage of approximately 22 percent of the maximum daily demand is typical for small residential areas.

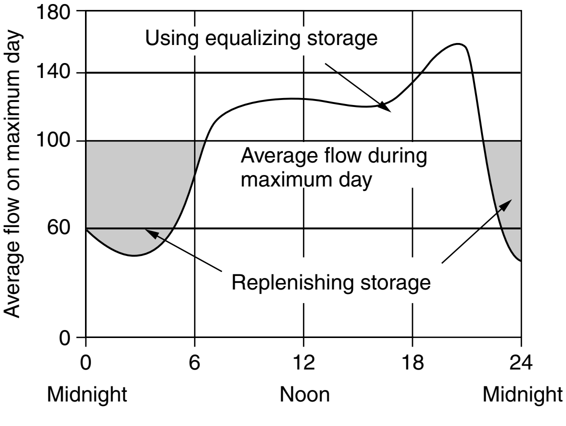

Figure 2. Hourly water use variation.

STORAGE TANK SHAPE AND VOLUME

Water towers can be made of concrete or steel and can take various forms. The most suitable form for concrete towers is a cylinder with a curved shaped bottom or with a flat bottom. Steel tanks may have a spherical or dome shaped bottom. The shape chosen is usually a compromise between function, construction and maintenance costs, and aesthetics.

The lowest water level in the tank is determined according to the pressure requirements in the pipeline. The pressure in the pipelines may vary depending on the type of community and pressure needs of different areas in a city. Typically, minimum acceptable water system pressures are 35 to 40 pounds per square inch (psi) and maximum pressures are 100 to 120 psi.

To keep pumping costs low, water depth in the tank is generally kept small. Due to structural considerations, the depth is kept equal to the diameter.

LOCATING STORAGE RESERVOIRS

A service reservoir stores the water and supplies it at the required pressure to the farthest point in the area. In view of the cost of pipelines and uniform pressure distribution, the reservoir should be located near the center of the service area.

In flat areas, it is relatively easy to build the water tower at the center. In hilly areas, however, it may be more advantageous to select the highest point for the construction of an elevated tank, which may lie at one end of the area instead of the center.

Apart from the center, the tank or tower can be situated between the area and the source of supply (pumping or gravity flow). When the service reservoir lies between the area and the source, all the water must pass through the elevated tank before flowing through the area (see Fig. 3a).

The pressure in the water supply system depends upon the water level in the service reservoir. A water supply system needs to guarantee a minimum pressure even at the most remote point in the area. Therefore, it is essential that the hydraulic gradient line always be above the required pressure.

When water is supplied from an impounded high-level reservoir, the service reservoir may function as a pressure-reducing device (see Fig. 3b). This reduces the possibility of damage to the pipes due to high hydrostatic pressure.

When the area lies between the source and the service reservoir, then most of the requirements are met by direct pumping and the excess water flows to the service reservoir (see Figs. 3c and 3d). In this system there may be larger fluctuations in the supply pressure.

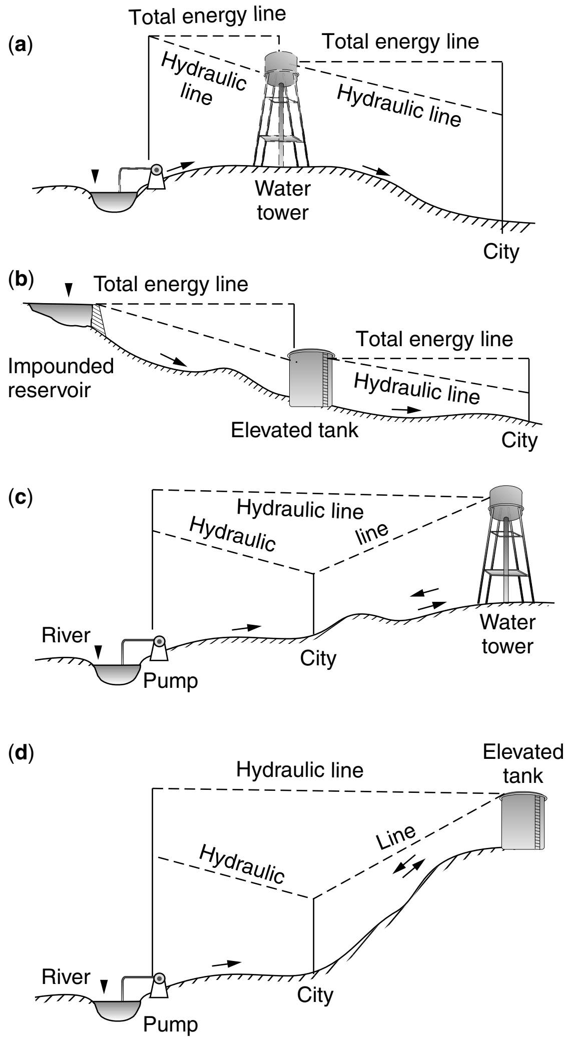

Figure 3. Service reservoir.

CONSTRUCTION MATERIALS

Most states permit steel and concrete construction materials. All piping, joints, and fittings should conform to American Water Works Association (AWWA) specifications. Welded steel water tanks should confirm to American National Standards Institute (ANSI)/AWWA Standard D100. Factory-coated bolted steel tanks should confirm to ANSI/AWWA D103. Wire and strand wound, circular, prestressed concrete tanks should confirm to ANSI/AWWA Standard D110.

The storage tanks should be painted or have cathodic protection. The AWWA standards for painting exclude the use of paints that might add toxic materials to the stored water. The paint, both external and internal, should comply with the standards prescribed by AWWA D101 and D102.

OTHER CONSIDERATIONS

All water reservoirs should be covered to protect the stored water against contamination. Overflow pipes should be brought down near the ground surface and discharged to minimize erosion. The storage structure should be designed so that there is water circulates. There should be a convenient access to the interior for cleaning, maintenance, and sampling. Rigid storage reservoirs should be vented.

READING LIST

Pizzi, NicholasG 1995. *Hoover's Water Supply and Treatment*, 12th Edn. National Lime Association: Arlington, VA.

HDR Engineering, Inc. 2001. *Handbook of Public Water Systems*. 2nd Edn. John Wiley & Sons, Inc.: New York, New York.

Hobbs, AubreyThomas (ed.) 1969. *Manual of British Water Engineering Practice*. Vol 2. W. Heffer and Sons, Ltd: Cambridge, England.

Middle Brooks, EJoe, et al. 1977. *Water Supply Engineering Design*. Ann Arbor Science Publishers: Ann Arbor, MI.

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- Tech Brief: Package Plants, item #DWBLPE63;
- Tech Brief: Water Treatment Plant Residuals Management, item #DWBLPE65;
- Tech Brief: Lime Softening, item #DWBLPE67;
- Tech Brief: Iron and Manganese Removal, item #DWBLPE70;
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WATER TREATMENT PLANT RESIDUALS MANAGEMENT

National Drinking Water
Clearinghouse

Water treatment plants produce a wide variety of waste products as well as safe drinking water. These residuals may be organic and inorganic compounds in liquid, solid, and gaseous forms depending on the source of raw water and the type of treatment processes, commonly, coagulation/filtration, precipitative softening plant, membrane separation, ion exchange, granular activated carbon.

The differences between the unit processes of the five plant types listed above characterize the type of residuals generated at a given facility. In the current regulatory climate, a complete management program for a water treatment facility should include the development of a cost-effective plan to remove and dispose of residuals. The following steps need to be considered when developing a comprehensive water treatment residuals management plan:

- Characterize form, quantity, and quality of the residuals;
- Determine appropriate regulatory requirements;
- Identify feasible disposal options;
- Select appropriate residuals processing/treatment technologies; and
- Develop a residuals management strategy that meets both the economic and noneconomic goals established for a water treatment facility.

WHAT ARE THE RESIDUALS CATEGORIES?

Water treatment plant residuals form when suspended solids in the raw water react with chemicals (e.g., coagulants) added in the treatment processes and associated process control chemicals (e.g., lime). Some potable water treatment processes generate residuals that are relatively easy to process and dispose of. For example, leaves, limbs, logs, plastic bottles, and other large floating debris separated from water during the initial screening process can be disposed of at conventional solid waste landfills. However, most other treatment processes produce more complex residual waste streams that may require advanced processing and disposal methods to protect human health and the environment.

The four major types of residuals produced from water treatment processes are:

Major Treatment Processes and Types of Residual Solids Treatment Processes (Robinson and Witko, 1991)

Coagulation/Filtration			
Typical Residual Waste Streams Generated	Typical Contaminant Categories	Typical Disposal Methods	Regulation Covering Disposal Method
Aluminum hydroxide, ferric hydroxide, or polyaluminum chloride sludge with raw water suspended solids, polymer and natural organic matter (sedimentation basin residuals)	Metals, suspended solids, organics, radionuclides, biological, inorganics	Landfilling Disposal to sanitary sewer/WWTP Land application Surface discharge	RCRA/CERCLA State and local regulations RCRA, DOT NPDES (CWA), state and local DOH
Spent backwash filter-to-waste	Metals, organics, suspended solids, biological, radionuclides, inorganics	Recycle Surface discharge (pumping, disinfection, dechlorination) Disposal to sanitary sewer/WWTP	State and local DOH NPDES (CWA), state and local regulations State and local regulations
Precipitative Softening			
Calcium carbonate and magnesium hydroxide sludge with raw water suspended solids and natural organic matter	Metals, suspended solids organics, unreacted lime, radionuclides	Landfilling Disposal to sanitary sewer/WWTP Land application	RCRA/CERCLA, state and local regulations State and local regulations RCRA, state and local regulations, DOT
Spent backwash filter-to-waste	Metals, organics, suspended solids, biological, radionuclides, inorganics	Recycle Surface Discharge (pumping, disinfection, dechlorination) Disposal to sanitary sewer/WWTP	State and local DOH NPDES (CWA), state and local regulations State and local regulations
Membrane Separation			
Reject streams containing raw water suspended solids (microfiltration), raw water natural organics (nanofiltration), and brine (hyperfiltration, RO)	Metals, radionuclides, TDS, high molecular weight contaminants, nitrates	Surface discharge (pumping, etc.) Deep well injection Discharge to sanitary sewer/WWTP Radioactive storage	RCRA, NPDES, state and local regulations RCRA, NPDES, state and local regulations State and local regulations RCRA, DOT, DOE
Ion Exchange			
Brine stream	Metals, TDS, hardness nitrates	Surface discharge Evaporation ponds Discharge to sanitary sewer/WWTP	RCRA, NPDES, state and local regulations RCRA, NPDES, state and local regulations State and local regulations
Granular Activated Carbon			
Spent GAC requiring disposal and/or reactivation, spent backwash, and gas-phase emissions in reactivation systems	VOCs, SOCs (nonvolatile pesticides), radionuclides, heavy metals	Landfill Regeneration (on/off site) Incineration Radioactive storage Return spent GAC to supplier	RCRA, CERCLA, DOT State and local air quality regulations (CAA) State and local air quality regulations (CAA) DOT, DOE
Stripping Process (Mechanical or Packed Tower)			
Gas phase emissions	VOCs, SOCs, radon	Discharge to atmosphere GAC adsorption of off-gas (contaminant type and concentration dependent)	State and local air quality regulations (CAA)
Spent GAC if used for gas-phase control	VOCs, SOCs radionuclides	GAC adsorption of off-gas (contaminant type and concentration dependent) Return spent to GAC to supplier	State and local air quality regulations (CAA)

Chart Key

CAA = Clean Air Act
CWA = Clean Water Act
CERCLA = Comprehensive Environmental Response, Compensation and Liability Act
DOE = Department of Energy
DOH = Department of Health
DOT = Department of Transportation
GAC = Granular Activated Carbon
NPDES = National Pollutant Discharge Elimination System
RCRA = Resource Conservation and Recovery Act
RO = Reverse Osmosis
SOC = Synthetic Organic Chemical
TDS = Total Dissolved Solids
VOC = Volatile Organic Compound
WWTP = Wastewater Treatment Plant

- *Sludges* (i.e., water that contains suspended solids from the source water and the reaction products of chemicals added in the treatment process). Presedimentation, coagulation, filter backwashing operations, lime soften-ing, iron and manganese removal, and slow sand and diato-maceous earth filtration all produce sludge.
- *Concentrate* (brines) from ion exchange regeneration and salt water conversion, membrane reject water and spent backwash, and activated alumina waste regenerant.
- *Ion exchange resins,* spent granular activated carbon (GAC), and spent filter media (including sand, coal, or diatomaceous earth from filtration plants).
- *Air emissions* (off-gases from air stripping, odor control units, or ozone destruction).

The chemical characteristics and contaminant concentration levels in these residual waste streams often impose the ultimate disposal options. Furthermore, it is reasonable to expect that as drinking water quality is increasingly regulated, higher removal efficiencies of more contaminants will be required. To achieve these higher efficiencies, water treatment plants (WTPs) will need to use more sophisticated treatment technologies. Of particular concern are cases in which residuals are characterized as either hazardous or radioactive waste. Depending on the raw water quality and treatment process removal efficiency, hazardous or radioactive characteristics could be exhibited in potentially any residual waste stream mentioned on page 1.

WHAT REGULATIONS GOVERN MANAGEMENT OF WATER TREATMENT PLANT RESIDUALS?

Identifying the regulations that affect various management practices may be difficult for water treatment utility managers. The difficulty is due to the many different types of wastes produced by WTPs and various types of waste disposal: direct discharge, discharge to wastewater treatment plants, disposal in landfills, land application, underground injection, disposal of radioactive waste, and treatment of air emissions.

At the federal level, the U.S. Environmental Protection Agency (EPA) has not established any regulations that are specifically directed at WTP residuals. Applicable regulations are those associated with the Clean Water Act (CWA); Criteria for Classification of Solid Waste Disposal Facilities and Practices (40 CFR, Part 257); the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund; and the Clean Air Act (CAA). The CWA limits direct discharges into a water course while the other legislation governs other methods of use and/or disposal of wastes. Most states are responsible for establishing and administering regulations that will meet the requirements of these acts. The regulation of wastes, therefore, is the responsibility of the states.

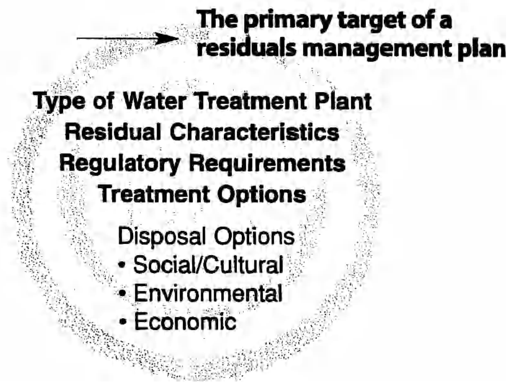

Figure 1. *Source*: Management of Water Plant Residuals.

HOW ARE RESIDUALS MANAGEMENT PLANS SELECTED?

To develop a residuals management plan, the WTP manager may start with a broad array of residuals processing and disposal options that can be narrowed through considering specific residuals characteristics and associated regulatory requirements. A focus on available disposal options further narrows the management alternatives.

Figure 1 illustrates the need for practical disposal options and treatment processes that will take into account economic and noneconomic factors of concerns to the community. The technical criteria used to select the final management plan differ from user to user; economic, cultural, social, and environmental factors are also site-specific, and are typically included in any final selection.

WHERE CAN I FIND MORE INFORMATION?

Information in this fact sheet was primarily obtained from:

(1) Management of Water Treatment Plant Residuals. American Society of Civil Engineers (ASCE) Manuals and Reports on Engineering Practice No. 88, American Water Works Association (AWWA) Technology Transfer Handbook, and U.S. EPA 625/R-95/008.

(2) Handbook of Practice: Water Treatment Plant Waste Management. American Water Works Association (1987). [This book is out of print but available in libraries.]

(3) Robinson, M.P., and J.B. Wiko. 1991."Overview of Issues and Current State-of-the Art Water Treatment Plant Waste Management Programs." 1991 Annual Conference Proceedings. AWWA Quality for the New Decade, Philadelphia, PA. June 23–27. [This book is out of print; however, copies of the article are avail able for a fee from AWWA.]

Management of Water Treatment Plant Residuals can be ordered from the AWWA. For more information, write the AWWA at 6666 W. Quincy Ave., Denver, CO 80235, or call (800) 926–7337. You may also view a selection of AWWA literature on their Web site at www.awwa.org/store.htm.

REVERSE OSMOSIS, PROCESS CHEMISTRY

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INTRODUCTION

The application of membranes to purify water provides a powerful means of producing high-purity water. In the total treatment of raw water, reverse osmosis (RO) is an important midstream process for fractionating feedwater into high-purity water and brine. The brine may be used to feed cooling towers and evaporators.

The RO process is sensitive to upstream treatments and itself impacts downstream operations. The almost infinite variety of contaminants that enter the membrane systems with the feedwater and the economic necessity to expend minimal resources on raw water pretreatment pose a major challenge to RO process chemistry design and control. RO process chemistry itself is important in understanding and controlling the quality of the product permeate water which may be further polished to remove trace contaminants to meet the ultrapure specifications needed in industries such as pharmaceuticals, microelectronics, and power generation. Presented here are the chemistry of feedwater membrane fouling mechanisms, composition of foulants, and chemicals used to prevent fouling.

FEEDWATER CHEMISTRY

Water that enters reverse osmosis systems comes from all imaginable sources. Presented in Table 1 is a list of sources that are differentiable by their quality and the significant chemistry in these waters that impacts the performance of RO systems.

Major physical occurrences in natural waters are the processes of erosion of the rocks that generate sand (50 microns −2 mm), silt (5–10 microns), clay (<5 microns), and submicron colloidal particles. Just as active a physical process is the growth, excretion, death, and decay of animals and microorganisms.

Table 1. Sources of Feedwater and Significant Chemistry that Impacts RO

Source Water	Significant Chemistry
1. Rain	Oxidation–reduction (e.g., $O_2 + NO_x$), acid–base (e.g., $CO_2 + H_2O$)
2. Springs	Dissolution, acid–base (acid rain + carbonate rocks)
3. Ponds, Lakes	Complex interactions of living and nonliving matter
4. Wells, aquifers	Dissolution–precipitation (e.g., $CaCO_3$, $CaSO_4$, $SrSO_4$, $BaSO_4$, silicates, iron and aluminum salts, sulfides), relatively low in organic matter
5. Rivers, municipal and industrial wastewater	Complexation interactions, precipitation
6. Oceans (99.4% of the earth's water including 2% as ice)	Biotic life, complexation interactions, precipitation

Some significant chemical processes occurring in these waters can be enumerated. Rain extracts oxygen, oxides of carbon, sulfur and nitrogen, and organic aerosol particles from the atmosphere. Spring water dissolves soluble matter, and the acidity of rainwater is neutralized by alkaline rocks such as limestone. Ponds and lakes are biotic reactors in which biomass is produced and accumulated, and complexation interaction of organic matter with inorganic particles occurs. Much of this particulate matter is retained in upper zones of the ground as water enters aquifers. The large surface areas of contact and the long times available for dissolution and precipitation allow water in aquifers to be equilibrated and fully saturated with respect to the composition of the minerals they are in contact with. Thus it is from the deep well source water that the greatest scaling potentials from foulants such as calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, silica, iron, and aluminum exist. We can compare the water in the lower sections of rivers to municipal and industrial waste streams in which complexation interactions of organic and inorganic particles predominate.

The chemistry of seawater is particularly interesting to note. It reflects the equilibrated end point of the processes that began in the surface waters just mentioned. Interestingly, the chemistry in the water undergoing concentration within RO systems models the transition of surface waters to highly saline seawater with respect to coagulation of colloidal matter. Heavy precipitation of biomass coagulated with silt and clay occurs in the delta region of major rivers. The quantity of the different components in seawater is not proportional to the quantity of the components that river water pours into the sea but is inversely proportional to the facility with which the components in seawater are insolubilized by chemical actions in the sea (1). Complexation interactions, precipitation of particles, and crystallization of salts of low solubility that began in ponds and lakes continue in the ocean.

Some of the types of colloids that exist in natural water, especially in the sea, are listed in Table 2. Polyphenolic complexes such as humic acid, lignin, and tannin are decay

Table 2. Colloidal Matter in Natural Water

Microorganisms
Biological debris (plant and animal)
Polysaccharides (gums, slime, plankton, fibrils)
Lipoproteins (secretions)
Clay (hydrous aluminum and iron silicates)
Silt
Oils
Kerogen (aged polysaccharides, marine snow)
Humic acid/lignins/tannins
Iron and manganese oxides
Calcium carbonate
Sulfur and sulfides

products of woody tissues of plants that are particularly noticeable in surface waters due to their tendency to foul RO membranes by themselves or coagulate with other foulants (2). Polysaccharides that constitute cell walls of microorganisms and plants and are excreted variously as gums, slimes, and biofilms are prominent in membrane fouling. In the ocean, they are added to polysaccharides from sea organisms, especially planktons (3), which become kerogen upon aging. It is believed that white materials called “marine snow” that has been observed falling in the deep oceans are these aged and ubiquitous polysaccharides (4).

MEMBRANE FOULING MECHANISMS

Feedwaters to RO systems typically are concentrated by a factor of 2–10 (50–90% recovery) during production of permeate water. For simplicity in classification, three classes of fouling (5–11) can be said to occur.

First, there is scaling. The solubility limits of various dissolved salts in the brine stream may be exceeded, leading to deposition and growth of crystals in the flow channels and membrane surface of the RO elements. This type of fouling is referred to as scaling. Most common examples of scales are calcium carbonate; sulfates of calcium, strontium, and barium; and calcium fluoride. In the examination of foulants (2) under the microscope, crystals have well defined shapes. Inhibitors injected into feedwaters to suppress crystallization are called antiscalants.

Second, there is colloidal fouling. Particulate matter that preexists in feedwater can aggregate and adhere to the membrane and brine flow channels due to increased concentration, salinity, compaction, flocculation, surface interactions, and other physical and chemical factors. The particles, such as silt, carbon fines, coagula, and microbial clusters, may be large enough to be removed by 1 to 5 micron RO prefilters, or they may be colloidal particles that escape filtration even with the standard 0.45-micron filters used in silt density index measurements. The colloids can be organic or inorganic or composites. Ferric, aluminum, and calcium hydroxides and silicic acid grow to increasing particle sizes by polymerization. Cross-linking and complexation of organic and inorganic polymers produce gels and amorphous foulants commonly seen on membranes (2,12). Biotic debris such as polysaccharides and dead cellular matter contribute largely to this type of foulant. We have found that anticoagulants and antideposition agents show promise in inhibiting this fouling process. Antifoulants then can be a term applied specifically in this particulate fouling context. In a broader sense, the term antifoulant is used in the field to include antiscalants as well (6).

Third, biofouling is a prominent source of fouling. True of all water treatment and distribution systems is the growth and anchoring of microorganisms. At times, moderate temperatures and minimal nutrient levels in RO waters can support explosive growth of microorganisms. Bacteria capable of cell division in 20 minutes can grow from a normal count per unit volume of water to millions in an 8-hour shift. Due to the tendency of bacteria to secrete polymers that anchor themselves to surfaces to facilitate growth as a biofilm, this fouling mechanism is unique and poses a serious threat to operation of RO systems (13). This threat is compounded by the great difficulty of treating and completely removing a biofilm from membrane surfaces.

COMPOSITION OF FOULANTS

The chemical composition of foulants correlated with their sources are given in the Reverse Osmosis, Membrane Foulants.

ANTIFOULANT DESIGN AND APPLICATION

The term antifoulant is used here in its broadest meaning covering scaling, particulate fouling, and microbial fouling—the three classes of fouling mechanisms discussed before. Strategies aimed at controlling each type of fouling are summarized here.

For scale control, the development and application of antiscalants is well known and reviewed in the field of boiling water and cooling water chemistry (6,14–16) and applied to boilers, evaporators, cooling towers, and cooling systems. Anionic polymers, polyphosphates, and organophosphorous compounds, sometimes referred to as threshold inhibitors and dispersants, are used in substoichiometric amounts, usually in the range of 1–5 mg/L in RO systems (17). By binding to surfaces of growing crystal nuclei, the rates of crystallization from supersaturated solutions are retarded, and crystal packing orders are modified. By this mechanism, crystallization rates are so retarded that although supersaturation of solutes in the water will eventually equilibrate through crystallization within the residence time of the water in the system, there is little or no scale formation. The uniqueness of RO among water conditioning systems is that residence time is very short (a few seconds), concentration of seed crystals is low, and temperature is constant. For this reason, higher levels of supersaturation without crystallization are possible. On the other hand, the limits of saturation and rates of scaling are hard to model, measure, and predict. Interference comes from other solutes in the water, organic or inorganic. Assumptions of RO fouling limits vary considerably among practitioners.

Controlling fouling by preexisting particulate matter is much more challenging due to the variety of types of potential foulants and the complexity of their interactions (1,2,8,10,12), with each other in the same water and with the membrane. The stability and agglomeration of colloidal particles is a subject of major importance in natural water (1) as well as in treating process water (16). Drawing on the basic science of colloids and testing of model foulants suggested by RO foulant analysis data (2), progress is made steadily by the development of antifoulants.

The literature on preventing and managing biofouling in water treatment systems, is extensive. Much of the art and science found useful generally is applicable to RO systems as well. Several factors peculiar to the RO system can be mentioned. Chemicals used to sanitize and clean the system have to be chemically compatible with the thin, salt-rejecting, polyamide barrier membrane. It is of prime concern that accumulation and exponential growth of microorganisms should not be allowed to occur within the system. Pretreatment of feedwater, adequate maintenance of upstream unit operations, continuous flow of water through the RO unit, a good monitoring and sanitization program, and use of preservatives during downtime (18) are important to this end. Normalized flow and differential pressure in the system are sensitive indicators of biofouling.

To prevent irreversible fouling, trend charting of normalized permeate flow, differential pressure, and salt rejection, and readiness to perform adequate cleaning are important aspects of system operation (see Reverse Osmosis, Membrane Cleaning). Immediate assistance should be sought when cleaning has been inadequate. Powerful new cleaners are now available that provide alternatives to membrane replacement in the worst cases of fouling.

BIBLIOGRAPHY

1. Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry*, 3rd Edn. John Wiley & Sons, New York, NY, p. 3.
2. Ning, R.Y. and Shen, P.T.L. (1998). Observations from analysis of reverse osmosis membrane foulants. *Ultrapure Water* **15**(4): 37–44.
3. Aluwihare, L.I., Repeta, D.J., and Chen, R.F. (1997). A major biopolymeric component to dissolved organic carbon in surface sea water. *Nature* **387**: 166–169.
4. Ritter, S.K. (1997). Chemistry on the high seas. *Chemical & Engineering News, Amer. Chem. Soc.* (October 27): 23–31.
5. Byrne, W. (1995). Chapter 3, *Reverse Osmosis*. Tall Oaks Publishing Inc., Littleton, CO, pp. 97–166.
6. Meltzer, T.H. (1993). *High Purity Water Preparation*. Tall Oaks Publishing Inc., Littleton, CO, pp. 485–487.
7. Potts, D.E., Ahlert, R.C., and Wang, S.S. (1981). A critical review of fouling of reverse osmosis membranes. *Desalination* **36**: 235–264.
8. Cohen, R.D. and Probstein, R.F. (1986). Colloidal fouling of reverse osmosis membranes. *J. Colloid Interface Sci.* **114**: 194–207.
9. Amjad, Z. (1987). Advances in scaling and deposit control for RO system. *Ultrapure Water* **4**(6): 34–38.
10. Zhu, X. and Elimelech, M. (1995). Fouling of reverse osmosis membranes by aluminum oxide colloids. *J. Environmental Engineering* **121**(12): 884–892.
11. Tracey, D. (1996). Membrane fouling—What is it? Where does it come from? and What does it mean? *Ultrapure Water* **13**(7): 47–53.
12. Ning, R.Y. and Stith, D. (1997). The iron, silica and organic polymer triangle. *Ultrapure Water* **14**(3): 30–33.
13. Ridgway, H.F., Rigby, M.G., and Argo, D.G. (1985). Bacterial adhesion and fouling of reverse osmosis membranes. *J. AWWA* **77**: 97–106.
14. Drew. (1994). *Principles of Industrial Water Treatment*. Ashland Chemical Co., Boonton, NJ, pp. 75–85; 183–186.
15. Betz. (1991). *Handbook of Industrial Water Conditioning*. Betz Laboratories, Trevose, PA, pp. 96–104; 181–185.
16. Kemmer, F.N. (Ed.). (1988). *The Nalco Handbook*, 2nd Edn. McGraw-Hill, New York, NY, pp. 3.14–3.15.
17. Darton, E.G. (2000). Membrane chemical research: centuries apart. *Desalination* **132**: 121–131.
18. Varnava, W., Silbernagel, M., Kuepper, T., and Miller, M. (1996). *Reverse osmosis element preservation study*, Proceedings of Biennial Conf., Amer. Desalting Assoc., pp. 308–327.

REVERSE OSMOSIS, MEMBRANE FOULANTS

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INTRODUCTION

Periodic cleaning of reverse osmosis (RO) membranes is generally accepted as a necessary routine maintenance operation in running water purification plants (1–3). Common foulants found in RO membrane elements include calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride, calcium phosphate, ferric hydroxide, aluminum hydroxide, silica, silt, polymers from natural sources, and synthetic polymers used in pretreatment. These foulants may occur singly or in most cases, in complex combinations. Single foulants are simpler to address in prevention and dissolving (except for barium sulfate) during cleaning. Complex foulants usually resulting from coagulation of colloidal particles, offer the greatest challenge in prevention and removal during cleaning.

A large body of data and observations from troubleshooting RO systems is summarized here. Complex foulants are extracted from membrane elements sent from plants across the world that need assistance. Qualitative tests and quantitative elemental analyses of these foulants, combined with a thorough review of the pretreatment chemistry, provide insights into the nature and the source of the foulants. Experience with the pattern of responses to various cleaners and successful resolution and elimination of fouling problems confirm the conclusions regarding the source of foulants and the mechanisms of formation in each specific situation. The following generalizations have been helpful in solving fouling problems and in selecting the most appropriate cleaning chemicals:

1. Organic matter usually contributes more than 10% of the mass of foulants; the majority of the samples contain 50–100% organic matter.
2. Biomass constitutes the major part of the organic content of the foulants.
3. Synthetic polymers used in water pretreatment can often be differentiated from biomass in foulants.
4. Anionic polymers used as antiscalants and dispersants can deposit on membranes and act to concentrate high valence metal ions (Fe, Al, Ca) on the membrane surface.
5. Colloidal silica and clays have complex and variable content of iron, aluminum, calcium, and magnesium.

6. Elemental phosphorous is associated with biomass, phosphate, and phosphonates.

The six generalizations separately presented below are derived from a synthesis of foulant analysis data and correlation with plant process chemistry and responses to cleaners. Positive outcomes in the plants have consistently been realized by applying them.

ORGANIC MATTER

Organic matter is defined as carbon-containing matter. Each foulant is washed by decantation with pure water, then dried at 120–130 °C. It is gravimetrically analyzed for carbon, hydrogen, and nitrogen (C,H,N) content by standard methods of pharmaceutical analysis, along with a quantitative ash test (furnace at 400–450 °C) to determine the percentage of inorganic matter. The percent total volatile or combustible elements (C,H,N and oxygen) from the ash test is considered organic matter, and it correlated well with C,H,N values along with the general oxygen atom content of biological and synthetic organic polymers commonly used in water pretreatment. The organic matter in 22 foulant samples analyzed by these methods, during a recent period has the values shown in Table 1. From the table, it is interesting to note that all samples contained at least 10% by weight of organic matter and that 73% of the samples contained 50–100% by weight of organic matter. Note that the foulants analyzed are representative of the more difficult to clean types of foulants. Foulants such as calcium carbonate, calcium sulfate, and ferric and aluminum hydroxides that are readily cleaned with generic acid cleaners are not represented. Organic matter, which includes biomass and polymers used in pretreatment, usually makes the foulant difficult to remove.

BIOMASS

Biomass refers to organic matter arising from living or dead organisms. In colloidal form, it can enter the RO system with the feedwater and then coagulates and accumulates on membrane elements. A more severe source of biomass is the exponential growth of viable organisms within the system (4) and the accumulation of the biofilm in the system due to the difficulties in removal (5). Such accumulation is usually promoted by inadequate maintenance sanitization procedures of the entire water processing system and stagnation during frequent or prolonged downtimes without preservative. Severe growths are often detectable by odor or slime on the internal surfaces in contact with water. Milder growths are detectable by microbial culturing and enzyme activity tests. Natural surface waters (lakes, rivers and sea), especially in warm regions, have very high levels of decaying or excreted plant and animal matter. High biomass content of foulants in the samples examined correlated with the factors mentioned, in the feedwater and in the plant.

Table 1. Organic Matter in RO Foulant Samples

Organic Matter (% by weight)	Number of Foulants Analyzed	
0–10%	0	
10–20	3	
20–30	2	
30–40	0	
40–50	1	27%
50–60	3	
60–70	3	
70–80	4	
80–90	5	
90–100	1	73%
	Total: 22	100%

SYNTHETIC POLYMERS

Synthetic polymers used in water pretreatment can often be differentiated from biomass in foulants. The absence of the characteristics of biomass—odor, visual and microscopic appearance, color, slime, microbial count, enzyme activity, presence of phosphates, sodium and potassium in ash—and the presence usually of a thin and even coating of colorless to tan gel suggest synthetic polymers. Severe flux reduction accompanied by an almost invisible film of organic material is the hallmark of poisoning by cationic polymers. Using Fourier transform infrared spectroscopy (FT-IR), if the reference spectrum of the suspect pretreatment polymer is available and the foulant spectrum is uncluttered, positive identification through "fingerprinting" is possible. Carryover of high molecular weight synthetic cationic, anionic and nonionic polymers used as coagulants in pretreatment often is flocculated with colloidal particles of complex compositions, carries more mass, and is less readily identifiable. Lower molecular weight polymers used as antiscalants often participate in these complexes and are deposited as foulants. Even in the absence of polymeric coagulants, low molecular weight polymers, used as antiscalants and dispersants, can and will deposit on membranes at a slower rate (see following section).

ANIONIC POLYMERIC ANTISCALANTS

Anionic polymers used as antiscalants and dispersants are known to be quite intolerant of multivalent cations such as ferric and aluminum ions. These ions act as ionic cross-linkers, causing even polymers in the molecular weight range of 1,000 to 2,000 daltons to flocculate. By a combination of gradual deposition and accumulation due to incomplete removal during routine cleaning, such foulants build up over several years and gradually concentrate high valence cations as an ion exchange resin would. As an example, the elemental composition of such a foulant is given in Table 2. This sample contains 52% volatile organic matter (C,H,N,O) and 48% inorganic ash. The carbon and hydrogen content of the foulant (23.67% and 3.73%, respectively) are in reasonable agreement with the theoretical polyacrylic acid composition (at 52%) of 26.4% carbon, 2.9% hydrogen, and 23.4% oxygen. Smaller amounts of coagulated nitrogen-containing polymers or biomass can account for the nitrogen content. The inorganic composition of the foulant is revealed by scanning electron microscopy with energy diffusive X-ray analysis (SEM-EDX). The instrument is calibrated to quantitate elements between the atomic numbers of 12–42, which correspond to magnesium to molybdenum in the periodic table. The lighter elements such as B,C,H,N,O, and F are not measured, so the percentage by weight values are relative for the range of atoms measured. As shown, the predominant cation is iron (44% relative), followed by calcium, aluminum, chromium, and magnesium. Bridging to phosphate, silicate, and sulfate anions is apparent.

COLLOIDAL SILICA AND CLAYS

Colloidal silica and clays refer to preexisting siliceous particles in the feedwater, which coagulate during passage through the reverse osmosis system and become deposited on the membrane as a foulant (1,6,7). Colloidal silica, also known as nonreactive silica, results in natural waters from the polymerization of silicic acid and reactive oligomeric species, which as a population is termed reactive silica. Reactivity is measured by and often referred to as reactivity toward molybdate ions by the same type of condensation reaction. Condensation of reactive silica with aluminum, iron, and calcium hydroxides forms clays. Clays in feedwaters result mainly from the erosion of rocks, however. It is stated (8) that the chemical composition of most clays is similar to the composition of the earth's crust: oxygen 49.9%, silicon 26.0%, aluminum 7.3%, iron 4.1%, calcium 3.2%, sodium 2.3%, potassium 2.3%, magnesium 2.1%, and all other elements 2.8%. Following erosion is sand (50 microns –2 mm), silt (5–10 microns), and clay (<5 microns), differentiated by particle sizes.

Depending on the extent of clarification and prefiltration of feedwaters, silt and clays often end up on the membranes. The silt density index (SDI) is a means of measuring particle load in the feedwater by timing the fouling of 0.45-micron test filters. In practice, feedwater with an SDI value greater than 5 would lead to high fouling rates in plants. The 0.45-micron filters are nominal filters, so it is likely that a significant fraction of clay entering with the feedwater is not detected by SDI monitoring.

Table 2. Elemental Composition of an Iron Acrylate Foulant

Component	Percent by Weight	
By gravimetric elemental analysis:		
Carbon	23.67	(absolute)
Hydrogen	3.73	
Nitrogen	3.26	
Ash (inorganic)	48.08	
By SEM-EDX (at. no. 12–42, Mg–Mo):		
Iron	44.0	(relative)
Calcium	15.0	
Phosphorous	13.0	
Silica	9.9	
Aluminum	8.8	
Sulfur	4.2	
Chromium	1.8	
Magnesium	1.7	
Total:	98.4	

Table 3. Elemental Composition of a Colloidal Silica Foulant

Component	Percent by Weight	
By gravimetric elemental analysis:		
Carbon	1.15	(absolute)
Hydrogen	0.67	
Nitrogen	0.02	
Ash (inorganic)	92.46	
By SEM-EDX (at. no. 12–42, Mg–Mo):		
Silicon	90.0	(relative)
Iron	3.6	
Aluminum	2.7	
Potassium	1.3	
Sodium	0.8	
Calcium	0.8	
Magnesium	0.6	
Sulfur	0.5	
Chlorine	0.3	
Total:	100.6	

Colloidal silica and clays are often encountered in analyses of foulants. They frequently appear in the presence of organic matter and accumulate in the flow channels of the membrane elements in significant masses. Occasionally, colloidal silica can severely foul membranes in amounts almost too minute to sample physically. The composition of one such example is given in Table 3.

PHOSPHOROUS

Phosphorous is detected in foulant samples by SEM-EDX. Relative amounts in the inorganic portions of 20 recent foulants surveyed ranged from 0–58% of the elements measured in these samples (mean = 14.6%, SD = 15.7%). Sources of phosphorous-containing matter can be correlated with a number of sources. Biomass generally contains measurable amounts of phosphates. Algal biomass in natural waters reportedly contains almost 1% elemental phosphorous (9). Phosphates, except those of sodium, potassium, and ammonium, are generally only slightly soluble in water. If phosphates are present in a feedwater to any appreciable extent, phosphate scales will likely form in a reverse osmosis system unless the water is acidified (2). Calcium phosphate has limited solubility at neutral pH and an even lower solubility at higher pH. Phosphates are widely used in agriculture and in laundry products, so it is common to find phosphate in silt and agricultural runoff. Municipal wastewater has phosphate concentrations usually in the range of 15–30 mg/L of phosphate ion (about 5–10 mg/L as phosphorous) (11). In addition to calcium phosphate, ferric and aluminum phosphates are particularly insoluble and can enter the reverse osmosis system in clay or colloidal form.

Other sources of phosphorous are found in the environment of the membrane itself. High pH membrane cleaners widely used for removing organic foulants are often formulated with trisodium phosphate and sodium tripolyphosphate (10). Incomplete cleaning is likely to deposit insoluble phosphates with residual foulants which accumulate over time. Another source is the commonly used generic antiscalant sodium hexametaphosphate (SHMP). Solutions of SHMP are hydrolytically unstable and generate phosphate ions and phosphate foulants (2). Even phosphonates can precipitate with high levels of calcium, iron, and aluminum and can participate in fouling.

CONCLUSIONS

These conclusions regarding the formation of RO foulants have been the basis of resolving many operating problems in RO plants. Hopefully, they will serve as a framework for further insights into making RO systems more stable in operation.

BIBLIOGRAPHY

1. Ebrahim, S. (1993). *Cleaning and Regeneration of Membranes in Desalination and Wastewater Applications: State-of-the-Art*. Vol. 1. Proc. IDA and WRPC World Conference, International Desalination Association, pp. 197–208.
2. Byrne, W. (1995). *Reverse Osmosis*. Tall Oaks Publishing Inc., Littleton, CO.
3. Veza, J.M. and Sadhwani, J. (1997). *Cleaning Methods for Reverse Osmosis Membranes*. Proc. IDA World Congress on Desalination and Water Reuse, Vol. 2, pp. 393–407, and references cited therein.
4. Ridgway, H.F. et al. (1984). Biofilm fouling of RO membranes—its nature and effect on treatment of water for reuse. *J. AWWA* **76**: 94–102.
5. Whittaker, C., Ridgway, H., and Olson, B.H. (1984). Evaluation of cleaning strategies for removal of biofilms from reverse-osmosis membranes. *Appl. Environ. Microbiol.* **48**(3): 395–403.
6. Ning, R.Y. and Stith, D. (1997). The iron, silica and organic polymer triangle. *Ultrapure Water* **14**(3): 30–33.
7. Zhu, X. and Elimelech, M. (1995). Fouling of reverse osmosis membranes by aluminum oxide colloids. *J. Environ. Eng.* **121**(12): 884–892, and references cited therein.
8. Kemmer, F.N. (Ed.). (1988). *The Nalco Handbook*, 2nd Edn. McGraw-Hill, New York, Section 4.9.
9. Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry*, 3rd Edn. John Wiley & Sons, New York, p. 887.
10. A survey of generic high pH cleaners recommended by all major membrane manufacturers that contain one or both of these reagents.
11. Reference 8, Chapter 36.

REVERSE OSMOSIS, MEMBRANE CLEANING

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INTRODUCTION

Reverse osmosis membrane cleaning has been extensively addressed over the years (1–7). Severe concentration of dissolved and suspended matter occurs when water is purified by using reverse osmosis (RO) membranes. Permeate recoveries of 50–90% correspond to 2–10-fold concentrations in the reject brine. Precipitation or crystallization of foulants can occur in the narrow brine flow channels within the membrane elements, leading to reduced membrane flux or increased differential pressure across the system, or both. Crystallization of salts or precipitation of colloidal matter occur more toward the back end of the system, and preexisting silt and flocculated organic matter can clog the leading elements of the system.

LIMITATIONS OF CLEANING

A practical procedure for maintenance cleaning is limited to recirculating cleaning solutions through the membrane elements. By a patented method (8) of membrane reconditioning, spiral wound elements, whose hard casing is removed, are routinely used in selecting effective cleaners for cleaning by recirculation. This allows visual inspection of the membrane surface after each cleaning test. It is apparent that, except for easily soluble foulants such as calcium carbonate or ferric and aluminum hydroxides, nearly all RO foulants are only slightly dissolved in even the best matched cleaning solutions by extensive soaking. Removal requires high tangential flow velocities and is usually partially effective especially where flow channels are clogged and large patches within the elements are inaccessible to the recirculating solution. For this reason, the need for cleaning should be minimized or completely eliminated by the new antiscalants and dispersants now available and adequate pretreatment and pilot testing of process designs. When cleaning is necessary, it should be performed at the earliest stages of fouling.

WHEN TO CLEAN

It is generally agreed among membrane manufacturers and practitioners that RO systems should be cleaned before the following performance changes are reached:

1. Loss of 10 to 15% in normalized permeate flow rate.
2. Increase of 10 to 15% in differential pressure.
3. Decrease of 1 to 2% in salt rejection.

If a cleaning procedure fails to restore system performance fully to reference start-up values, it is certain that continued use of the same cleaning procedure will lead to an accelerating decline in system performance and increased cleaning frequency. For this reason, it is important to address two issues at this point: (1) find an improved cleaning procedure, or (2) investigate possible improvement of pretreatment to avoid membrane fouling. Continue cleaning and process improvement efforts until the RO performance is stable.

CHOOSING CLEANERS

Major membrane manufacturers generally define five types of foulants for which various generic chemicals

Table 1. Cleaning Solutions Formulated from Generic Chemicals in Concentrations Recommended by Major Membrane Manufacturers[a,b]

Types of Foulants-	Acid-Soluble Foulants	Biofilm, Bacterial Biological Matter	Oils and Organic Matter	Organic and Inorganic Colloids	Silica and Silicates
Fluid Systems	1% citric acid	1% STPP (TFC only) 1% EDTA.Na$^+$ 1% TSP 1% Borax (TFC only) 0.1% Triton X-100 (CA only)			–
Hydranautics	2% citric acid 0.1% Triton X-100 or Tergitol 8, etc.	2% STPP 0.26% SDDBS pH 7.5	0.5% Na Perborate 0.1% TritonX-100 or Tergitol 8 etc.	2% STPP 0.8% EDTA.Na$^+$ 0.1% Triton X-100 or Tergitol 8, etc.	–
Filmtec	0.2% HCl or 0.5% H_3PO_4 or 2.0% citric acid or 0.2% sulfamic acid	1% EDTA.Na 0.1% NaOH to pH = 12 or following pH = 12 solutions: 0.05% Na-DDS or 0.1% STPP + 1% EDTA.Na, or 0.1% TSP + 1% EDTA.Na		0.1% NaOH 0.05% Na-DDS pH = 12	–
Desal	HCl pH = 3 or citric acid pH = 2	1% TSP 1% STPP 0.1% Na-DDS 1% EDTA.Na pH = 8–11.5			–
Permasep	0.5% HCl (pH 2.3 min) or 0.5% H_3PO_4 (pH 2.3 min) or 0.2% sulfamic acid or 2% citric acid, pH = 4 or 2% citric acid 2% Na_2EDTA NH_4OH to pH = 4 or 1% $Na_2S_2O_4$ or 1% NaHMP	1% Na_2EDTA 0.1% NaOH pH = 11 max	0.3% NaPerborate 0.25% Na-DDBS pH = 10 or 1% Na_2EDTA 1% STPP 1% TSP, pH = 11 or 2% STPP 0.25% Na-DDBS pH = 10 or 1% NaHMP	0.3% NaPerborate 0.25% Na-DDBS pH = 10 or 2% STP 0.25% Na-DDBS pH = 10 or 1% NaHMP	0.5% NaOH, pH = 11 or 1% Na_2EDTA 0.1% NaOH, pH = 11 or 0.3% Naperborate 0.25% Na-DDBS pH = 10 or 2% STPP 0.25% Na-DDBS pH = 10

[a] Reference (10).

[b] STPP = sodium tripolyphosphate; EDTA.Na = sodium salt of ethylenediaminetetraacetic acid; TSP = trisodium phosphate; Triton X-100 and Tergitol 8 = nonionic surfactants; Na-DDS = sodium dodecylsulfate; Na-DDBS = sodium dodecylbenzenesulfonic acid; Na_2EDTA = disodium salt of ethylenediaminetetraacetic acid; NaHMP = sodium hexametaphosphate.

are recommended for blending at the site where cleaning solutions are prepared. The five types of foulants are (1) acid-soluble foulants, (2) biofilm/bacterial slime/biological matter, (3) carbon-containing oils/organic matter, (4) dual organic and inorganic coagulated colloids, and (5) silica and silicates. The recommended generic chemicals and concentrations in the cleaning solutions to be prepared are given in Table 1 for the five respective types of foulants. Proprietary booster cleaners are commercially available to fortify the effectiveness of these generic cleaners that are formulated at the site. For convenience and technical support, a large variety of proprietary RO membrane cleaners are available from chemical suppliers that specialize in RO operations.

CLEANING STRATEGIES

Experience has shown that within the same class of foulants, responses to the same cleaning solution can vary considerably. Elemental analyses of foulants and cleaning studies have shown that more than one type of foulant can be present on the membrane at the same time, requiring sequential cleaning with different cleaners. Sometimes even the order of cleaners used would make a significant difference. All this is to say that the choice of cleaners and the cleaning procedure to be used is an empirical science. For a given set of conditions in a plant, cleaning efficiencies are improved by trials over time. The progress of improvement can be greatly accelerated by conducting off-line cleaning studies on single elements.

When a better cleaning method is needed in the plant, the following are the alternative strategies:

Strategy 1: The plant has a history of using generic cleaning chemicals, and modest improvement in effectiveness is needed. Consider purchase of proprietary booster cleaners.

Strategy 2: Significant cleaning improvement is needed. Look for a proprietary cleaner supplier who has cleaning expertise. Option 1:

Based on prior knowledge of the characteristics of the foulant on hand and consultation with the supplier, select a combination of cleaners for trial in the plant. Option 2: Send one to three fouled elements to a specialist for a cleaning study, foulant analysis, and a review of plant performance history and pretreatment processing. Document the findings and pilot cleaning results using a recommended improved cleaning procedure. Simultaneously, address recovery of the plant and avoidance of repeated fouling. Option 3: Send all fouled elements for off-site cleaning by a specialist.

Strategy 3: All cleaning efforts by recirculation of cleaning solutions have failed. Consider nonroutine methods such as using proprietary membrane conditioning liquids or a patented membrane reconstruction process by which the membrane bundle is unrolled, cleaned leaf by leaf, then restored with a new hard casing. Both methods are offered by King Lee Technologies (9).

ON-LINE CLEANING PROCEDURE

There are six steps in cleaning membrane elements in place in RO systems:

1. Mix cleaning solution.
2. Low flow pumping. Pump preheated cleaning solution to the vessels at a low flow rate (about half of that shown in Table 2) and low pressure to displace the process water. With the RO concentrate throttling valve completely open to minimize pressure during cleaning, use only enough pressure to compensate for the pressure drop from feed to concentrate. The pressure should be low enough that essentially no permeate is produced. Low pressure minimizes redeposition of dirt on the membrane. Dump the concentrate, as necessary, to prevent dilution of the cleaning solution.
3. Recirculate. After the process water is displaced, cleaning solution will be present in the concentrate stream. Recirculate the concentrate to the cleaning solution tank, and allow the temperature to stabilize.
4. Soak. Turn the pump off, and allow the elements to soak. Sometimes, a soaking period of about 1 hour is sufficient. For difficult to clean foulants, an extended overnight soaking period of 10–15 hours is beneficial. To maintain a high temperature during an extended soaking period, use a slow recirculation rate (about 10% of that shown in Table 2).
5. High flow pumping. Feed the cleaning solution at the rates shown in Table 2 for 30–60 minutes. The high cross-flow rate flushes out the foulants removed from the membrane surface by the cleaning; minimal or no permeation through the membrane avoids compacting the foulant. If the elements are heavily fouled (which should not be a normal occurrence), a flow rate 50% higher than that shown in Table 2 may aid cleaning. At higher flow rates, excessive pressure drop may be a problem. The maximum recommended pressure drops are 20 psi per element or 60 psi per multielement vessel, whichever value is more limiting.

   Note: In this cleaning mode, foulants are generally partially dissolved in the cleaner and partially dislodged physically from the membrane and flow channels without dissolving. An in-line filter removes the recirculated particles and should be monitored for cartridge replacement.
6. Flush out. Prefiltered raw water can be used for flushing out the cleaning solution, unless there will be corrosion problems such as seawater corroding stainless steel piping. To prevent precipitation, the minimum flush temperature is 20°C.

   Additional Notes: The pH should be monitored during acid cleaning. The acid is consumed when it dissolves alkaline scales. If the pH increases more than 0.5 pH units, add more acid.

Table 2. Recommended High Recirculation Flow Rates During Cleaning

Feed Pressure,[a] psig	Element Diameter, inches	Feed Flow Rate per Vessel (gpm)
20–60	2.5	3–5
20–60	4	8–10
20–60	6	16–20
20–60	8	30–40

[a] Dependent on the number of elements in the pressure vessel.

MULTISTAGE SYSTEMS

For tapered multistage systems, the flushing and soaking steps can be performed simultaneously in the entire array. The high flow rate recirculation step, however, should be carried out separately for each stage, so that the flow rate is not too low in the first stage and too high in the last. This can be accomplished either by using one cleaning pump and operating one stage at a time or by using a separate cleaning pump for each stage.

CONTROL AND IMPROVEMENT OF CLEANING PROCESS

To ensure complete recovery of membrane performance by cleaning, the system performance should be adequately controlled by trending of normalized flux, differential pressure, and salt rejection to (1) trigger cleaning when any monitored parameters change from normal baseline by 10–15%, (2) record the trended parameters before and after each cleaning, and (3) initiate improvement actions for better cleaning if membrane performance does not fully recover. A change in responsiveness to a previously effective cleaning process signals a change in the fouling pattern that requires immediate attention.

If partial cleanings are allowed to continue, the system performance will decline at an increasing rate and will become increasingly difficult to recover.

In-place cleaning processes are improved primarily by the choice of cleaning chemicals and the order of the application sequence. Depending on the composition of the complex foulants, when two or more cleaners are found necessary, often the order in which they are used is important. Also critical, but to lesser extents, are the variables of time, temperature, and cross-flow rate.

Through a thorough review of the water and pretreatment chemistry, analyses of the foulant composition and source, and customized selection of antiscalants, dispersants, and high performance cleaners, both fouling avoidance and reliable plant performance can be attained.

BIBLIOGRAPHY

1. Veza, J.M. and Sadhwani, J. (1997). *Proceedings IDA World Congress* **2**: 393.
2. Amjad, Z., Pugh, J., and Zuhl, R.W. (1996). *Ultrapure Water* **13**(7): 27.
3. Byrne, W. (1995). *Reverse Osmosis*. Tall Oaks Publishing, Littleton, CO.
4. Ebrahim, S. (1994). *Desalination* **96**: 225.
5. Hickman, C.E. (1991). *Proceedings Membrane Proc. Conf., Amer. Water Works Assoc.*, p. 329.
6. Tragardh, G. (1989). *Desalination* **71**: 325.
7. Whittaker, C., Ridgway, H., and Olson, B.H. (1984). *Appl. Environ. Microbiol.* **48**: 395.
8. U.S. Patent No. 5,250,118 (1993). C.L. Netwig and D.L. Kronmiller. Method of Removing Foulants and Restoring Production of Spiral-Wound Reverse Osmosis Cartridges
9. *Membrane conditioners and the reconstruction service are unique from King Lee Technologies*, San Diego, CA (www.kingleetech.com).
10. *Technical Bulletins from several major membrane manufacturers provide guidance on membrane cleaning procedures and generic cleaning chemicals: Koch-Fluid Systems and Hydranautics*, San Diego, CA; Dow-Filmtec, Midland, MI; Desal/Osmonics, Minneapolis, MN; and DuPont-Permasep, Wilmington, DE.

APPLICATION OF RISK ASSESSMENTS IN CRAFTING DRINKING WATER REGULATIONS

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INTRODUCTION

Assessments of adverse health outcomes and estimations of health risks from contaminants of drinking water are used at several points in the overall development of U.S. drinking water regulations. They are applied during the extensive discussions surrounding consideration of a contaminant's risk and approaches to risk mitigation, and in the required elements of National Primary Drinking Water Regulation (NPDWR) proposals, support documents, and final rules. Risk assessments are of several types with substantially different intents and characteristics. No one approach fits all applications. The type of assessment chosen depends on the application and the nature and availability of relevant data.

The regulatory process starts with the identification of a constituent as either a possible contaminant of drinking water or as having some adverse toxicological or pathogenic properties. Available health data are then collected and analyzed, leading to the possible development of a toxicological profile of adverse health outcomes and dose–response characteristics. This is then coupled with occurrence data and exposure estimates to provide an estimate of national public health impact. If a decision is made to move forward on a NPDWR, more refined assessments are then used to develop maximum contaminant level goals (MCLGs). Separate assessments are used to help identify possible maximum contaminant levels (MCLs) or treatment techniques consistent with public policies. In some cases, risk assessments may comprise regulatory elements themselves, such as sanitary surveys or comprehensive performance evaluations. Finally, risk assessments are necessary as formal components of regulatory supporting documents to help estimate risk reductions and quantify public health benefits. Some of these assessments, particularly those associated with public health policies and legal requirements, are highly constrained in form and content. Additionally, while the art and science of environmental risk assessment continue to evolve, we still have substantial uncertainty and imprecision in these estimates. Effective interpretation of these risk products requires some understanding of their purpose and form. This chapter details these applications and presents some examples.

Disclaimer: The views expressed in this chapter are those of the author and do not necessarily represent those of the USEPA.

RISK ASSESSMENT APPROACHES FOR DRINKING WATER REGULATIONS

In risk management activities to ensure the safety of drinking water, assessments of health risk are performed to answer questions posed in the management process (Fig. 1). Examples include broad questions such as “What is the nature and magnitude of waterborne disease in the United States?”—answers to which can help define where the safety of drinking water fits into the overall considerations of public health, or identify particular situations (e.g., undisinfected wells, crossconnections) that are associated with disease. More familiarly, risk assessments can address narrower questions such as “What is the risk that oral ingestion of hexavalent chromium will cause lung cancer?” or “What is the likelihood of *Cryptosporidium* illnesses from a turbidity spike in an unfiltered surface water system?” where the answers might help define regulatory actions. Specific questions, such as “What is the likely differential number of cancers prevented between a MCL for arsenic at

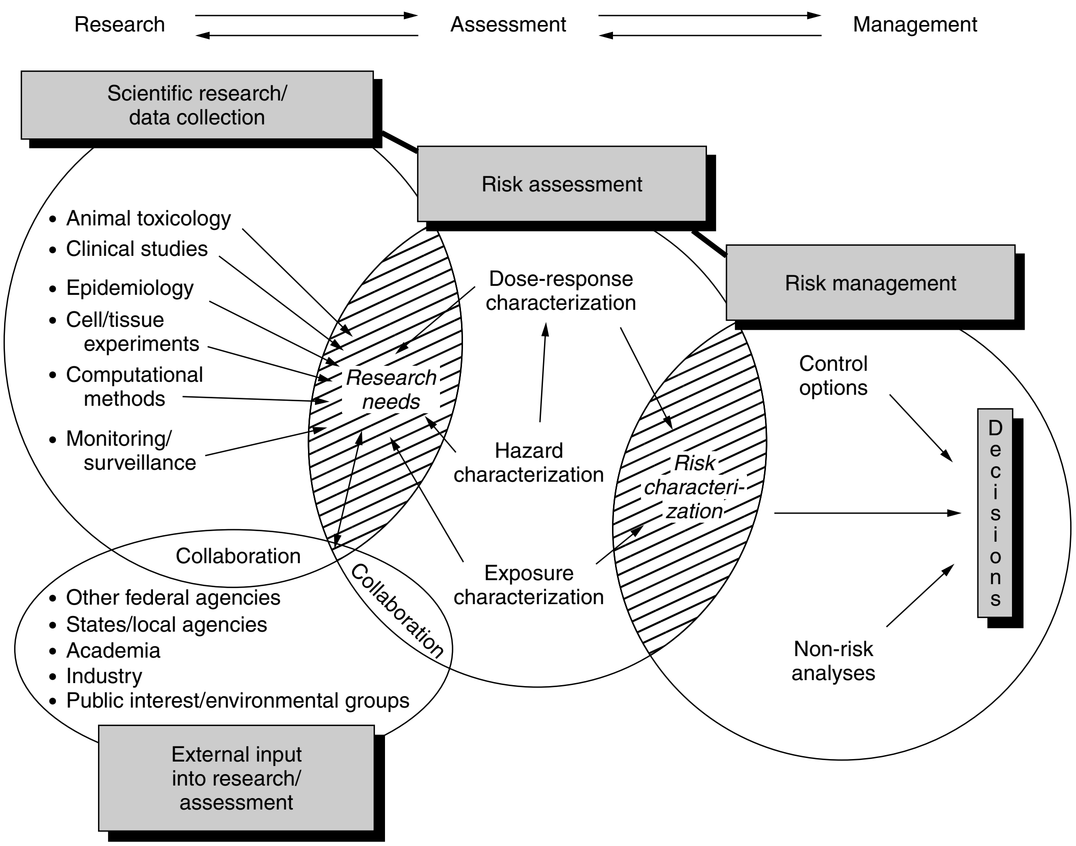

Figure 1. Integration of data collection, risk assessment, and risk management [*Source*: Farland (1)].

3 μg/L and one at 5 μg/L?" or "What are failure modes in the operation of an upflow clarifier?" may need to be answered to compare or determine possible solutions to the identified problems.

Risk assessment approaches for drinking water health and regulatory questions fall into three main types: those based on epidemiologic data, those calculated using mathematical risk models, and those based on analysis of systems and components. Epidemiologic and risk model approaches have been described more completely in earlier chapters, so only their applicability to regulatory development is addressed here. For this purpose, it is important to remember that there are substantial and important limitations to these approaches and that the conclusions from such assessments must be considered with due caution by those using the information. In addition, management decisions are often required in the face of uncertainty and lack of information. Risk assessments can provide useful information, but seldom give clear, unambiguous answers.

With respect to epidemiologic data, information from waterborne disease outbreaks, intervention studies, or controlled experiments on humans can be used directly to both quantitatively and qualitatively describe risks. However, the precision and accuracy of epidemiologic data typically limit these assessments to situations where excess risks (risks above background levels) are about 1% or greater. More often, epidemiologic studies of large groups or populations can describe only effects greater than 10–100% or more. In general, causal associations between contaminants and effects are considered significant only when effects are severalfold higher than background levels. Therefore, risk assessments done directly from these data can generally describe risks and answer risk questions only to this level of resolution. Because public health questions for drinking water often involve situations where risks are substantially below epidemiologic resolution, this approach is frequently inappropriate.

Perhaps the most familiar form of risk assessment is based on mathematical models used to extrapolate existing data to make quantitative estimates relevant to other situations. This well-known approach, first described by the National Academy of Sciences (NAS) in 1983 (2), organizes the process of human health risk assessment into four steps: hazard identification, dose–response assessment, exposure assessment, and risk characterization (Fig. 2). Hazard identification involves an evaluation of whether exposure to a substance would produce an adverse or otherwise undesirable effect. The data used to make such a determination usually come from animal studies. In some instances, human data may be available for the contaminant of interest. Dose–response assessment involves a more quantitative evaluation of the empirical evidence relating a specific exposure dose to the effect of interest. In particular, the available data are examined to determine the relationship between the magnitude of the exposure and the probability of the observed effect.

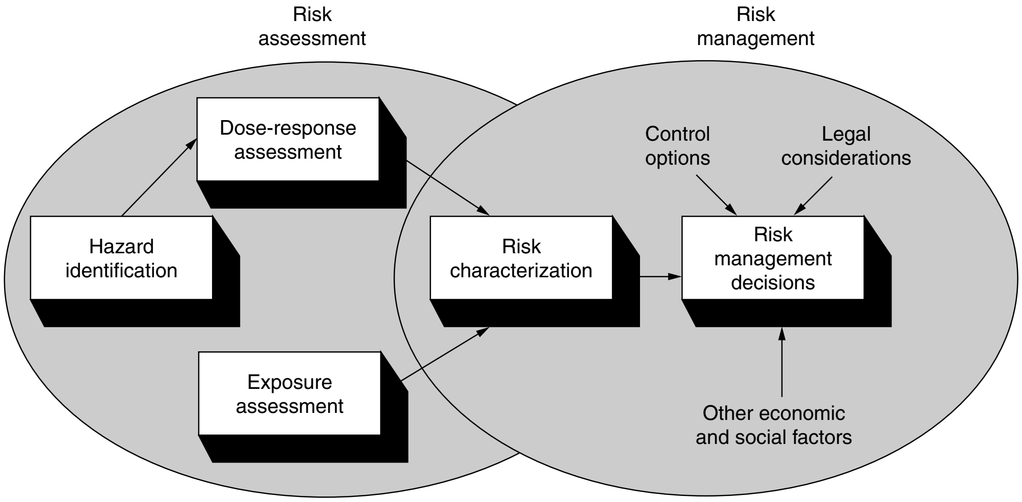

Figure 2. NAS risk assessment paradigm (left circle) and risk management (right circle) [*Source*: USEPA (3)].

Exposure assessments involve an evaluation of contaminant occurrence data, characterization of the environmental fate and transport of the contaminant from the source to the exposed population by different media (e.g., air, water, food), and physiological considerations of different exposure routes (e.g., ingestion, inhalation, dermal contact).

These toxicity and exposure products are combined in the risk characterization. The risk characterization describes the overall nature and magnitude of risk posed to human populations exposed to a particular contaminant. Included in the description is a discussion of what is known and not known about the hazards posed by the substance, what models were used to quantify the risk and why they were selected, assumptions and uncertainties associated with the qualitative and quantitative aspects of the assessment, and general level of confidence in the assessment.

A caution with these is that, while the calculated results are often presented as point value expressions of risk, it must be recognized that the farther the extrapolation from the original data, the more uncertainty and less precision in the results. The animal data themselves result from what are essentially small, highly controlled epidemiologic studies, and thus have the resolution limitations noted above. In addition, experimental variation may be 10% or greater. Because these studies are most often conducted with high exposures to the contaminants of interest and generate high risks, models are used to extrapolate the data to answer questions about lower environmental exposures and/or risks. These models have inherent limitations that magnify uncertainties. Exposure estimates likewise have substantial variation and uncertainty. The net result is that quantitative estimates of risk cannot describe a defined point risk for a certain exposure, but instead a range of possible risks. These ranges tend to increase with increasing model complexity to frequently span orders of magnitude. Most often, the range includes zero.

A third approach to risk assessment is based on analysis of an entire system or operation to identify vulnerabilities that could allow contaminants to reach the consumer. It is based on standard engineering design assessment approaches used to identify failure modes, judge probabilities of occurrence, and describe consequences. These have been adapted to focus on vulnerabilities in systems or operations that could result in human exposure to contaminants. This approach begins with a full description of the system or flow diagram of the process. Points where contamination can occur are identified. The likelihood and consequences of contamination at these points are described. From such an assessment, management actions can focus on controlling high-impact situations (Fig. 3). In the food industry, hazard assessment critical control point (HACCP) programs have been put into place to protect the public from, among other things, contaminated shellfish and other food items. Sanitary surveys, source water vulnerability assessments, and comprehensive performance evaluations (CPEs) are examples of this type seen in the drinking water industry. This is also the approach used for water system security and counterterrorism assessments. As currently practiced, these are qualitative, rather than quantitative in nature. Once the system is described and vulnerabilities identified, probabilities and consequences are typically rated on the basis of best professional judgment and using categories such as “high, medium, or low” or “minor, significant, or catastrophic.” The end result may be a list of vulnerabilities with some rankings for risks and consequences. Managers can use this information to identify problem areas and prioritize activities. Although not commonly practiced, it should be noted that such system analysis approaches are open to quantification of risks (4).

RISK MANDATES FROM THE SAFE DRINKING WATER ACT

The Safe Drinking Water Act (SDWA), as amended in 1986 and 1996 (5) has language that directs the U.S. Environmental Protection Agency (USEPA) to establish

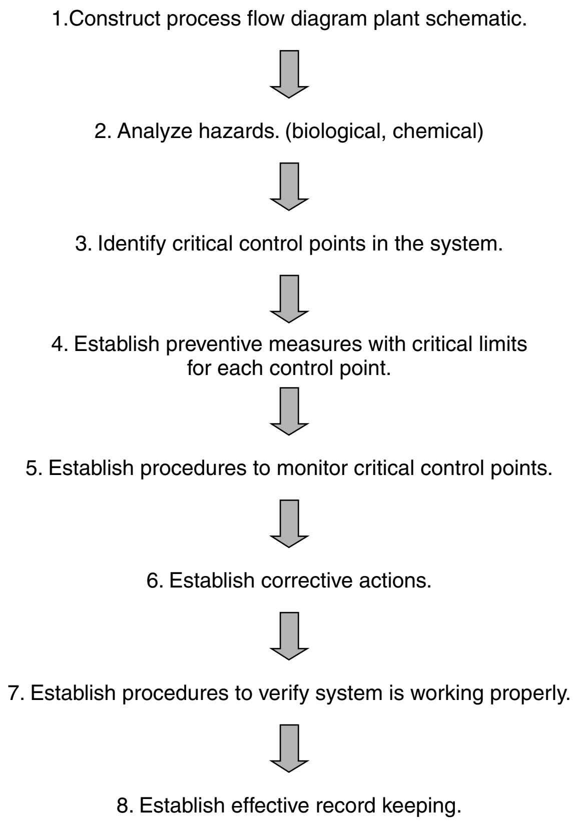

Figure 3. Hazard assessment critical control point (HACCP) risk assessment approach.

MCLGs for contaminants of public health concern for drinking water: "Each maximum contaminant level goal established under this subsection shall be set at the level at which no known or anticipated adverse effects on the health of persons occur and which allows an adequate margin of safety." These goals, which are not enforceable themselves, are to be used to set the enforceable NPDWRs (5):

> Each national primary drinking water regulation for a contaminant for which a maximum contaminant level goal is established under this subsection shall specify a maximum contaminant level for such contaminant which is as close to the maximum contaminant level goal as is feasible. ... For the purposes of this subsection, the term "feasible" means feasible with the use of the best technology, treatment techniques and other means which the Administrator finds, after examination for efficacy under field conditions and not solely under laboratory conditions, are available (taking cost into consideration).

In addition, a provision added to the Act in 1996 specifies priorities for selecting contaminants for rulemaking to

> take into consideration, among other factors of public health concern, the effect of such contaminants upon subgroups that comprise a meaningful portion of the general population (such as infants, children, pregnant women, the elderly, individuals with a history of serious illness, or other subpopulations) that are identifiable as being a greater risk of adverse health effects due to exposure to contaminants in drinking water than the general population.

In addition, the Act specifies that USEPA shall document health risks, opportunities for risk reductions, and benefits and costs of mandating these reductions and make these available for public comment. This health risk reduction and cost analysis (HRRCA) is a required component of the regulatory process.

By this and other language, Congress described both the necessary characteristics of risk assessments for drinking water regulations and the broad principles for managing these risks. It can be seen that by their words, Congress established a precautionary policy with regard to drinking water safety. The MCLG was to be set conservatively with respect to risk to more vulnerable individuals. The MCL was to be set to reflect the MCLG, with the additional considerations for technical feasibilities and costs.

These broadly stated goals set directions, but were not sufficiently described to be used for specific regulatory decisions. USEPA evolved operational interpretations of Congressional intentions for both the MCLG and for the acceptable public health risks associated with MCLs and treatment techniques following the 1986 amendments. These have been used consistently for NPDWRs from that time. Following the 1996 amendments, USEPA developed additional approaches for the benefit and cost analyses for the HRRCA.

DEVELOPING MCLS AND TREATMENT TECHNIQUES

The SDWA grants the USEPA Administrator the authority to publish a MCLG and promulgate a NPDWR for a contaminant if the contaminant may have an adverse effect on the health of persons, the contaminant is known or likely to occur in drinking water with a frequency or level of health concern, and there is a meaningful opportunity for health risk reduction. Development of a NPDWR normally begins with the identification of a drinking water contaminant. As provided in the SDWA, USEPA must list candidate contaminants for regulation on a periodic basis (6). Following listing, more detailed health, occurrence, exposure, and treatment technology information is gathered. When adequate information becomes available, a determination is made on whether to go forward with development of a NPDWR proposal (7). This determination uses a protocol developed and recommended to USEPA by the National Drinking Water Advisory Council (NDWAC). The health risk information is combined with occurrence data (levels, frequency, national distribution, persistence, etc.) and exposure estimates to predict the national number of individuals exposed above advisory levels. This risk assessment forms the basis for USEPA's determination if regulation would provide a meaningful opportunity for health risk reduction.

Maximum Contaminant Level Goals

Once the decision is made to move forward, the MCLG is determined. MCLGs are risk assessment products developed by USEPA Office of Water and Office of

Research and Development. MCLGs are strictly health-based levels. They are developed and set at contaminant levels believed to be without appreciable health risk to individuals, to be consistent with the provision "set at the level at which no known or anticipated adverse effects on the health of persons occur." Additionally, they must address the concern for the protection of sensitive subpopulations. Therefore, risk assessments used to develop MCLGs must at a minimum provide an estimate for a zero-risk exposure level for humans who may be more sensitive to the contaminant. While these risk assessments are caveated to be upper bounds for estimated risks, such that the true risks may be less or even zero, the assessments do not have to, nor are they designed to, estimate the full range of true risks to the average individual.

MCLG risk assessments use the available toxicologic and epidemiologic health study data. The data are evaluated with respect to the nature of the adverse health effects from the contaminant, the strength of evidence for causal relationships, and their quality. Depending on the outcome, a dose–response estimate is made. As noted above, these data are almost always limited in quantity and quality, yielding substantial ranges for uncertainty. USEPA has chosen as a matter of policy to work to risks at the more conservative end of these ranges, in order to comply with the provision that the MCLG "allows an adequate margin of safety" in the face of these uncertainties. Therefore, poorer-quality data will lead to more stringent quantitative descriptions of risk.

For chemicals that produce adverse health effects and are not considered to be carcinogenic (noncarcinogens), the MCLG is based on the *reference dose* (RfD), which is defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. In practice, the RfD is set at a plausible zero-risk level. USEPA assumes that a physiological threshold exists for noncancer health effects from chemical contaminants, below which the effect will not occur. Thus the MCLG will be a nonzero number.

Depending on the quality of the available toxicity data, the RfD is usually derived from an experimental no-observed-adverse-effect level (NOAEL), identified as the highest dose in the most relevant study that did not result in a known adverse effect. The adverse effects chosen may themselves be mild and without clinical significance, but typically represent early stages in progression to more serious disease. In order to extrapolate from the data to human exposures protective of sensitive subpopulations, the NOAEL is divided by various uncertainty factors to derive the RfD. These uncertainty factors conservatively account for the variation in human response to the contaminant, extrapolation to human responses if animal data were used, the nature of the studies, data quality, and relevance. The result of this is that the RfD may differ from the NOAEL by as little as a factor of 3 (e.g., nitrate, arsenic) or as much as $\geq$1000 (e.g., methyl bromide, chlorobenzene). The RfD takes the form of dose ingested per unit body weight per day (μg kg^{-1} day^{-1}). RfDs that have been reviewed and agreed on by consensus within USEPA are listed in USEPA's Integrated Risk Information System (IRIS).

The RfD, which is based on the total daily amount of contaminant taken up by a person on a body weight basis, is converted to a drinking water equivalent level (DWEL) concentration and adjusted for the percentage contribution of other sources [relative source contribution (RSC)] of the contaminant besides drinking water (air, food, etc.) to arrive at the MCLG. This calculation traditionally assumes a lifetime consumption of 2 L of drinking water per day by a 70-kg adult, which is about the upper 90th percentile consumption level. More recent USEPA regulatory risk assessments, such as those for arsenic, have considered different drinking water consumption rates in addition to this default value to represent specific populations (infants, agricultural workers) and situations (8).

A different approach is taken for contaminants that may be carcinogenic. USEPA assumes as a default position that no toxicity threshold exists for induction of cancer and thus, there is no absolutely safe level of exposure. Until relatively recently, once it was determined that a contaminant is a known or probable human carcinogen, the MCLG was automatically set at zero. USEPA has now revised its guidelines for cancer risk assessments to reflect the increasing understanding of the several steps in the progression of cancer (9,10). Some contaminants have been reevaluated for their carcinogenicity using the current draft version of these guidelines. A good example is chloroform (6), which is now considered a carcinogen only at very high exposures associated with tissue damage, such that a threshold is indicated. This allows calculation of a nonzero MCLG using a margin of exposure (MoE) approach. As with RfDs, these determinations of carcinogenicity and their associated dose–response assessments that have been reviewed and agreed on by consensus within USEPA are listed in IRIS.

An alternative approach is used for situations where the data on carcinogenicity of a contaminant are equivocal or too scanty to make a clear judgment. These contaminants are termed "possible human carcinogens." For these, the MCLG may be derived from their relevant noncancer health effects as described above. The resulting RfD is divided by an additional uncertainty factor of 10 as a margin of safety for the possible carcinogenicity.

In a vein similar to that for carcinogens, microbial pathogens and indicator organisms are also assigned a MCLG of zero as a matter of policy, from the consideration that one infective unit (oocyst, cyst, virus particle, bacterium) could be sufficient to cause an infection. The available data on infectivity are supportive for this assumption for the pathogenic viruses studied and for the protozoa, *Giardia* and *Cryptosporidium*. While it is less clear that this is so for pathogenic bacteria, the data cannot exclude this possibility.

Identifying Candidate MCLs

Once the MCLG is established, it is combined with information on contaminant occurrence, treatment technologies, and analytical methods to suggest and evaluate possible regulatory criteria for further discussion. Although the MCLG is a regulatory value, it is not enforceable; the NPDWR is the enforceable regulatory element.

One element in the standard setting process is to determine whether the NPDWR should be a MCL or a treatment technique. An enforceable MCL can be established to control exposure to a contaminant when appropriate analytical methods exist to quantify the contaminant and determine compliance at the MCL. When methods are not available, as for certain microbial exposure situations, treatment techniques may be established that do not directly measure exposure, but use other indicators for compliance.

Two risk considerations come into play in the process of setting a MCL to reduce a contaminant as close as feasible to the MCLG. The first has to do with MCLGs of zero. It is impossible to quantify a contaminant or confirm treatment to a zero exposure. Therefore, MCLs must be above zero, and thus have some risk. A risk benchmark is used to identify appropriate safe drinking water exposures. These guide selection of analytical techniques, treatment approaches, and, ultimately, the MCL choices. This benchmark is based on a consideration of de minimus or “acceptable” risk. As a matter of policy, USEPA Office of Water has used an acceptable risk range for chemical carcinogens from one additional cancer per million people to one additional cancer per 10,000 people exposed to the contaminant over a lifetime (8,11). For pathogenic microorganisms, an acceptable risk of one additional infection per 10,000 people exposed per year has been used (12,13).

These allowable exposures are estimated from the associated dose–response curves. For carcinogens, this dose–response assessment uses models to extrapolate from the available data to zero exposure–zero risk, defining a curve that is essentially linear at low exposures. The resulting “cancer slope factor” allows for a convenient probability analysis of risks to individuals associated with different exposures. The exposures for the acceptable risk range are taken directly from the curve. However, as noted above, the uncertainties increase substantially in these extrapolations. USEPA traditionally uses the 90th percentile upper bound of the modeled results to minimize the possibility that risks in this exposure range are not greater than estimated. The end result of this is that the risk from a lifetime consumption of water at a given level is unlikely to be greater than estimated, is more likely substantially less, and may be zero.

A similar probabilistic risk approach is used for microbial contaminants. The dose–response models used for microbial risk assessments are somewhat more complex in that they must be selected to account for the particulate nature of the infective material in the environment. The modeled exposures are then used for further risk management.

For contaminants with noncancer health risks, the MCLG is used as the starting point for determining a MCL. Because this uses a “bright line” reference point (the DWEL), exposures need only be estimated and compared to the MCLG. However, since this is nonprobabilistic, alternative MCLs cannot be considered on the basis of risks. For most noncarcinogens, the MCL is set equal to the MCLG.

The estimated risks associated with different exposures are then matched against the existing environmental exposure levels to determine the magnitude of the public health problem to be solved. As discussed in other chapters, the additional considerations for treatment technologies and their feasibility and the availability of appropriate analytical methods are factored in at this point.

Health Risk Reduction and Cost Analysis

The second application of risk assessment in the development of a MCL or treatment technique is in the estimation of public health benefits to be gained by regulation. This is used in the management discussions leading up to a regulatory proposal. Under the SDWA of 1986, it was necessary to consider only analytical and treatment feasibility in establishing the MCL. However, a cost benefit assessment was produced as an element of the regulatory impact analysis (RIA). The 1996 revisions to the SDWA required USEPA to explicitly consider costs and benefits in determining the MCL. Therefore, an expanded HRRCA is now required as part of a regulatory proposal. To estimate benefits for different MCLs or treatment requirements, the risks to an individual at the resulting exposure levels must be multiplied by estimates of the number of individuals in the United States exposed to the different levels. In practice, a relationship between the number of individuals exposed versus exposure level is first produced, then further manipulated to account for existing and proposed treatment controls. This relationship may be calculated stepwise or by using Monte Carlo simulations based on exposure distributions. From this, the number of cancers or microbial illnesses avoided at a given regulatory level can be estimated. These “body counts” can be matched with information on the costs of treating the associated diseased and the dollar value of avoiding illness to give quantitative information on the monetary benefits of the regulation. These benefits are then matched against the implementation and compliance costs to utilities and oversight agencies (14). From a risk assessment perspective, it must be remembered that carcinogen dose–response curves represent upper-bound risks; thus estimates of the number of cancers based on these curves are also upper-bound values for any given exposure level.

This approach is most useful for benefits from reducing cancer or microbial illness risks. This is both because these disease endpoints are recognizable and definitive and because the impacts are quantifiable from their probabilities. This is not so for noncancer risks from chemicals. Because these are described by nonprobabilistic, zero-risk DWELs associated with subclinical health effects of indeterminate public health importance, it is difficult to quantify or assign monetary value to the benefits of reducing exposures to these chemicals.

Risk Assessments as Regulations

Risk assessments can comprise regulatory elements themselves. These may apply directly to utilities or secondarily through requirements on primacy agencies. The type of risk assessments currently required in NPDWRs are all qualitative system analyses. These include treatment system sanitary surveys found in the Total Coliform Rule (15) and Interim Enhanced Surface Water Treatment Rule (IESWTR) (16), the watershed sanitary surveys in the Surface Water Treatment Rule (SWTR) (12), and the CPEs, also in the IESWTR. These all require on-site evaluations to determine sources of contamination and vulnerabilities to failures that could compromise water quality. These analyses are similar to the HACCP process used by the National Aeronautics and Space Administration (NASA) and U.S. Department of Agriculture (USDA) to protect foods.

Australia has taken a more formal HACCP approach to protect their drinking water. Termed the “framework for management of drinking water quality,” it is to be incorporated into the Australian Drinking Water Guidelines (17). The approach includes a systematic and comprehensive analysis of the entire route of water from source to tap (Table 1). This analysis leads to identification of hazards, sources of hazards, and associated risks. These are addressed in the subsequent institution of protective measures to yield multiple barriers to contamination. The emphasis of the HACCP approach is on proactive protection, rather than reactive responses.

Regulatory Reviews of NPDWRs

The 1996 SDWA Amendments required that USEPA review all existing NPDWRs every 6 years to determine if information available subsequent to promulgation would support regulatory revision. Congress stipulated that all such revisions must maintain, or provide for greater, protection of the health of persons. USEPA, working with the NDWAC, developed a protocol for these reviews, driven largely by reevaluations of health risk information (7). USEPA principally considered whether any new evaluation of oral ingestion risks could lead to revision of the MCLG. This approach allows the Agency to use up-to-date risk assessment approaches in its reevaluations, which will include a wider range of possible adverse health outcomes (reproductive and developmental) and better characterizations of carcinogenicity. The potential here is that some carcinogens would be reclassified in such a way that their MCLs could be relaxed while maintaining the same level of health protection to the public. The reclassification of chloroform as a threshold carcinogen is an example. This would recognize that improved risk assessments could reduce the scientific uncertainties that led to excessively stringent NPDWRs.

Table 1. Australian Framework for Management of Drinking Water Quality

First element
Commitment to drinking water quality management
System analysis and management
Assessment of the drinking water supply system
Planning preventive strategies for water quality management
Implementation of operational procedures and process control
Verification of drinking water quality
Incident and emergency response
Supporting requirements
Employee awareness and training
Community involvement and awareness
Research and development
Documentation and reporting
Review
Evaluation and audit
Review and continual improvement

FUTURE OUTLOOK

Risk assessments are used both formally and informally at several points within the regulatory process. They serve specific purposes and mandates and may have severe constraints on their representations of risk. While assessments may be qualitative or quantitative in nature, they are always limited by the available information and our current abilities to understand disease processes and predict outcomes. They will always be inexact. Recognizing and accepting their limitations is important for making sound regulatory decisions. An increased awareness of how risk assessments may be used will improve future regulatory discussions.

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BIBLIOGRAPHY

1. Farland, W.H. (2000). *Current and Proposed Approaches to Assessing Children’s Cancer Risk*. USEPA/National Institute of Environmental Health Sciences Workshop: Information Needs to Address Children’s Cancer Risk. March 30 and 31. USEPA Office of Research and Development, Washington, DC.
2. National Academy of Sciences. (1983). *Risk Assessment in the Federal Government: Managing the Process*. National Academy Press, Washington, DC.
3. USEPA. (1999c). *Research and Development: Fiscal Years 1997–1998 Research Accomplishments*. USEPA Office of Research and Development, Washington, DC.
4. Buchanan, R.L. and Whiting, R.C. (1998). Risk assessment: A means for linking HACCP plans and public health. *J. Food Protect.* **61**(11): 1531–1534.
5. *Title XIV—Safety of Public Water Systems*; Sec. 1412(b), National Drinking Water Regulations: Standards; 42 USC Sec. 300g.
6. USEPA. (1998a). Announcement of the drinking water candidate list; notice. *Fed. Reg.* **63**: 10273–10287.
7. USEPA. (2002a). National primary drinking water regulations; announcement of the results of EPA’s review of existing drinking water standards and request for public comment. *Fed. Reg.* **67**: 19029–19090.
8. USEPA. (2001a). National primary drinking water regulations; arsenic and clarifications to compliance and new source contaminants monitoring; final rule. *Fed. Reg.* **66**: 6976–7066.
9. USEPA. (1999b). *Draft Guidelines for Carcinogen Risk Assessment*. NCEA-F-0644. USEPA, Washington, DC.

10. USEPA. (2001b). Notice of opportunity to provide additional information and comment. Draft revised guidelines for carcinogen risk assessment. *Fed. Reg.* **66**: 59593–59594.
11. USEPA. (1998d). National primary drinking water regulations: disinfectants and disinfection byproducts; final rule. *Fed. Reg.* **63**: 69390–69476.
12. USEPA. (1989a). Drinking water; national primary drinking water regulations; filtration, disinfection; turbidity, giardia lamblia, viruses, legionella, and heterotrophic bacteria; final rule. *Fed. Reg.* **54**: 27486–27541.
13. USEPA. (1998c). National primary drinking water regulations: interim enhanced surface water treatment; final rule. *Fed. Reg.* **63**: 69478–69521.
14. USEPA. (1999a). Health risk reduction and cost analysis for radon in drinking water: notice. *Fed. Reg.* **64**: 9560–9599.
15. USEPA. (1989b). Drinking water; national primary drinking water regulations; total coliforms (including fecal coliforms and *E. coli*); final rule. *Fed. Reg.* **54**: 27544–27568.
16. USEPA. (1998b). National primary drinking water regulations: disinfectants and disinfection byproducts notice of data availability; proposed rule. *Fed. Reg.* **63**: 15606–15692.
17. Australian Department of Health and Ageing. (2001). *Framework for Management of Drinking Water Quality: A Preventative Strategy from Catchment to Consumer*. National Health and Medical Research Council, Canberra, Australia.

READING LIST

USEPA. (1986). *The Risk Assessment Guidelines of 1986*. EPA/600/8-87/045. USEPA, Washington, DC.

USEPA. (2002b). Announcement of preliminary regulatory determination of priority contaminants on the drinking water contaminant candidate list. *Fed. Reg.* **67**: 38222–38244.

POTENTIAL RISKS OF WATERBORNE TRANSMISSION OF *ESCHERICHIA COLI* O157:H7

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Escherichia coli O157:H7 can be transmitted by any route where fecal contaminated material is ingested. These routes may include foodborne, waterborne, person-to-person, and animal-to-person. Epidemiological investigations during outbreaks have identified that only a small number of organisms is needed to cause infection (i.e., 10–200 organisms) (3). This low infectious dose combined with the possibility of *E. coli* O157:H7 infections that do not show symptoms allows direct person-to-person transmission via poor hygiene.

The most well-documented route of *E. coli* O157:H7 transmission is foodborne. Several outbreaks have occurred from consumption of undercooked ground beef either in restaurants or within individual homes. In addition to meat, other foods have been implicated, including mayonnaise, unpasteurized apple juice, fermented hard salami, lettuce, vegetable sprouts, yogurt, and milk. Contamination of these foods may have occurred due to improper hygiene among food handlers or by contact between uncooked foods and raw meats contaminated with *E. coli* O157:H7. There is also the possibility of direct contamination of produce in the fields with manure from infected animals (4).

An increasingly common route of transmission is waterborne via recreational or municipal water sources. Several *E. coli* O157:H7 outbreaks have been linked to use of recreational waters. Typical sources of recreational water outbreaks may be fecal contaminated material entering a lake and lake water ingested by swimmers or by children with diarrhea contaminating pool water, usually with an insufficient level of chlorine. Outside Portland, Oregon, 59 individuals were infected after swimming in a recreational lake in 1991 (5). A water park outbreak in Georgia in 1998 resulted in dozens of infections and the death of one child. The outbreak was linked to contamination from a child with diarrhea combined with low chlorine levels in the pool water (6).

In addition to these recreational water outbreaks, several incidents have occurred with drinking water. A list of outbreaks linked to contaminated drinking water is shown in Table 1.

The first municipal waterborne *E. coli* O157:H7 outbreak occurred in Missouri in 1989 (7); more than 240 people were infected, and four individuals died. It was suspected that the outbreak occurred from backflow during two water main breaks, leading to intrusion of the pathogen. The most publicized waterborne outbreak of *E. coli* O157:H7 occurred in May 2000 in Walkerton, Ontario, Canada. Approximately 1350 cases of gastroenteritis were reported in individuals exposed to Walkerton municipal water, and overall, it was estimated that the number of cases associated with Walkerton exceeded 2300 individuals. Stool samples confirmed 167 cases of *E. coli* O157:H7 infection; 65 individuals were hospitalized, and 27 individuals developed hemolytic uremic syndrome. Four deaths were directly due to the *E. coli* outbreak in Walkerton, and *E. coli* O157:H7 was a contributing factor leading to three additional deaths. During the outbreak, a supply source well was contaminated with coliform bacteria and *E. coli* O157:H7. This well was prone to surface contamination, especially following flooding conditions, which is what preceded the Walkerton incident. Furthermore, environmental testing of livestock farms, especially a farm adjacent to this well, indicated the presence of *E. coli* O157:H7 infections in the livestock (16,17).

This most common drinking water treatment is disinfection with chlorine. Susceptibility of various strains of *E. coli* O157:H7 to chlorine disinfection has

Table 1. Outbreaks of *E. coli* O157:H7 from Drinking Water

Year, Location	# Infected	Description	Reference
1989, Missouri, U.S.	243	Two water main breaks may have led to backflow in an unchlorinated municipal water supply leading to four deaths	(7)
1990, Scotland	4	O157 contamination of reservoir water supply	(8)
1990, Japan	42	O157 cultured from tap and well water	(9)
1995, Scotland	6	Sewage contaminated a public water supply	(10)
1995, Minnesota, U.S.	33	Contaminated spring water used as drinking water source at campgrounds	(11)
1997, Washington, U.S.	4	Contaminated chlorinated groundwater supply at a trailer park	(12)
1998, Illinois, U.S.	3	Well water contaminated by cattle feces	(12)
1998, Wyoming, U.S.	157	Contamination of a spring and two wells that were municipal water sources	(13)
1999, Texas, U.S.	22	Inadequately chlorinated city well water	(14)
1999, New York, U.S.	127	Septic system contaminated a well used for drinking water at fairgrounds, resulting in 2 deaths	(15)
2000, Utah, U.S.	102	Illness among those drinking from an irrigation system	(14)
2000, Ohio, U.S.	29	Possible backflow at fairgrounds from animal barn to food vendor taps	(14)
2000, Walkerton, Ontario, Canada	167	Improper chlorination of municipal well water contaminated with O157 from surface water runoff resulted in seven deaths	(16,17)

been examined in several studies, and except for an occasional resistant strain (18), the organism can be rapidly inactivated by low levels of chlorine disinfectant and shows no unusual tolerance to chlorine.

According to a Water Quality Disinfection Committee survey (19), it was determined that United States water utilities must maintain a median chlorine residual of 1.1 mg/L and a median exposure time of 45 minutes before the point of first use in the distribution system. Based on these guidelines, it seems unlikely that *E. coli* O157:H7 would survive conventional water treatment practices in the United States at these levels of chlorination. Had appropriate chlorine residual levels been maintained, many of the aforementioned drinking water outbreaks, such as the Walkerton event, would have been avoided. In nondisinfected drinking water, *E. coli* O157:H7 demonstrates environmental survival and chlorine susceptibility similar to wild-type *E. coli* (20), which suggests that wild-type *E. coli* could be an adequate indicator organism for fecal contamination of water.

The United States Environmental Protection Agency regulates systems that operate at least 60 days per year and serve 25 people or more or have 15 or more service connections as public water systems under the Total Coliform Rule. This compliance monitoring of tap water for all public water systems can indicate whether the system is contaminated or vulnerable to fecal contamination, if it fails to identify specifically the presence of *E. coli* O157:H7. Existing detection methods for *E. coli* O157:H7 are intended for analyses of clinical specimens or food products, which are expected to contain large numbers of organisms. These methods lack sensitivity for detecting low numbers of contamination in environmental samples and typically require long (20–48 hour) incubation periods for analyzing small sample volumes. To ensure that public water systems can rapidly respond to contamination from this significant human pathogen, there is an urgent need for rapid detection methods for *E. coli* O157:H7 in water. The reader is referred to the article entitled "Understanding *Eschericia coli* O157:H7 and the need for rapid detection in water" by Bukhari, Weihe, and LeChevallier for further discussion of rapid methods for detecting *E. coli* O157:H7 in water.

BIBLIOGRAPHY

1. Boyce, T., Swerdlow, D., and Griffin, P. (1995). Current concepts: *Escherichia coli* O157:H7 and the hemolytic-uremic syndrome. *N. Engl. J. Med.* **333**: 364–368.
2. Shelton, D. and Karns, J. (2001). Quantitative detection of *Escherichia coli* O157 in surface waters by using immunomagnetic electrochemiluminescence. *Appl. Environ. Microbiol.* **67**: 2908–2915.
3. Willshaw, G.A., et al. (1994). Vero cytoxin-producing *Escherichia coli* O157 in beefburgers linked to an outbreak of diarrhea, haemorrhagic colitis and haemolytic uraemic syndrome in Britain. *Lett. Appl. Microbiol.* **19**: 304–307.
4. Mead, P. and Griffin, P. (1998). *Escherichia coli* O157:H7. *Lancet* **352**: 1207–1212.
5. Keene, W.E., et al. (1994). A swimming-associated outbreak of hemorrhagic colitis caused by *Escherichia coli* O157:H7 and *Shigella sonnei*. *N. Engl. J. Med.* **331**: 579–584.
6. Gilbert, L. and Blake, P. (1998). Outbreak of *Escherichia coli* O157:H7 infections associated with a waterpark. *Georgia Epidemiol. Rep.* **14**: 1–2.
7. Swerdlow, D.L., et al. (1992). A waterborne outbreak in Missouri of *Escherichia coli* O157:H7 associated with bloody diarrhea and death. *Ann. Intern. Med.* **117**: 812–819.

8. Dev, V., Main, M., and Gould, I. (1991). Waterborne outbreak of *Escherichia coli* O157. *Lancet* **337**: 1412.
9. Akashi, S., et al. (1994). A severe outbreak of haemorrhagic colitis and hemolytic uremic syndrome associated with *Escherichia coli* O157:H7 in Japan. *Eur. J. Pediatr.* **153**: 650–655.
10. Jones, I. and Roworth, M. (1996). An outbreak of *Escherichia coli* O157 and Campylobacteriosis associated with contamination of a drinking water supply. *Public Health* **110**: 277–282.
11. Levy, D., Bens, M., Craun, G., Calderon, R., and Herwaldt, B. (1998). *Surveillance for waterborne-disease outbreaks—United States, 1995–1996*. CDC Surveillance Summaries. MMWR 47 (No. SS-5): pp. 1–33.
12. Barwick, R., Levy, D., Craun, G., Beach, M., and Calderon, R. (2000). *Surveillance for waterborne-disease outbreaks—United States, 1997–1998*. CDC Surveillance Summaries. MMWR 49 (No. SS-4): pp 1–35.
13. Olsen et al. (2002).
14. Lee, S., Levy, D., Craun, G., Beach, M., and Calderon, R. (2002). *Surveillance for waterborne-disease outbreaks—United States, 1999–2000*. CDC Surveillance Summaries. MMWR 51 (No. SS-8): pp. 1–43.
15. New York Department of Heath. (2000). Health commissioner releases *E. coli* outbreak report. Available: <www.health.state.ny.us/nysdoh/commish/2000/ecoli.html> (cited November 2003).
16. Hrudey, S.E., Payment, P., Huck, P.M., Gillham, R.W., and Hrudey, E.J. (2003). A fatal waterborne disease epidemic in Walkerton, Ontario: Comparison with other waterborne outbreaks in the developed world. *Water Sci. Technol.* **47**: 7–14.
17. O'Conner, D.R. (2002). Report of Walkerton Inquiry: Part 1- The events of May 2000 and related issues. Available: <http://web.utk.edu/~hydro/Geol685/Walkerton_Summary.pdf> (cited November 2003).
18. Zhao, T., Doyle, M.P., and Zhao, P. (2001). Chlorine inactivation of *Escherichia coli* O157:H7 in water. *J. Food Prot.* **64**: 1607–1609.
19. Water Quality Disinfection Committee. (1992). Survey of water utility disinfection practices. *J. Am. Water Works Assoc.* **84**: 121–128.
20. Rice et al. (1992).

SLOW SAND FILTRATION

National Drinking Water
Clearinghouse

First used in the U.S. in 1872, slow sand filters are the oldest type of municipal water filtration. Today, they remain a promising filtration method for small systems with low turbidity or algae-containing source waters. Slow sand filtration does not require pretreatment or extensive operator control—which can be important for a small system operator with several responsibilities

WHAT IS SLOW SAND FILTRATION?

Slow sand filtration is a simple and reliable process. Slow sand filters are relatively inexpensive to build, but they do require highly skilled operators (Fig. 1).

The process percolates untreated water slowly through a bed of porous sand, with the influent water introduced over the surface of the filter, and then drained from the bottom.

Properly constructed, the filter consists of a tank, a bed of fine sand, a layer of gravel to support the sand, a system of underdrains to collect the filtered water, and a flow regulator to control the filtration rate. No chemicals are added to aid the filtration process.

ADVANTAGES

Design and operation simplicity—as well as minimal power and chemical requirements—make the slow sand filter an appropriate technique for removing suspended organic and inorganic matter. These filters also may remove pathogenic organisms.

Slow sand filtration reduces bacteria, cloudiness, and organic levels—thus reducing the need for disinfection and, consequently, the presence of disinfection byproducts in the finished water. Other advantages include:

- Sludge handling problems are minimal.
- Close operator supervision is not necessary.
- Systems can make use of locally available materials and labor.

Slow sand filters also provide excellent treated- water quality (See Table 1). Slow sand filters consistently demonstrate their effectiveness in removing suspended particles with effluent turbidities below 1.0 nephelometric turbidity units (NTU), achieving 90 to 99 + percent reductions in bacteria and viruses, and providing virtually complete *Giardia lamblia* cyst and *Cryptosporidium* oocyst removal.

LIMITATIONS

Slow sand filters do have certain limitations. They require a large land area, large quantities of filter media, and manual labor for cleaning.

Table 1. Typical Treatment Performance of Conventional Slow Sand Filters

Water Quality Paramenter	Removal Capacity
Turbidity	<1.0 NTU
Coliforms	1–3 log units
Enteric Viruses	2–4 log units
Giardia Cysts	2–4 + log units
Cryptosporidium Oocysts	>4 log units
Dissolved Organic Carbon	<15–25%
Biodegradable Dissolved Organic Carbon	<50%
Trihalomethane Precursors	<20–30%
Heavy Metals	
Zn, Cu, Cd, Pb	>95–99%
Fe, Mn	>67%
As	<47%

Source: Adapted from Collins, M.R. 1998.

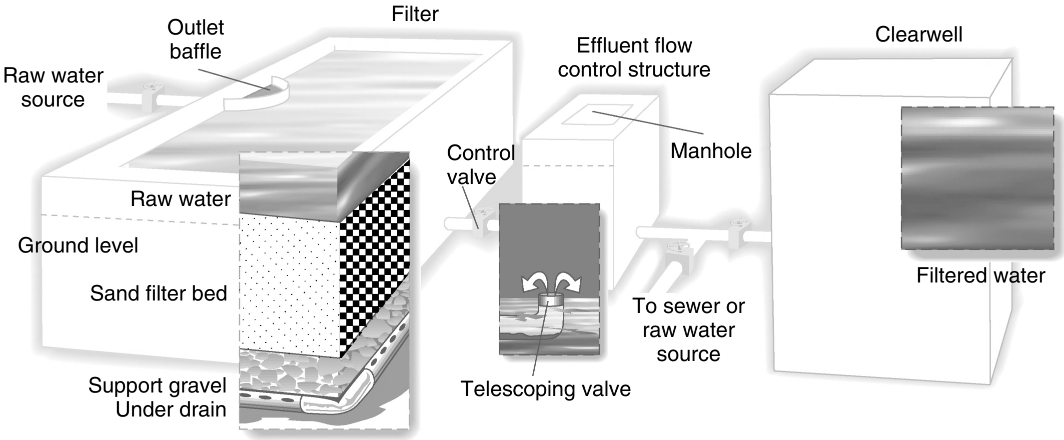

Figure 1. Slow sand filter.

Water with high turbidity levels can quickly clog the fine sand in these filters. Water is applied to slow sand filters without any pretreatment when it has turbidity levels lower than 10 NTU.

When slow sand filters are used with surface waters that have widely varying turbidity levels, infiltration galleries or rough filters—such as up- flow gravel filters—may be used to reduce turbidity.

Waters with a very low nutrient content may impair turbidity removal since some nutrients must be present that promote biological ecosystem growth within the filter bed.

Slow sand filters do not completely remove all organic chemicals, dissolved inorganic substances, such as heavy metals, or trihalomethane (THM) precursors—chemical compounds that may form THMs when mixed with chlorine. Also, waters with very fine clays are not easily treated using slow sand filters.

A granular activated carbon (GAC) sandwich filter is a modified slow sand filter that removes organic material. This filter uses a base sand layer that is approximately 1 foot deep, an intermediate GAC layer approximately 0.5 feet, and a top sand layer approximately 1.5 feet deep. This modified slow sand filter effectively removes pesticides, total organic carbon, and THM precursors.

Slow sand filters are less effective at removing microorganisms from cold water because as temperatures decrease, the biological activity within the filter bed declines.

PROCESS DESCRIPTION

Slow sand filters require a very low application or filtration rate (0.015 to 0.15 gallons per minute per square foot of bed area, depending on the gradation of the filter medium and the quality of the raw water). The removal action includes a biological process in addition to physical and chemical ones (Table 2).

A sticky mat of biological matter, called a “schmutzdecke,” forms on the sand surface, where particles are trapped and organic matter is biologically degraded. Slow sand filters rely on this cake filtration at the surface of the filter for particulate straining. As the surface cake develops during the filtration cycle, the cake assumes the dominant role in filtration rather than the granular media.

Pilot testing is always necessary when designing slow sand filters. Currently, engineers are not able to predict the performance of a slow sand filter with a specific quality of raw water. Operation of a small pilot filter, preferably over several seasons of the year, will insure adequate performance of the full-scale plant.

Remember, after the designer sets the parameters—such as the plant filtration rate, bed depth, and sand size—there is little a plant operator can do to improve the performance of a slow sand filter that does not produce satisfactory water.

Slow sand filter pilot plant testing does not have to be expensive. Pilot plant testing has been done using manhole segments and other prefabricated cylindrical products, such as filter vessels.

Slow sand filter pilot facilities operate over long periods of time—up to a year—but the level of effort can be quite low, consisting of daily checks of head loss, flow rate, water temperature, and turbidity and taking coliform samples.

Since the purification mechanism in a slow sand filter is essentially a biological process, its efficiency depends upon a balanced biological community in the schmutzdecke. Therefore, filters should operate at a constant rate. When operation is stopped, the microorganisms causing bacteriological degradation of trapped impurities lose their effectiveness. Intermittent operation disturbs the continuity needed for efficient biological activity.

Allowing the filter to operate at a declining rate is one way of overcoming this problem. Declining rate filtration produces additional water, which is generally satisfactory. Moreover, the declining-rate mode may be applied during overnight operation, resulting in significant labor savings.

Storing filtered water is essential at a slow sand filter plant for two reasons. First, because of the importance of establishing biological activity, using chlorine ahead of the filter is inappropriate, and the operator must provide disinfectant contact time in a storage basin. Second, storage is needed for production equalization and demand.

Table 2. Design Summary of a Slow Sand Filter

Design Parameters	Recommended Range of Values
Filtration rate	0.15 $m^3/m^2 \cdot h$ (0.1–0.2 $m^3/m^2 \cdot h$)
Area per filter bed	Less than 200 m^2 (in small community water supplies to ease manual filter cleaning)
Number of filter beds	Minimum of two beds
Depth of filter bed	1 m (minmum of 0.7 m of sand depth)
Filter media	Effective size (ES) = 0.15–0.35 mm; uniformity coefficient (UC) = 2–3
Height of supernatant water	0.7–1 m (maximum 1.5 m)
Underdrain system	
Standard bricks	
Precast concrete slabs	Generally no need for further hydraulic calculations
Precast concrete blocks with holes on the top	
Porous concrete	
Perforated pipes (laterals and manifold type)	Maximum velocity in the manifolds and in laterals = .3 m/s
	Spacing between laterals = 1.5 m Spacing of holes in laterals = 0.15 m Size of holes in laterals = 3 mm

Source: Vigneswaran, S. and C. Visvanathan, 1995.

MONITORING AND OPERATION REQUIREMENTS

A slow sand filter must be cleaned when the fine sand becomes clogged, which is measured by the head loss. The length of time between cleanings can range from several weeks to a year, depending on the raw water quality. The operator cleans the filter by scraping off the top layer of the filter bed. A ripening period of one to two days is required for scraped sand to produce a functioning biological filter. The filtered water quality is poor during this time and should not be used.

In some small slow sand filters, geotextile filter material is placed in layers over the surface. In this cleaning method, the operator can remove a layer of filter cloth periodically so that the upper sand layer requires less frequent replacement.

In climates subject to below-freezing temperatures, slow sand filters usually must be housed. Uncovered filters operating in harsh climates develop an ice layer that prevents cleaning. Thus, they will operate effectively only if turbidity levels of the influent are low enough for the filter to operate through the winter months without cleaning. In warm climates, a cover over the slow sand filter may be needed to reduce algae growth within the filter.

Before cleaning a slow sand filter, the operator should remove floating matter, such as leaves and algae. When one unit is shut down for cleaning, the others are run at a slightly higher rate to maintain the plant output.

After cleaning, the unit is refilled with water through the underdrains. This water can be obtained from an overhead storage tank or by using water from an adjacent filter. When the clearwell is designed, the temporary reduction of plant output should be considered, ensuring that sufficient water is available for the users.

Once the filter is cleaned, the microorganisms usually re-establish and produce an acceptable effluent. In cooler areas, ripening may take a few days. Even then, if the effluent's turbidity is sufficiently low, the water supply can be resumed after one day with adequate chlorination.

Slow sand filter monitoring and operation is not complicated. Daily tasks include reading and recording head loss, raw and filtered water turbidity, flow rates, and disinfectant residual. If necessary, the operator should adjust the flow to bring water production in line with demand.

In addition, with the promulgation of the Surface Water Treatment Rule, each day the operator needs to use the flow data and disinfectant residual data to calculate contact time values and determine if disinfection is sufficiently rigorous. These duties may require one to two hours unless automated.

WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1993. *Back to Basics Guide to Slow Sand Filtration*. Denver: American Water Works Association.

American Water Works Association. 1994. *Slow Sand Filtration: International Compilation on Recent Scientific and Operational Developments*. Denver: American Water Works Association.

Clark, R. M., and D. A. Clark. 1995. *Drinking Water Quality Management*. Lancaster, Pennsylvania: Technomic Publishing Company.

Collins, M. R. 1998. *"Assessing Slow Sand Filtration and Proven Modifications." In Small Systems Water Treatment Technologies: State of the Art Workshop*. NEWWA Joint Regional Operations Conference and Exhibition. Marlborough, Massachusetts.

National Research Council. 1997. *Safe Water from Every Tap: Improving Water Services to Small Communities*. Washington, DC: National Academy Press.

U.S. Environmental Protection Agency. 1990. *Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities*. Washington, DC: Office of Water. EPA/625/5-90/025

U.S. Environmental Protection Agency. 1998. *Small System Compliance Technology List for the Surface Water Treatment Rule and Total Coliform Rule*. Washington, DC: Office of Water. EPA/815/R/98/001.

Vigneswaran, S. and C. Visvanathan. 1995. *Water Treatment Processes: Simple Options*.

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APPROACHES FOR SECURING A WATER DISTRIBUTION SYSTEM

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The world focus on water security has been extremely heightened since the attack on the World Trade Center on September 11, 2001. The thinking behind the new focus is in response to terrorist threats on our drinking water and infrastructure in general. This heightened focus is generally a public response—citizens wanting something to be done to make them safer than they are currently. But water related security issues are not new.

INHERENT RISKS

Catastrophic events involving water have been taking place regularly throughout history. On April 1, 1913, hundreds of homes in Portsmouth, Ohio, were washed away when a 69-foot wall of water washed through from a flood on the Great Miami River. More than 120 people were killed, and there was a subsequent smallpox outbreak. On Cape Cod, Massachusetts, treated sewage disposal has formed a contaminated plume of ground water that today is slowly spreading into drinking water wells through the shallow gravel and sand soil composition. Droughts take place on a regular cycle related to various weather systems (1).

The possibilities of things that could go wrong are impossible to list—a fact that points to a reality that has to be faced. There is no way to stop things from happening to your water systems. And though there are a number of things you can do to reduce the risk, the most important step to take is preparing in advance for the time when something does happen.

DRINKING WATER SPECIFICS

Water arrives at the consumer through a network of pipes that ultimately link to the water supply or treatment facility. However, to achieve maximum control over the system, for instance, in case of pipe failures or unusual demand patterns (such as fire flows), water supply networks are generally designed as complicated, looped systems, wherein each individual tap may be capable of receiving water from several sources and intermediate storage facilities. This means that the water from any given tap can arrive through several different routes and can be a mixture of water from several sources. The routes and sources for a given tap can vary over time, depending on the pattern of water use (2).

The Association of State Drinking Water Administrators devised a security vulnerability checklist for a water distributor to use as a guideline for security (3). It includes a list of critical components, such as shown in (Fig. 1): ground water, surface water, purchased water, buildings, pumps, treatment equipment and supplies, laboratories, chemicals, storage tanks, power supplies, auxiliary power supplies, pipes, valves, buildings, computers, files, work vehicles, telephones, and dispatch radios.

Citizens have always been concerned about who is watching the water and how and when they would be told if something went wrong. In 1993, there was a an outbreak of *Cryptosporidium*—an intestinal protozoan—that infested the Milwaukee water supply and sickened more than 400,000 people (4). The cause of the infestation was not determined, but it is thought that it related to storm water runoff across pasture land that fed cattle—known for carrying this protozoan. *Giardia* is another germ that can often be found in the water supply.

Except for freak accidents or intentional attacks on the system, U.S. drinking water is thoroughly tested and is safe to drink. The maximum contaminant levels are frequently tested on a prescribed schedule, and it is treated with chlorine and chloramines to kill germs. Of course, people not on the public water supply need to take steps on their own to ensure that there are no contaminants. There are many countries that do not treat water or test it—and in those countries, the risk of serious disease is much higher.

The Danish government hired the Danish Hydraulic Institute (DHI) to secure the water system for their country. The end result of that study, again, was that it cannot be done (Fig. 2). So steps were then taken to prepare responses in case of accidental or intentional contamination. One of the methods being used there is called Artificial Recharge Technology—a mixing of water sources to dilute the supply, so that it can be flushed to reduce contaminants quickly and eventually to remove them (5).

GOVERNMENT ACTIONS

The states have had money available for loan for many years through the EPA Superfund. This is a loan that has to be paid back over 20 years. This money can be used for fencing, cameras, and other physical security and also for software models and other emergency action planning tools. By the year 2004, all water distribution utilities serving approximately 3000 customers or more

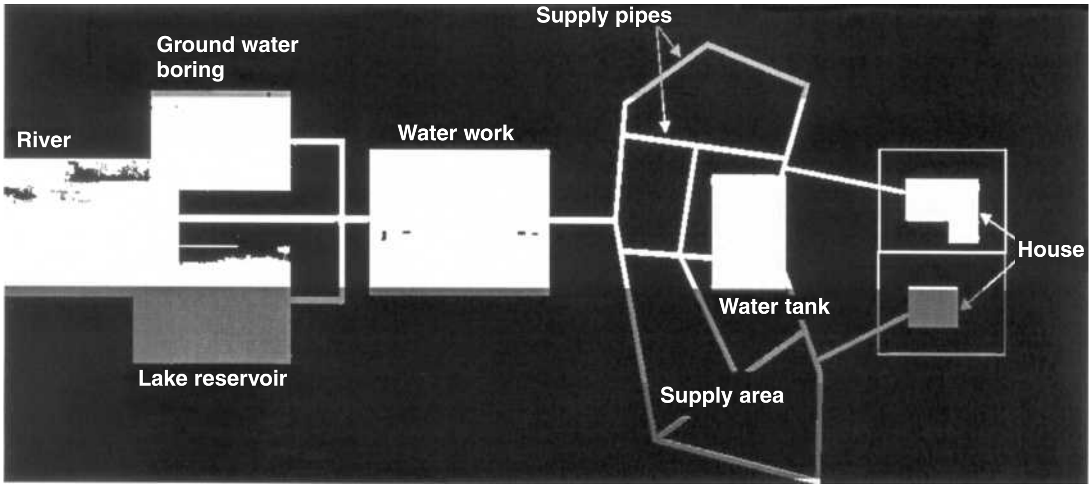

Figure 1. Components of a water system.

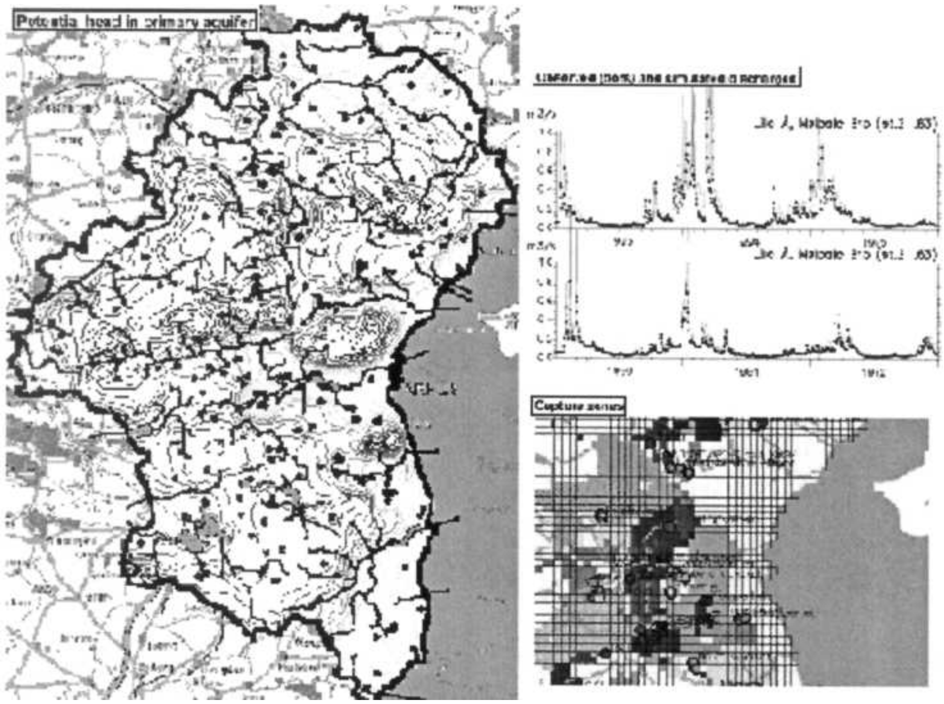

Figure 2. Aarhus, Denmark, water supply system data as seen in the emergency response planning software screen.

will be required to have written emergency action plans filed with the government.

These formal requirements for water utilities will be followed by formal requirements for wastewater utilities, and voluntary compliance by the wastewater utilities is expected to take place prior to formal implementation. In response to the need to establish these documents, many organizations have created written guidelines, as well as various training schemes. Sandia National Labs has been designated as the official resource for vulnerability assessment training (6). Many other private firms have been trained by Sandia to train others to perform these assessments.

Water security issues were addressed formally during the Clinton administration as just one part of a needed focus on all our infrastructure systems. In the White Paper printed by the U.S. Department of Justice, the Presidential directive states, "Critical infrastructures are those physical and cyber-based systems essential to the minimum operations of the economy and government ... these infrastructures have become increasingly automated and interlinked. These same advances have created new vulnerabilities to equipment failures, human error, weather and other natural causes, and physical and cyber attacks. Addressing these vulnerabilities will necessarily require flexible, evolutionary approaches that span both the public and private sectors, and protect both domestic and international security. . .non-traditional attacks on our infrastructure and information systems may be capable of significantly harming both our military power and our economy" (7). Even in this document written in 1998, our government was requiring emergency action plans.

The Environmental Protection Agency (EPA) is, today, setting up the training, the grants, and the documentation for water agencies to meet their required vulnerability assessments and emergency action plans (8). Every water and wastewater agency is coming out with its own version of training aid documents, and commercial software packages are available from many companies to facilitate the planning process (Fig. 3). At least one commercial company, DHI, offers additional discounts to government buyers to hold down the cost of this compliance (www.dhigroup.com). There is also freeware available from the U.S. government. So lack of tools is not an issue for suppliers to prepare themselves.

TAKING ACTION

Whether it is a terrorist threat, flood, drought, earthquake, hurricane, or other natural catastrophe, there are logical steps to take to reduce the risk in any situation:

1. Identify the resources at risk and label them.
2. Determine who is responsible as a caretaker of each resource—and make sure they know it.
3. Measure the degree of risk.
4. Monitor the condition of the resource frequently.
5. Develop contingency plans.

First determine the water resources in your realm that are susceptible to loss or destruction—water supply, bridges, or treatment plants. Make an inclusive list. Figure 1 shows all the components of a water supply system—it is more than the waterworks plant. Be sure that the surrounding community is aware of the resources—posting signage, for example, that a water supply is not for dumping, and other things that might seem obvious to some are not so obvious to others. We are all caretakers of our environment. Many catastrophic events can be avoided simply by educating those who are in the area about proper care of their resources. Running out of water is a very scary possibility, and the public should be informed and trained in water conservation tactics—especially in time of droughts.

Second, identify the responsible person for each item you listed—it could be an organization, individual, or a department. Ensure that they know the full scope of their responsibility. They may know they are responsible, say, for water distribution—but have they been acknowledged as responsible for safety for that system? Ensure that they have been empowered to take needed steps to secure it. These are organizational issues generally that have to be met by some level of municipal government. The responsible parties must have the proper authority for exercising their duty.

Third, the responsible authority should measure the resource. They should get a firm grasp of the magnitude of their responsibility—both the physical size and the number of people involved. They need to know what condition it is in today. If steps can be taken to make them less vulnerable, they should be taken. It is impossible to improve the condition of anything if you do not know what condition it is in now. Measure it, and determine what shape it should be in to satisfy the community it serves (Fig. 4). Then take steps to get it in shape.

Fourth, monitoring the current condition can vary greatly depending on the vulnerability of the resource. If it is a condition that can be watched, then someone should be checking the vulnerability or watching for safety reasons. For instance, water quality samplers can be installed to check, at any interval desired, the condition of any water supply. Simple fences can keep out unwanted visitors. Periodic inspections to keep things at optimum condition are easily performed.

Fifth, contingency planning is multiphased. It should be determined if there are adequate resources, in the way of tools and manpower, to manage the system in the event of a catastrophe. Contingency plans should exist

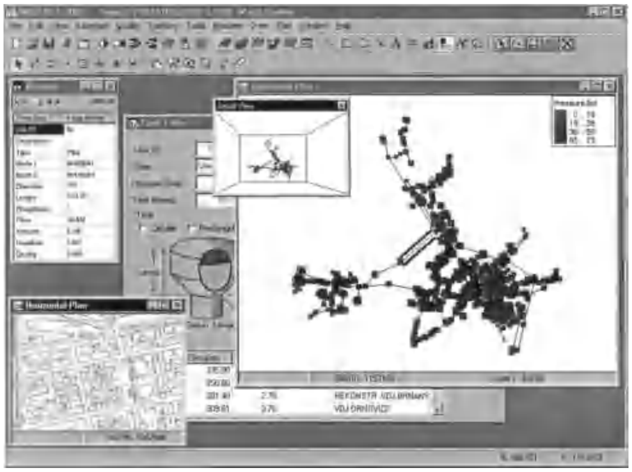

Figure 3. Use of a commercial software package to prepare action plans.

Figure 4. Monitoring the data from a storm drain flow monitor.

that can be readily executed. Authorities should know of the contingency plans—how to locate them and how to execute them. Models can be developed of water supplies and wastewater collection systems that can then be used to show a multitude of “what if” scenarios. For water distribution systems, the use of a model is key to creating proper emergency response plans.

The American Water Works Association published the Manual of Water Supply Practices M19, which includes the section “Emergency Planning for Water Utility Management” (9). In chapter 5 of this document, it states that the basic principles of an emergency action plan are that it should “(1) use or reference existing resources, (2) be concise and logical, and (3) be coordinated with other agencies.” There is a great push to implement SCADA (supervisory control and data acquisition) systems to watch the operation of a water system in real time—even monitoring the water quality, so it is important that these automated systems have built into them the ability to notify officials in case of sudden change and emergency. Many systems simply monitor and react without human notification. For introduction of toxins and protection of public health and safety, this would not be acceptable to the public, nor should it be.

In summary, I quote the AWWA from the *Security Analysis & Response for Water Utilities*: “A completed security assessment and response plan is useful only if the utility staff and supporting agencies maintain continued vigilance” (10). Ongoing training of staff, ongoing review of the emergency system, along with periodic drills of implementation of emergency actions are vital to successful performance of any emergency action planning.

BIBLIOGRAPHY

1. Hosner, M. (2002). Five steps to risk reduction. *Water 21 Mag.* 54–55.
2. Hosner, M. (2002). Use of a computer model to help secure a water system in Denmark. *cover, EH&S Software News Online* **XI**(5).
3. *Association of State Drinking Water Administrators, National Rural Water Association, “Security Vulnerability Self-Assessment Guide for Small Drinking Water Systems”*, May 30 2002.
4. Symons, J. M. (2001). *Plain Talk About Drinking Water*, 4th Edn. American Water Works Association, pp. 5, 25.
5. Brun, A. (2000). Artificial recharge technologies. *Programme for Part A: Environment and Sustainable Development*, Official Journal of the European Communities **C(2000)3118**.
6. AWWA. Mainstream—*AWWA seeks $2.5 million from Congress for security training*. September/October 2002, p. 5.
7. US Department of Justice *www.usdoj.gov/criminal/cybercrime/white_pr.htm*, White Paper, “The Clinton Administration’s Policy on Critical Infrastructure Protection: Presidential Decision Directive 63,” May 22, 1998.
8. US Environmental Protection Agency, *www.epa.gove/safewater/security*, “What is being done to protect the nation’s water infrastructure?”
9. AWWA. (2001). *Emergency Planning for Water Utilities, a manual of water supply practices, M19*, 4th Edn.
10. AWWA. (2001). *Security Analysis & Response for Water Utilities*. p. iii.

WATER SECURITY: AN EMERGING ISSUE

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One of the most pressing global issues is the increase in world population and its impact on the availability of freshwater. Freshwater is generated, transported, and stored within confined river basins. In 1992, the Dublin conference, Assessment, CFWA, was considered, where water was regarded as an economic good, and in 1994, the United Nations Commission for Sustainable Development proposed that a comprehensive assessment of the freshwater resources of the world should be undertaken (1). Climate change adds further risks and uncertainties to the global picture, requiring adaptive management in water resources based on monitoring and re-evaluation (2). A global-scale assessment of water resources and their use was performed in the framework of the 1997 United Nations Comprehensive Assessment of the Freshwater Resources of the World (3). Since 1970, global water demand has risen at an estimated rate of 2.4% per annum, with much higher trends in developing countries because of increasing urbanization and water-intensive agricultural activities (4). Developing countries are home to the overwhelming proportion of the world’s 2.6 billion people without access to clean water, a figure that is expected to significantly increase in the next decades (5). The relationships between water quantity and environment have been overlooked in the past. A need exists for a new dimension of the impending water crisis (6). For example, in India, it is expected that severe water crises will occur by the year 2025 (7).

MODELS FOR PREDICTION OF GLOBAL WATER AVAILABILITY

Identification of the links between rapidly growing populations and shrinking freshwater supplies is the essential first step in making water use sustainable. Various models are proposed for prediction of water usage based on climate data. Even water security has been correlated with food security by modeling (8). Yates (9) presented an integrated assessment model for continental scale runoffs where the limiting data for the spatial and temporal variability of freshwater resources is the constraint. An analysis of Western Europe’s and Africa’s freshwater runoff, which spans a range of climate variability, was performed at varying levels of spatial aggregation and at both monthly and annual time steps. Model results showed that regional runoff characteristics were lost beyond a data aggregation of $1^\circ \times 1^\circ$ resolution. A macroscale hydrological model, designed to simulate stream flow from climatic inputs over a large geographic domain, has been proposed by Arnell (10). In the case of

Hydrological Model of WaterGAP 2 (WGHM), the model tuning has aimed at achieving a good representation of the long-term average discharges (11). It has a strong positive effect on the performance of all proposed water availability indicators.

WATER SOURCE AND RESOURCES

The prevention of water contamination is always a preferable scenario instead of attempting to remove contaminants once they have entered the aquatic environment. Although it is likely that some contamination events will always occur, a large proportion of water resources can be secured through protection and good water resource management; efficient design, operation, and management of water supplies; and regular and thorough surveillance activities. Water source protection is a mixture of case-specific measures of a particular area to protect individual sources. It also involves wider ranging measures, which are designed to protect the larger water resource bodies on a provincial, national, or regional (international) basis, which always requires guidelines such as state-level or provincial-level guidelines up to international treaties to ensure sustainable management of resources. Surface water sources and resources are far more open to contamination, and potential sources for contamination are generally far larger than for groundwater. Thus, any measures taken to protect surface water resources will generally encompass a far wider geographical region than measures designed to protect groundwater resources. At a global level, the advanced scientific methods, such as GIS applications and remote sensing techniques, quantify the existing water resources and help in formulating a sustainable management scheme by considering both water uses and environmental protection (12). Groundwater is an important source of drinking water. In its natural state, groundwater is generally of high microbiological quality with little or no contamination. The relative purity of groundwater in its natural state is largely a result of infiltration through the soil and unsaturated layers of rock, although some groundwaters do have high levels of harmful chemicals, such as fluoride and arsenic (7).

THREATS TO WATER RESOURCES

The water resources can be at threat because of natural geological disturbances or anthropological activities, which are making water unsafe for human consumption. Various anthropogenic activities exist that are making water resources unsafe, such as selenium pollution, which is a globally identified phenomenon and is associated with the most basic agricultural practices to the most high-tech industrial processes (13).

The prevention of contamination of groundwaters by persistent mobile contaminants is an essential element in the protection of groundwater resources. Generally, where aquifers are overlain by a substantial unsaturated zone and have high primary porosity and reasonable permeability, they tend to be less vulnerable to pollution. In industrial cities, initial development led to a decrease in the groundwater levels and subsequent accumulation of contaminants in the unsaturated zone. However, further developmental activities that have occurred there, or maybe elsewhere using different water sources, sometimes leads to a recovery of groundwater levels owing to desorption of contaminants and groundwater pollution, which has led the concept of “Groundwater Protection Zones” where acceptable land uses are defined in order to protect the underlying groundwater. Many factors exist that influence the shape of the zone: the nature of the aquifer (which are very rarely isotropic); the number of rivers in the zone; the condition of rivers (whether influent, effluent, perched, or changing); and the number and location of other abstraction points within the zone. The more rivers associated with the aquifer, the greater the distortion and extension of the zone.

In general, water can become contaminated at the original water source, during treatment, in the pipes that distribute water from a treatment facility to homes and businesses, or in containers. Surface water (rivers or lakes) can be exposed to acid rain, storm water runoff, sewage overflow, pesticide runoff, and industrial waste. This water is cleansed somewhat by exposure to sunlight, aeration, and micro-organisms in the water. Groundwater (aquifer) generally takes longer to become contaminated, but the natural cleansing process also may take much longer because it moves slowly and is not exposed to sunlight, aeration, or aerobic (requiring oxygen) micro-organisms. Groundwater can be contaminated by disease-producing pathogens, leachate from landfills and septic systems, careless disposal of hazardous household products, agricultural chemicals (fertilizers, pesticides, herbicides), industrial chemicals, and leaking underground storage tanks. Water distribution systems contain living micro-organisms and nutrients that enter a system with raw water during water treatment failures or from leaks, cross-connections, and back-flows. Bacterial growth may also occur at or near the pipe surfaces (biofilms), the interface with suspended particulates, and within the water itself. Besides microbes, other contaminates occurring in drinking water can include: (a) organics (trihalomethanes and other disinfection byproducts), which are formed when chlorine and other water disinfectants combine with naturally occurring organic matter; pesticides, including herbicides, insecticides, and fungicides; and volatile organic chemicals; and (b) inorganics (arsenic, barium, chromium, lead, mercury, and silver). The Centre for Science and Environment, New Delhi, India, has also expressed concern over the contamination of pesticides in bottled water.

WATER SECURITY AND ITS RELATION TO FOOD SECURITY AND AGRICULTURE

The International Food Policy Research Institute has developed a 2020 Vision of *a world where every person has economic and physical access to sufficient food to sustain a healthy and productive life, where malnutrition is absent, and where food originates from efficient, effective, and low-cost food and agricultural systems that are compatible with* *sustainable use and management of natural resources*. The major challenges observed to this Vision 2020 are ignorance to water security (14). The Indian national consultation program (15) also projected the World Water vision for the year 2025. Projections for world agriculture in the first half of the twenty-first century vary widely, largely depending on assumptions of yield growth. The pattern of yield growth for major crops is logistic, and not exponential. This pattern is consistent with ecological limits on soil fertility, water availability, and nutrient uptake (16).

Agriculture demands more water than any other activity. Although the total amounts of water made available by the hydrologic cycle provide enough freshwater for the world's current population, most of this water is concentrated in specific regions, leaving other areas water deficient. Therefore, the "Virtual water" concept has been introduced for water-short countries in recent years. These countries can minimize their use of water and achieve food security at the same time by importing a portion of their food requirements from other areas or countries where water resources are adequate and available at a lower cost (17). Similarly, a Water Poverty Index has been proposed, which integrates water stress and scarcity and physical estimates of water availability with socioeconomic variables (18). The effect of usage of virtual water has been analyzed nicely in a case study where, by taking six southern Mediterranean countries, the water-food challenges facing water-scarce countries and the implications for the world food economy have been discussed. By accounting for the volume of virtual water embedded in food imports into the countries concerned, a close relationship between water endowment and food import dependence has been elaborated. The results of this case study highlight that food imports are imperative for compensating water resource deficiency and that water scarcity-related food imports will continue to have an impact on food economy (19).

Globally, water is likely to become an increasingly critical resource issue in the developing world. In the coming time, the forces of globalization with technological revolution will influence the trans-boundary management of water as equity. The world is moving into a new kind of economy as well as into a new kind of society, where we need new mindsets and knowledge to resolve increasingly complex and interrelated continental issues. The water sector is no exception to this development.

BIBLIOGRAPHY

1. Björklund, G. and Kuylenstierna, J. (1998). The comprehensive freshwater assessment and how it relates to water policy world wide. *Water Policy* **1**: 267–282.
2. Sophocleous, M. (2004). Global and regional water availability and demand: Prospects for the future. *Natural Resources Res.* **13**: 61–75.
3. Raskin, P., Gleick, P., Kirshen, P., Pontius, G., and Strzepek, K. (1997). Water futures: Assessment of long-range patterns and problems, *Comprehensive Assessment of the Freshwater Resources of the World*. Stockholm Environment Institute, Stockholm, Sweden.
4. Clarke, R. (1993). *Water: The International Crisis*. MIT Press, Cambridge, MA.
5. Jong-Wook, L. and Bellamy, C. (2004). In: *WHO/UNICEF Joint Monitoring Program for Water Supply and Sanitation Report*.
6. Lundqvist, J. (2000). Physics and chemistry of the earth, Part B. *Hydrol. Oceans Atmosphere* **25**: 259–264.
7. Gordon, B., Mackay, R., and Rehfuess, E. (2004). *Inheriting the World: The Atlas of Children's Health and the Environment* WHO.
8. Kamara, A. and Sally, H. (2003). Water for food, livelihoods and nature: Simulations for policy dialogue in South Africa. *Phys Chem Earth, Parts A/B/C* **28**: 1085–1094.
9. Yates, D.N. (1997). Approaches to continental scale runoff for integrated assessment models. *J. Hydrol.* **291**: 289–310.
10. Arnell, N.W. (1999). A simple water balance model for the simulation of streamflow over a large geographic domain *J. Hydrol.* **217**: 314–335.
11. Döll, P., Kaspar, F., and Lehner, B. (2003). A global hydrological model for deriving water availability indicators: Model tuning and validation. *J. Hydrol.* **270**: 105–134.
12. Zacharias, I., Dimitriou, E., and Koussouris, T. (2003). Developing sustainable water management scenarios by using thorough hydrologic analysis and environmental criteria. *J. Environ. Manage.* **69**: 401–412.
13. Lemly, A.D. (2004). Aquatic selenium pollution is a global environmental safety issue. *Ecotoxicol. Environ. Safety* **59**: 44–56.
14. Pinstrup-Andersen, P. and Pandya-Lorch, R. (1998). Food security and sustainable use of natural resources: A 2020 Vision. *Ecologic Econom.* **26**: 1–10.
15. ICID. (2003). *Indian National Consultation Program of International Commission on Irrigation and Drainage and Country Policy Support Program Report*. Nov. 21–22, New Delhi, India.
16. Harris, J.M. and Kennedy, S. (1999). Carrying capacity in agriculture: global and regional issues. *Ecologic Econom.* **29**: 443–461.
17. Allan, J.A. (1998). Virtual water: a strategic resource, global solutions to regional deficits. *Ground Water* **36**: 545–546.
18. Sullivan, C. (2002). Calculating a water poverty index. *World Develop.* **30**: 1195–1210.
19. Yang, H. and Zehnder, A.J.B. (2002). Water scarcity and food import: a case study for southern mediterranean countries. *World Develop.* **30**: 1413–1430.

READING LIST

Rosegrant, M.W. and Perez, N.D. (1995). *Water Resources Development in Africa: A Review and Syntheses of Issues, Potentials and Strategies for the Future*. International Food Policy Research Institute (IFPRI), Washington, DC.

GUIDE TO SELECTION OF WATER TREATMENT PROCESSES

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Selecting the appropriate treatment process is a critical step in providing safe, reliable, good quality drinking water at a cost-effective price.

This article provides guidance in selecting appropriate treatment processes taking into account raw water quality and costs.

RAW WATER QUALITY AND TESTING

There is a need for raw water quality data covering an extended period sufficient to show seasonal and extreme events to make a sound decision on appropriate treatment processes.

Ideally, the parameters listed in Table 1 should have data collected as set out.

In practice, the extent of data set out in Table 1 is rarely available. In these cases, immediate intensive periods of testing are essential to develop as much understanding of the raw water characteristics as possible in advance of selecting treatment processes. Adjacent similar water sources are possible sources of indicative data. In addition, risk assessment techniques can identify potential hazard parameters even where sampling data are limited. For some possible contaminants, it is appropriate to assess risk rather than sampling because measurements may not be representative. This approach involves examining possible sources of contaminants in the catchment and then calculating the risk or approximate concentration that might occur in the raw water.

Before any process is finally selected, it is important to carry out treatability testing on the actual source water. All waters have subtle differences, and these can have a significant effect on process selection and performance. As a minimum, coagulation jar tests should be performed.

Testing is particularly important for correct sizing and cost analysis of competing options to take account of actual conditions. For example the amount of coagulant and other chemical usage can have a significant influence on the cost-effectiveness of a coagulant-based conventional process versus, say, microfiltration. Conversely, although it can be assumed that microfiltration achieves excellent particle and protozoa removal reliably, its performance in terms of fouling and sustainable flux rate can only be determined realistically by pilot testing the water to be treated. Pilot testing is always recommended, if feasible, particularly for large projects.

THE BENCHMARK PROCESS

To allow comparison between process options, particularly on a cost basis, it is appropriate to define a "benchmark" process.

The benchmark process is based on the most commonly used treatment configuration in the world, coagulation/clarification/granular media filtration.

A typical process flow schematic is shown in Fig. 1.

Within the benchmark, there can also be considerable variation between clarifier and filtration types. An indication of types of clarifier available and their basic characteristics are set out in Table 2.

Modern granular media filters typically operate at 10 to 15 m/h in postclarifier configurations, although there are examples of deep-bed higher rated filters operating under suitable conditions. There is a wide variation in granular media filter designs. Table 3 sets out some examples at both ends of the spectrum.

Table 1. Minimum Sampling Regime for Raw Water

Surface Water	Groundwater (Not Significantly Influenced by Surface Water)
Initially and then annually • Complete scan of WQ parameters. From this, additional parameters may be added or removed from the weekly/monthly testing regime. *Weekly* • Turbidity • True colour • Alkalinity • pH (at sample point) • Temperature (at sample point) • Conductivity *Monthly* • *Cryptosporidium* / *Giardia* • Total coliforms • *E.coli* • Iron • Manganese • DOC • Calcium (component of hardness) • Magnesium (component of hardness) *Special* • Short-term intensive testing of certain 'suspect' parameters depending on circumstances for example hourly measurement of turbidity on flashy river; pesticides or C*ryptosporidium* after storm;	*Initially and then annually* • Complete scan of WQ parameters. From this, additional parameters may be added or removed from the monthly/quarterly testing regime. *Monthly* • Turbidity • pH (at sample point) • Calcium (component of hardness) • Magnesium (component of hardness) • Iron • Alkalinity • Temperature (at sample point) • Conductivity *Quarterly* • True color • Manganese • Total coliforms (monthly if detected) • *E.coli* (monthly if detected) *Potential Concerns* • Parameters sometimes found in groundwaters include — Nitrate — Radionuclides — Hydrogen sulfide — Arsenic — Other suspect parameters, for example, pesticides

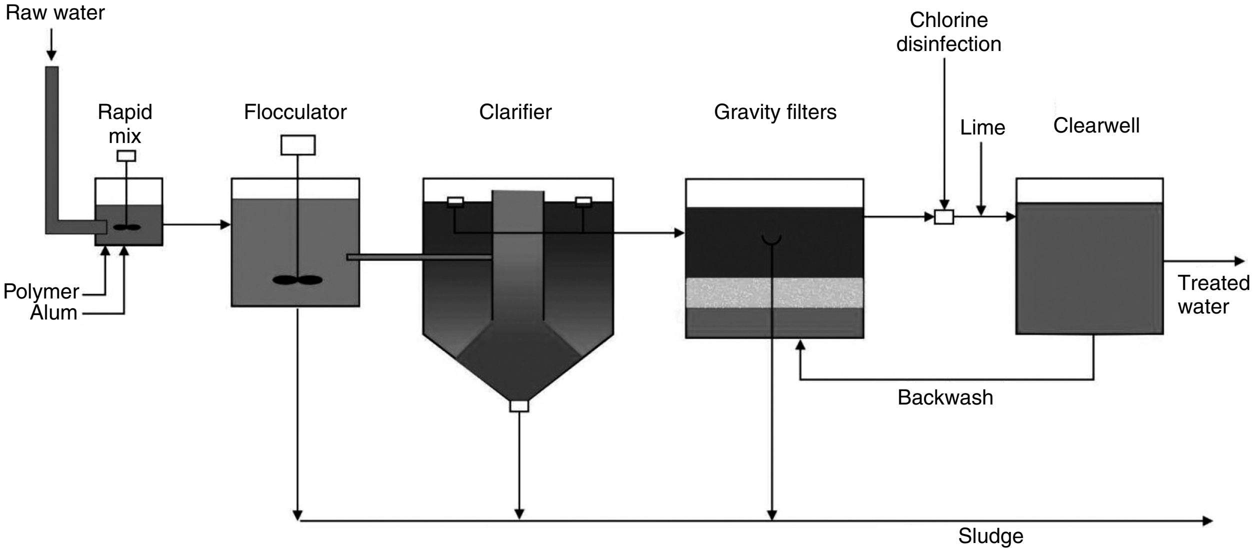

Figure 1. The “Benchmark” process.

Table 2. Clarifier Options in “Benchmark” Process

Clarifier Type	Typical Loading Rate m/hr	Minimum Flocculation		Comment
Horizontal flow sedimentation	1.5	2 stage, 15 minutes	}	Sedimentation particularly suited to waters with high solids load
Radial flow sedimentation	1.5	2 stage, 15 minutes	}	
Sludge blanket clarifier	2.5	NA	}	
Sludge recirculation contact clarifier	3.0	15 minutes	}	
Pulsation type	3.0	NA	}	
Dissolved air flotation (DAF)	10	2 stages, 10 minutes		• Suited to colored, algal-laden, impounded raw water • Can be located in-filter
Tube settler	5	2 stages, 15 minutes		Loading rate depends on spacing and depth of tubes. Often retrofitted to increase plant capacity
Ballasted sand	30	1 stage, 10 minutes		Proprietary process
Sirofloc	10	2 stages, 10 minutes		Proprietary process

Table 3. Granular Media Filter Arrangements

Media	Typical Grading and Depth	Typical Loading Rate	Comment
Monomedia (sand)	600 mm of 0.6 m effective size	6 m/h	Typical old style rapid gravity filter designs
Monomedia (sand or anthracite)	2000 mm of 2 mm effective size	Up to 24 m/h	e.g., 3000 ML/day direct filtration plant at Prospect, Sydney, Australia
Dual media (typically anthracite/sand)	1500 mm of 1.5 mm anthracite on 300 mm of 0.8 mm sand	12–18 m/h	Also used in direct filtration configuration (i.e., no preclarification)
Dual media (typically anthracite/sand)	Wide range of anthracite sand combinations are in use	8–14 m/h	Finer grading used in postclarifier configurations

GUIDE TO PROCESS SELECTION

Table 4 provides a summary guide to selecting the most applicable treatment process, given particular water quality problems. The parameters covered focus on challenges that occur in raw waters. They do not include parameters that are created through treatment and distribution. Therefore, parameters such as disinfection by-products like trihalomethanes (THMs), lead (usually a corrosion product), and soluble aluminum (usually a residual of alum coagulation) are not included.

Table 4 focuses on primary treatment needs and does not consider residual disinfection requirements.

The “primary process candidates” focus on processes that can cost-effectively provide very good removal efficiency of the parameter in question, so that water

Table 4. Water Treatment Process Selection Guide

Water Quality Parameter	Primary Process Candidates	Relative Cost	Comments	Other Process Candidates
		Biological		
Bacteria	Chemical disinfection	0.1	Chlorine, chlorine dioxide, chloramine, and ozone are the main disinfectants. Cost is based on chlorine.	
	Ultraviolet disinfection	0.2	Good pretreatment often required.	
	Microfiltration	1.3		
Virus	Chemical disinfection	0.1		Reverse osmosis
	Ultraviolet disinfection	0.2	Some viruses can be relatively resistant	
Giardia	Benchmark	1.0	Filtered water turbidity of better than 0.3 NTU and preferably 0.1 NTU is required.	Reverse osmosis
	Chemical	0.1	Most practical choices are chlorine, chlorine dioxide, and ozone. Cost is based on chlorine.	
	Ultraviolet disinfection	0.2	Good pretreatment often required.	
	Microfiltration	1.3		
Cryptosporidium	Benchmark	1.0	Filtered water turbidity of better than 0.3 NTU and preferably 0.1 NTU is required.	Reverse osmosis
	Ultraviolet disinfection	0.2	Good pretreatment often required.	
	Microfiltration	1.3		
Algae	Benchmark	1.0	High algae levels needs a suitable clarifier process, e.g., DAF. See “Organics” for algal taste, odor and toxins.	
		Aesthetics		
Turbidity	Benchmark	1.0		Reverse osmosis
	Microfiltration	1.3		
Color	Benchmark	1.0		
	Ozonation	0.5	Practical limit to color removable	
	Nanofiltration	2.0	Pretreatment required	
Hardness	Lime softening	1.2		
	Ion exchange (cation)	0.7	Need also to consider pretreatment requirements, if any	
	Nanofiltration	2.0	Pretreatment required	
Iron	Benchmark	1.0		Lime softening
	Oxidation/filtration	0.8		Activated alumina
Manganese	Oxidation/benchmark	1.1	Potassium permanganate commonly used	Lime softening
	Catalytic filtration	0.8	Chlorination ahead of Mn-coated filter media	
	Benchmark/high pH	1.1	Coagulation at high pH	
Hydrogen sulfide	Aeration	0.3		
		Organics		
DOC	Benchmark	1.0		
	Ion exchange (anion)	0.9		
	Nanofiltration	2.0		
Algal tastes & odors	Granular activated carbon	0.6—1.0	Cost depends on bed life; bed life uncertain: testing required	
	Powdered activated carbon	0.2—0.4	Cost depends on dose and period of use	
	Ozonation	0.5	Sometimes used in conjunction with hydrogen peroxide	
Algal toxins	Chlorination	0.1	Effective on many hepatotoxins	Nanofiltration
	Ozonation	0.5	Sometimes used in conjunction with hydrogen peroxide	

(*continued overleaf*)

Table 4. (*Continued*)

Water Quality Parameter	Primary Process Candidates	Relative Cost	Comments	Other Process Candidates
	Ozone/biological activated carbon	1.0		
	Granular activated carbon	0.6—1.0	Bed life uncertain; testing required	
	Powdered activated carbon	0.2—0.4	Dose setting can be difficult	
Pesticides	Ozonation	0.5	Sometimes used in conjunction with hydrogen peroxide	Reverse osmosis
	Ozone/biological activated carbon	1.0		
	Granular activated carbon	0.5—2	Bed life uncertain	
	Powdered activated carbon	0.2—0.5	Dose setting can be difficult	
Organic chemicals generally	Aeration	0.3—1	Only for highly volatile compounds	
	Granular activated carbon	0.5—2	Cost highly sensitive to bed life; testing required	
Inorganics				
Antimony	Benchmark	1.0		Reverse osmosis
Arsenic	Oxidation & benchmark	1.1		
	Oxidation & lime softening	1.3		
	Activated alumina	0.9		
	Ion exchange (anion)	0.9		
Barium	Lime softening	1.2		Reverse osmosis
	Ion exchange (cation)	0.7		
Beryllium	Benchmark	1.0		Reverse osmosis
	Lime softening	1.2		
	Activated alumina	0.9		
Boron	Ion exchange (anion)	0.9		
	Reverse osmosis	2.5		
Cadmium	Benchmark	1.1	Ferric coagulation at high pH	Reverse osmosis
	Lime softening	1.2		
Chromium (III)	Benchmark	1.0		
	Lime softening	1.2		
	Ion exchange (cation)	0.9	Anion for Cr(VI)	
	Reverse osmosis	2.5	OK for Cr(VI)	
Cyanide	Oxidation and benchmark	1.1		Reverse osmosis
Fluoride	Activated alumina	0.9		
	Reverse osmosis	2.5		
Mercury (inorganic)	Benchmark	1.0	Ferric coagulant preferred	Reverse osmosis
	Granular activated carbon	0.5—1.0	Cost depends on bed life	
	Lime softening	1.2		
Nitrate	Ion exchange (anion)	0.9		
	Reverse osmosis	2.5		
Sulfate	Ion exchange (anion)	0.9		
	Reverse osmosis	2.5		
Selenium	Ion exchange (anion)	0.9		Reverse osmosis
	Activated alumina	0.9		
Silver	Benchmark	1.0		
	Lime softening	1.2		
TDS	Reverse osmosis	2.5	Brackish water	
	Electrodialysis	3.0		
	Distillation	5.0	Very dependent on energy cost	
Radiological				
Uranium	Benchmark	1.0	Waste disposal is an issue	
	Lime softening	1.2	Waste disposal is an issue	
	Ion exchange (cation)	0.9	Waste disposal is an issue	
Radon	Aeration	0.3		
	Granular activated carbon	0.5—1.0	Depends on bed life	
Radium	Lime softening	1.2	Waste disposal is an issue	
	Ion exchange (cation)	0.9	Waste disposal is an issue	
	Reverse osmosis	2.5	Waste disposal is an issue	

quality objectives can be met. Processes that provide only limited removal are generally not listed. The focus is also on the most readily available technologies.

The "relative cost" column indicates life-cycle cost in comparison with the "benchmark" treatment process. The cost relativity is indicative only and depends on plant scale, the site and local conditions, and costs. "Other process candidates" list potential processes which would not normally be selected for the water quality parameter in question but are listed to provide guidance if that particular process is also a good primary candidate for another water quality parameter of concern.

As a reference, the expected range of life-cycle cost for the benchmark process in developed countries is of the order of US$0.15 to US$0.40 per kL (2003); the variation depends mainly on scale—the larger scale plant has lower unit costs.

Examples of Application

Example 1: Braided River from Farming Catchment and High Base Flow. A source water drawn from a braided river suffers from elevated turbidity after storms and is suspected of *Cryptosporidium/Giardia* and bacteria/contamination from farming in the catchment.

From Table 4, microfiltration is suitable for all identified contaminants, as is the combination of the benchmark process plus disinfection (either chemical or UV). From this, the prime process candidates are therefore

- benchmark plus disinfection
- microfiltration

Example 2: Highly Turbid Tropical River in Unprotected Catchment. In this case, the water quality parameters of concern and corresponding process selections are

Cryptosporidium: benchmark, UV, MF
Turbidity: benchmark, MF
Color: benchmark, ozonation
Virus: disinfection, UV
Bacteria: disinfection, UV, MF
Iron: benchmark, oxidation/filtration.

Looking at these technology selections suggests selecting the benchmark process plus disinfection would most cost-effectively deal with all of the parameters of concern.

Example 3: Algal-Prone Surface Water Reservoir from a Compromised Catchment. In this case, the parameters of concern are turbidity, algae, DOC, color, *Cryptosporidium*, bacteria, virus, iron, manganese, taste and odor, and toxins.

Using the same procedure as previously highlights the potential to select a process train consisting of the benchmark process plus ozone/BAC.

Example 4: Groundwater. This groundwater has problems of elevated arsenic, iron, and manganese. From Table 4, the benchmark process with oxidation would be an appropriate selection.

Testing the most likely process selections obtained through the guidance process is always important to confirm achievable performance and likely actual costs. In evaluating the final short list of process options, factors like local skills, cost and availability of materials, level of support services, and waste management constraints, need to be taken into account.

READING LIST

EPA. (1990). *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Plants*. Office of Drinking Water, USEPA, Cincinnati, OH.

AWWA. (1994) *Water Quality and Treatment*, 4th Edn. McGraw-Hill, New York.

www.epa.gov

www.usbr.gov

Department of Natural Resources & Environment. (1997). *Low Cost Water Treatment for Small Towns*. Report No. WQ97.001. Melbourne, Australia.

SOURCE WATER ASSESSMENT

U.S. Geological Survey

FREQUENTLY ASKED QUESTIONS

What is a Source Water Assessment?

A source water assessment is a study and report, unique to each water system, that provides basic information about the water used to provide drinking water.

What Will My Assessment Tell Me?

- *Where My Drinking Water Comes From*. Source Water Assessments identify the area of land that most directly contributes the raw water used for drinking water.
- *What Could Pose a Threat to My Drinking Water Quality*. Assessments identify the major potential sources of contamination to drinking water supplies. This information is used to determine how susceptible the water system is to contamination.

Is This Information Available?

The results of an assessment will be provided to the public to help communities plan for protection activities. Information about the assessment will be included in the yearly consumer confidence report you receive from your water utility.

Does My Water System Have a Source Water Assessment?

Every state is moving forward to implement assessments of its public water systems, as required under a new

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federal Safe Drinking Water Act program called the Source Water Assessment Program (SWAP). Assessments must be completed by 2003 for every public water system—for major metropolitan areas and the smallest towns, including schools, restaurants, and other public facilities that have wells or surface water supplies. Assessments will not be conducted for drinking water systems that have less than fifteen service connections or that regularly serve less than twenty-five individuals, since these are not considered public water systems.

Who is Paying for These Assessments?

Source water assessments and protection measures are eligible uses of the Drinking Water State Revolving Fund (DWSRF) set-asides. States may use the funds for a mixture of source water related local assistance activities. For example, funds are available for Land Acquisition and Conservation Easements.

SOURCE WATER ASSESSMENTS

The source water assessment programs created by states differ since they are tailored to each state's water resources and drinking water priorities. However, each assessment must include four major elements:

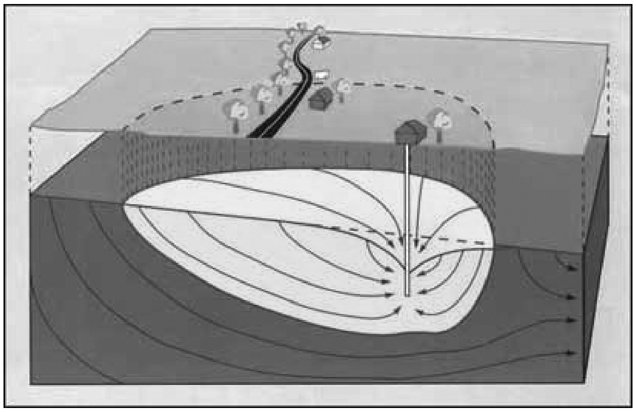
- delineating (or mapping) the source water assessment area,
- conducting an inventory of potential sources of contamination in the delineated area,
- determining the susceptibility of the water supply to those contamination sources, and
- releasing the results of the determinations to the public.

These steps are described in more detail below, with information on how citizens and organizations can join in the assessment process. More information about the SWAP program is available. Our SWAP Contact List has state specific contacts and links to State web sites.

Source Water Assessment Using Geographic Information Systems: This document provides guidance to states, municipalities, and public water utilities for assessing source waters using geographic information system (GIS) technology.

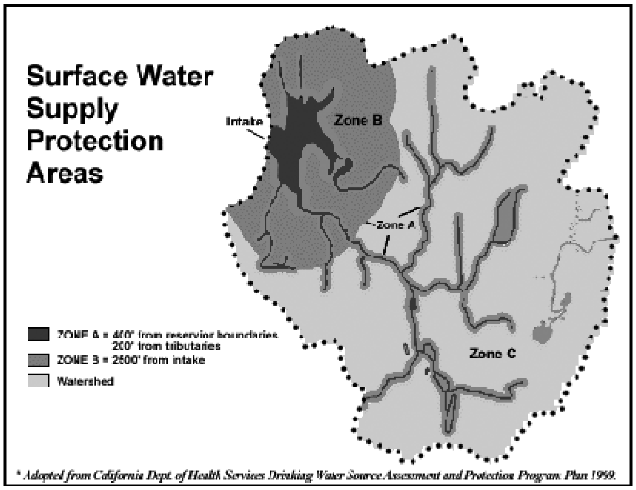
STEP 1: DELINEATE THE SOURCE WATER ASSESSMENT AREA

For each ground water well or surface water intake that supplies public drinking water, the land area that could contribute water and pollutants to the water supply must be delineated, or mapped. Significant potential sources of contamination will then be identified in this delineated area during Step 2 of the assessment process.



For ground water supplies, states commonly use information about the flow of underground water to delineate source water assessment boundaries. This results in a map of land areas where, if pollutants are spilled or discharged on the surface, they could filter through the soil to the ground water and be drawn into a particular well. Some states may use a simpler mapping approach, by drawing a circle of a certain radius around the well.

For a community that uses surface water from a stream, river, lake, or reservoir, the land area in the watershed upstream of the intake is identified on the map. A watershed boundary is drawn using a topographic map, and includes the land areas where rain or melted snow flows over or through the ground and eventually enters the water source upstream of the water system's intake.



* Adopted from California Dept. of Health Services Drinking Water Source Assessment and Protection Program Plan 1999.

Diagram2

Some states plan to divide the watershed area into segments—areas closest to the intake where most types of contamination sources can impact the water supply, and other more distant areas. The entire watershed up to the state's boundaries is required to be delineated, but the inventory of potential pollution sources may be more detailed in segments that are closer to the intake.

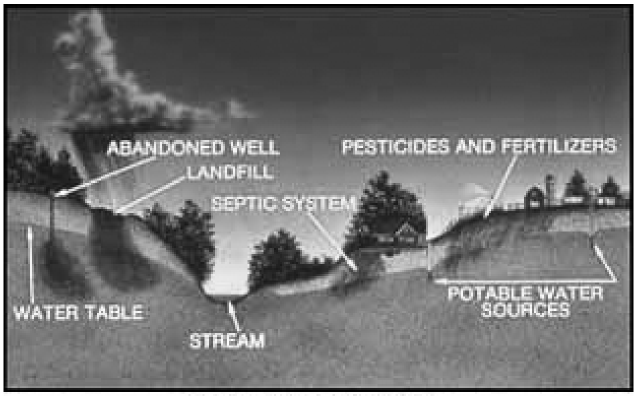
After the state has completed its assessment for a water system, the community may decide to undertake protection efforts for targeted sources of contamination. An initial step could be to expand upon the state's delineation process. Particularly for smaller ground water systems, where states may not have the resources to conduct a detailed delineation, additional scientific methods can be used to more accurately delineate the area that contributes ground water to the well.

Community members can seek assistance from the environmental sciences, geology, or engineering departments of local colleges, or from environmental consulting firms to assist in creating more detailed delineations. Sometimes these services are provided by professors, graduate students, or local firms for a reduced fee or none at all. In addition, local water resource information is often available from other sources such as the federal Natural Resource Conservation Service, the United States Geological Survey, and the state's Cooperative Extension Service.

For more information on delineation see Reliable Sources—Delineation.

STEP 2: CONDUCT AN INVENTORY OF POTENTIAL SOURCES OF CONTAMINATION

Community groups can become especially involved in the second step of an assessment—identifying potential sources of pollutants that could contaminate the water supply. This inventory usually results in a list and a map of facilities and activities within the delineated area that may release contaminants into the ground water supply (for wells) or the watershed of the river or lake (for surface water sources).



Contamination Sources

Some examples of the many different types of potential pollutant sources include landfills, underground or aboveground fuel storage tanks, residential or commercial septic systems, storm water runoff from streets and lawns, farms that apply pesticides and fertilizers, and sludge disposal sites.

Some states are asking communities to conduct the inventory themselves, in order to obtain detailed information about potential contaminant sources. Others will use computer databases and focus the inventory on land uses and activities that are currently mapped or regulated. Although this approach may not address sources of contaminants that are not currently regulated, such as smaller livestock areas or auto salvage yards, the database inventories could include industries and sewage treatment plants that discharge wastewater, hazardous waste sites, mining operations, particular land use categories (such as industrial, agricultural and urban areas), and various facilities that have environmental permits.

Community groups such as watershed organizations, local environmental committees or scout troops can enhance the state's assessment by conducting site-specific inventories of potential pollutant sources that may not be on state databases or maps. Local inventories may provide information on abandoned dump sites, businesses with septic tanks or floor drains such as dry cleaners or car repair shops, pesticide mixing and storage areas, golf courses, and other land uses that may release pollutants to ground water or surface water. Community groups can coordinate their local inventory with the state's assessment process or can enhance a completed assessment with a more detailed inventory.

A helpful document to aid community groups is EPA's "Drinking Water Contaminant Source Index" which is a list of potential contaminant sources and the pollutants they can release. Additional resources about contamination are available at Reliable Sources—Contaminant Source Inventory.

STEP 3: DETERMINE THE SUSCEPTIBILITY OF THE WATER SUPPLY TO CONTAMINATION

For the susceptibility analysis, the state combines the inventory results with other relevant information to decide how likely a water supply is to become contaminated by identified potential sources of contamination. This critical step makes the assessments useful for communities, since it provides information that local decision-makers may use to prioritize approaches for protecting the

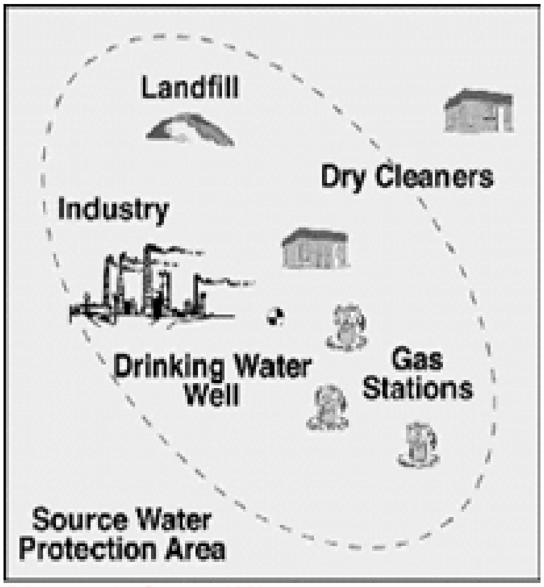


Diagram3: Ground Water

drinking water supply. Local information provided to the state by local community groups about contaminant sources, water resource characteristics, or environmental management practices may be used in the susceptibility determination process. Some states prioritize the potential for contamination from identified potential contamination sources or specific chemicals that could pollute the water. Other states assign susceptibility rankings of high, medium or low to the water sources.

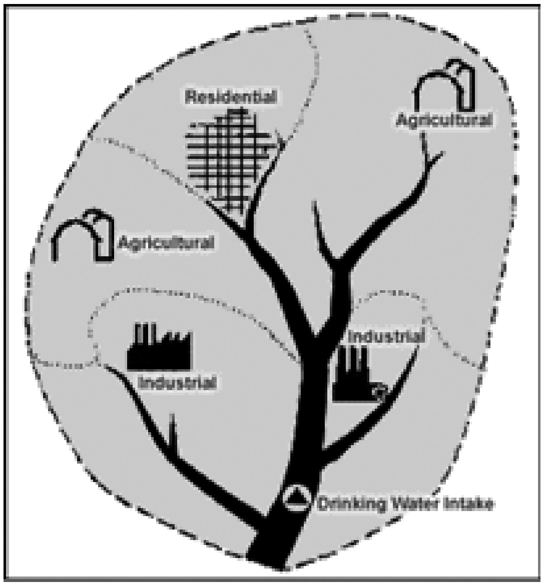


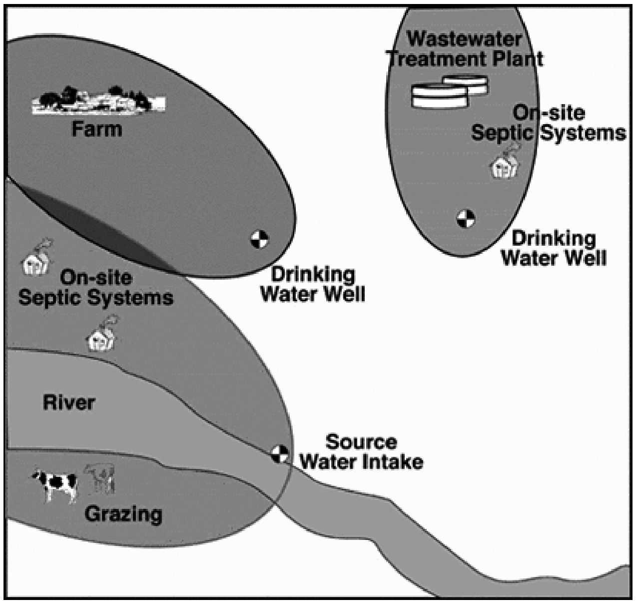
Diagram4: Surface Water

For more information on susceptibility see Reliable Sources—Susceptibility Determination.

STEP 4: RELEASE THE ASSESSMENT RESULTS TO THE PUBLIC

After a state completes the assessment of a particular water system, it will summarize the information for the public. Such summaries help communities understand the potential threats to their water supplies and identify priority needs for protecting the water from contamination. States will make the assessment summaries available to the public in a variety of ways. Some states plan to convene public workshops, while others will have copies available in public libraries and from local government offices or water suppliers. Many also plan to post the assessment summaries on the Internet. The results of the assessments will also be included in the annual water quality reports that community water systems are required to prepare for their customers. Community groups can convene local meetings to discuss the results and begin the process of protecting the drinking water source.

For more information on results see Reliable Sources—Public Availability.



USING THE ASSESSMENT

Whether using the state's assessment or expanding it into a more detailed local assessment, communities can use information gathered through the assessment process to create a broader source water protection program. Community groups and local officials, working in cooperation with local, regional, and state government agencies can plan how to manage identified potential contamination sources and prevent new contaminant threats in the source water assessment area.

Communities use a wide array of different source water protection methods to prevent contamination of their drinking water supplies. One management option involves regulations, such as prohibiting or restricting land uses that may release contaminants in critical source water areas. Along with regulations, many communities hold local events and distribute information to educate and encourage citizens and businesses to recycle used oil, limit their use of pesticides, participate in watershed cleanup activities, and a multitude of other prevention activities. Another aspect of a source water protection program can be the purchase of land or creation of conservation easements to serve as a protection zone near the drinking water source. For an effective protection program, communities should consider using a variety of prevention measures.

EPA's fact sheet, Community Involvement in Source Water Assessments, explains the four steps of source water assessments; how communities can participate in the assessment process; and how communities can utilize assessment information for source water protection. A downloadable version (PDF, 180 kb) is available.

HELPFUL CONTACTS

EPA, State and other contacts are also available to help you.

Your local water supplier may also have more information about opportunities to become involved in the source water assessment process. EPA can provide some local information about your drinking water system. You can also call the number on your water bill or contact your local health department for information on your water supplier.

HYDRAULIC DESIGN OF WATER DISTRIBUTION STORAGE TANKS

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Water distribution storage ensures the reliability of supply, maintains pressure, equalizes pumping and treatment rates, reduces the size of transmission mains, and improves operational flexibility and efficiency. Numerous decisions must be made in designing a storage tank, including size, location, type, and expected operation. There are several key considerations in the hydraulic design of water storage tanks.

Equalization is the primary purpose for constructing water distribution storage tanks. Water utilities like to operate treatment plants at a relatively constant rate, and wells and pumping stations generally work best when pumped at a steady rate. However, water use in most utilities varies significantly during the course of the day. These variations in use can be met by continuously varying source production, continuously varying pumping rates, or filling and draining storage tanks.

Filling and draining storage tanks is much easier operationally and is generally less expensive than other methods. Facilities that serve portions of a distribution system that has storage tanks generally need to be sized only to meet maximum daily demands; storage tanks provide water during instantaneous peak demands. Maintaining adequate pressure in a water distribution system is very important. To a great extent, the elevation of water stored in a tank determines the pressure in the pipes directly connected to the tank. The larger the tank volume, the more stable the pressure in the distribution system, despite fluctuations in demand or changes in pump operation. If distribution storage were not used, larger water transmission mains and larger treatment plant capacity would be required by most utilities to provide water needed for fire fighting. Especially in smaller systems, storage tanks are a much more economical and operationally reliable means for meeting the short-term large demands placed on a water supply system during fire fighting. In addition to fires, emergencies such as power outages, breaks in large water mains, problems at treatment plants, and unexpected shutdowns of water supply facilities can cause failure of the water system if sufficient water is not available in storage. Water storage tanks meet demands during emergencies.

Figure 1. Ground-level water storage tank (*Source*: Columbian TecTank).

Figure 2. Traditional multicolumn elevated storage tank (*Source*: Caldwell Tank, Inc.)

Besides equalization, pressure maintenance, and fire and emergency storage, other factors such as energy consumption, water quality, hydraulic transient control, and aesthetics should be considered in designing water distribution storage tanks. Tanks enable utilities to store energy as well as water for later use. To the extent that equalization storage slows down the velocity (and friction losses) in large transmission mains, the energy used to pump water is reduced by having distribution storage tanks that equalize pumping. Tanks may affect water quality in two general ways: (1) through chemical, physical, and biological processes that occur as water ages while stored in the tank and (2) through external contamination of water in tanks.

Figure 3. Composite elevated storage tank (*Source*: Caldwell Tank, Inc.).

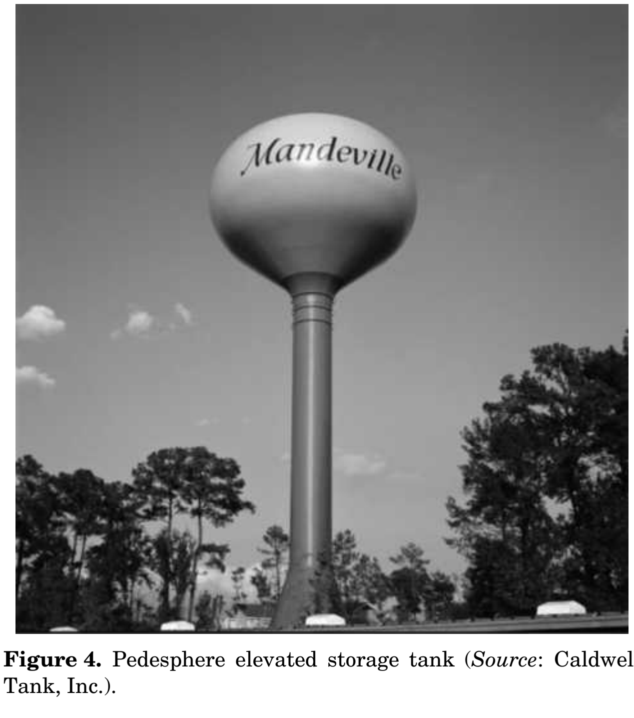

Figure 4. Pedesphere elevated storage tank (*Source*: Caldwell Tank, Inc.).

Some water quality problems can be eliminated by proper design and maintenance. In recent years, because of the concern for microbial regrowth and formation of disinfection byproducts, protecting the water quality in the storage tanks has become increasingly important. Another important consideration in designing water distribution storage tanks is controlling hydraulic transients. Changes in velocity in water mains can result in "water hammer." A water storage tank is effective in dampening the extreme high or low pressure caused by a transient. Sometimes the aesthetics of storage tanks becomes important. Tanks should be designed to satisfy the aesthetic considerations of stakeholders without sacrificing the purpose of the tank and the efficiency of the system's operation.

Depending on the topography and local environmental conditions, storage tanks may be located above, on, or below the ground. Underground tanks or reservoirs are constructed of reinforced concrete. Small ground-level tanks are usually earth-lined with gunite, asphalt, or some synthetic membrane. Large surface tanks are concrete-lined (Fig. 1). Most large surface tanks are covered to prevent contamination by bird, animal, and human wastes. Elevated water storage tanks are usually constructed of steel or concrete. Common shapes for elevated storage tanks are illustrated (Figs. 2–4).

READING LIST

HDR, Inc. (2001). *Handbook of Public Water System*, 2nd Edn. John Wiley & Sons, New York.

May, L.W. (Ed.). (1999). *Water Distribution System Handbook*. McGraw-Hill, New York.

Peavy, H.S., Rowe, D.R., and Tchobanoglous, G. (1985). *Environmental Engineering*. McGraw-Hill, New York.

Qasim, S.R., Motley, E.M., and Zhu, G. (2000). *Water Works Engineering*. Prentice-Hall, Upper Saddle River, NJ.

SYSTEM CONTROL AND DATA ACQUISITION (SCADA)

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Technical Assistance
Consultant

As small water systems continue to struggle to become more efficient, technology provides good ways to improve operations. Nowhere is this more apparent than in the application of control and communications systems—namely SCADA [System Control and Data Acquisition]—and their ability to provide system and information management that can help utilities meet regulatory requirements, reduce operating costs, and improve customer service. A water distribution system transports water from the treatment facility to the user. The distribtion system should supply water, without impairing its quality, in adequate quantities and at sufficient pressures to meet system requirements

WHAT IS SCADA?

A SCADA system consists of a computer placed at a central location, communications equipment, programmable logic controllers, sensors, and other devices that when put together, will monitor and control equipment and processes in a utility, such as a water system. Remote sites, equipped with remote telemetry units (RTUs), can be located as close as within the same building or as far away as across the country. RTUs measure a variety of conditions and parameters, including tank levels, temperature, voltage, current, volumes, and flow rates, and report back to a central processing unit (CPU). This technology is widely accepted in the water and wastewater industries as a reliable and efficient control system.

SCADA EQUIPMENT ENHANCES WATER OPERATIONS

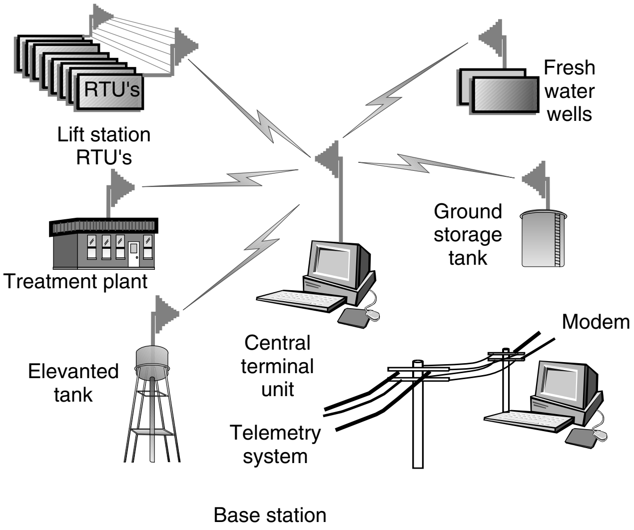
Functions that the SCADA system can perform include: remote monitoring of well levels and control of their pumps, and monitoring flows, tank levels, or pressures in storage tanks. A SCADA system can also monitor water quality characteristics, such as pH, turbidity, and chlorine residual, and control the addition of chemicals. In the distribution system, SCADA can supervise and control the water pressure of networks, assure water pressure is uniformly distributed, lower the leakage rate, and store data for future analysis.

SCADA is not a new technology by any means, but significant innovations and improvements have been achieved since its introduction. By automating many routine tasks, a SCADA system frees the plant operator to perform other duties, such as addressing state and federal reporting requirements. In fact, SCADA can assist in mandated reporting because it can store various activities and information on the computer. Graphs and reports can be generated automatically using the data collected remotely from the field. These reports are important in inferring production and consumption patterns, data that help manage the water resources more efficiently. Stored information also proves invaluable when producing the annual Consumer Confidence Reports required under the 1996 Safe Drinking Water Act (SDWA) Amendments.

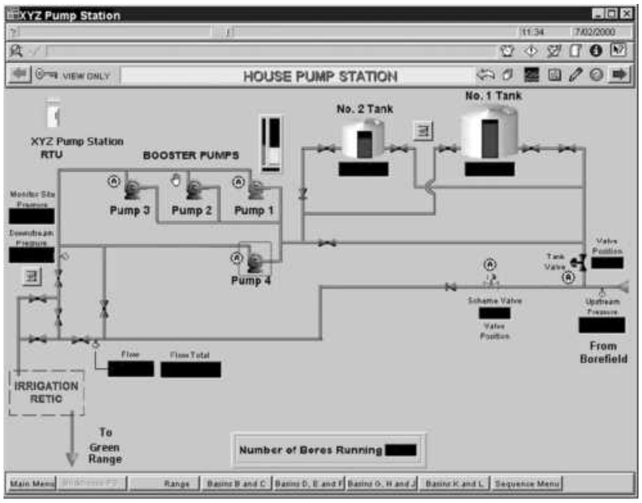
SCADA is useful in an emergency situation. Immediately following an incident, an operator can be notified via personal pager and increase response capability dramatically. SCADA provides multipurpose utility management, operating flexibility and more complex system control. SCADA keeps an eye on the entire system from one place.

SCADA PROVIDES COST-EFFECTIVE CONTROL AND MONITORING FOR SMALL WATER SYSTEMS

Because of its cost, smaller systems often viewed SCADA as a luxury item. But water system management has become complex and SCADA has become more advanced yet, paradoxically less expensive, making SCADA a viable option. Initial installation costs, which are often high, typically pay for themselves in a short time through direct labor and vehicle cost savings, as well as increased efficiency.



SCADA system



SCADA allows water operators to monitor the entire distribution system from one location

Due to a low tax base, many small communities have limited financial resources for drinking water system management and operation. Thus, it is difficult for operators to maintain extensive manual monitoring to ensure the system complies with complex regulations. These small systems, therefore, frequently violate (monitoring/reporting violations) the SDWA and its amendments, according to the National Research Council.

One solution to keeping up with ever more stringent requirements is for several small communities to pool their resources. The U.S. Environmental Protection Agency is evaluating the option of using remote telemetry, called an "electronic circuit-rider," that allows one qualified operator to monitor and control the operation of several small treatment systems from a centrally located computer. Using such a system can optimize the time spent taking daily readings out in the field. For onsite inspection and maintenance efforts, the RTS allows the operator to visit only the problematic systems. The results expected from an appropriately designed and successfully deployed remote monitoring and control system include enhanced water quality, compliance with existing water quality regulations, and reduced operating and maintenance costs for small communities.

SECURITY MEASURES ARE A CONCERN

Experienced computer hackers can access SCADA systems that operate over the Internet and deactivate process alarms, change chemical parameters, start and stop equipment, and so on. The results of such an intrusion can be devastating to the general public and to plant employees.

Many system managers installed protection as part of their "Y2K" contingency plans. The likelihood of a terrorist cyber attack is less likely than a cyber attack from a disgruntled employee. Fortunately, there are steps a system can take to minimize a security breech.

SCADA COMPONENTS AND TERMINOLOGY

Distributed Control System (DCS): An integrated system made up of many subsystems that are remotely located. Each subsystem can operate independently.

Modem (MOdulator DEModulator): Used to convert signals in one form to another. This is generally used for communication between computers and other devices over telephone lines or radio.

Programmable Logic Controller (PLC): A microprocessor-based controller, usually with multiple inputs and outputs and a program to perform control functions

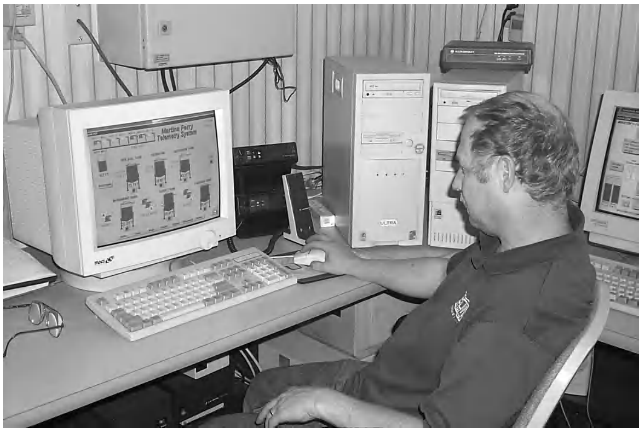
Remote Telemetry Unit or Remote Terminal Unit (RTU): A microprocessor device with multiple inputs and outputs connected to field instruments and devices. The RTUs translate these signals to digital form and transmit the same to central location by radio or telephone lines.

The National Infrastructure Protection Center (NIPC), located in the Federal Bureau of Investigations headquarters in Washington, D.C., shares information with public and private sector owners and operators of critical infrastructures. The NIPC monitors, warns, and investigates unlawful acts involving computer and information technologies. The agency manages computer intrusion investigations and supports law enforcement related to cyber crimes.

Best practices regarding the security of SCADA operation include:

- Internal threats are usually the main security challenge. The key to managing internal threats is understanding who might do what and why.
- Log-ins should be traceable and a strong password authentication process used.
- Suggest that a utility consider fiber optics to each of its remote facilities. This is the best solution in terms of bandwidth and security.
- Suggest taking a look at commercially available tools for monitoring computers and having a security team review activity weekly to verify that only authorized users are accessing the system.

WHAT SHOULD BE CONSIDERED WHEN BUYING A SCADA SYSTEM?


John Barkey, plant operator for Martin's Ferry, Ohio, inspects the water levels of the system's storage tanks from his desk

Selecting the appropriate SCADA system software is all-important. The software program should be capable of performing every task needed to operate and maintain water treatment and the distribution system. Its use in many similar applications should prove its reliability. Make sure the hardware supplier and the software developer can guarantee prompt, efficient, and cost effective support. The manufacturer should have experience in the water and wastewater industry and be able to provide service, replacement parts, and support for the system when needed.

To expedite the selection of specific devices/components for an RTS that monitors and controls a small drinking water facility, prepare a list of features associated with the particular water treatment facility. Identify the water quality parameters and types of monitoring that are key to the specific operation. For example, monitor residual chlorine to verify disinfection operations. Next, review the regulatory compliance requirements and consider them when reviewing manufacturers' specifications and discussing the applicability of their device or system. Finally, select the monitoring device.

It is important to document the pump characteristics, operational functions, and the physical dimensions of the treatment system before selecting components to monitor flow rates, pressure, electrical usage, or other process functions. Know facility specifications when contacting technical representatives of process monitoring/control devices. Component selection must be based on the plant's operational characteristics.

Data acquisition and telemetry components can be purchased as package items, but again, identify an inventory of what devices will be used on line and what options exist for transmitting data in the locality of the treatment plant before contacting suppliers.

FOR MORE INFORMATION

Booth, R., D. Ryan, and C. Hewell. 2001. *Technical Security and Countermeasures White Paper for Water Utilities*. Washington, DC: The National Council for Public-Private Partnerships.

Lebeau, L. W. 1997. "Automation Project Floods Water Department with Useful Data." *Water Engineering* *and Management*. Des Plaines, IL: Scranton Gilette Communications.

Madabhushi, B. S. 2000. “Can SCADA benefit small systems?” *Water Sense*. 6, no. 2. Morgantown, WV: National Drinking Water Clearinghouse.

National Research Council. 1997. *Safe Water From Every Tap*. Washington, DC: National Academy Press.

Pollack, A. J., A. S. Chen, R. C. Haught, and J. A. Goodrich. 1999. *Options for Remote Monitoring and Control of Small Drinking Water Facilities*. Columbus, OH: Batelle Press.

Rossmiller, R., and M. C. Moaveni. 2000. “Water Utility Mixes Technology and Creativity for Control and Communications Solution.” Water Engineering and Management. Des Plaines, IL: Scranton Gilette Communications.

To learn more about the National Infrastructure Protection Center (NIPC), write to the NIPC, 935 Pennsylvania Avenue, NW, Washington, D.C. 20535-0001, call toll free (888) 585–9078, or e-mail nipc.watch@fbi.gov. *Information is also available on the NIPC Web site at* www.nipc.gov.

For further information, to comment on this fact sheet, or to suggest topics, contact Dr. Lahlou via e-mail at *lahloum@hotmail.com*.

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To order this product, call the NDWC at the numbers listed at the bottom of this ad and ask for item #DWPKPE71. **The item is free.** Additional copies of fact sheets are also free; however, postal charges may be added. You can also order copies of one or all of the free *Tech Briefs* listed below.

Tech Brief: Disinfection, item #DWBLPE47;
Tech Brief: Filtration, item #DWBLPE50;
Tech Brief: Corrosion Control, item #DWBLPE52;
Tech Brief: Ion Exchange and Demineralization, item #DWBLPE56;
Tech Brief: Organics Removal, item #DWBLPE59;
Tech Brief: Package Plants, item #DWBLPE63;
Tech Brief: Water Treatment Plant Residuals Management, item #DWBLPE65;
Tech Brief: Lime Softening, item #DWBLPE67;
Tech Brief: Iron and Manganese Removal, item #DWBLPE70;
Water Conservation Measures Fact Sheet, item #DWBLPE74;
Tech Brief: Membrane Filtration, item #DWBLPE81;
Tech Brief: Treatment Technologies for Small Drinking Water Systems, item #DWPSPE82;
Tech Brief: Ozone, item #DWBLPE84;
Tech Brief: Radionuclides, item #DWBLPE84;
Tech Brief: Slow Sand Filtration, item #DWBLPE99;
Tech Brief: Ultraviolet Disinfection, item #DWBLPE101;
Tech Brief: Leak Detection and Water Loss Control, item #DWBLPE102;
Tech Brief: Diatomaceous Earth Filtration for Drinking Water, item #DWBLPE108.

SETTLING TANKS

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INTRODUCTION

Settling tanks (clarifiers) are an integral part of every wastewater treatment plant. These treatment facilities are used to remove solids from the wastewater by gravity sedimentation in quiescent conditions. Each settling tank has two functional zones—a clarification zone, where the process of gravity sedimentation occurs, and a thickening zone where the settled solids are accumulated forming a dense layer of sludge (sludge blanket). Settling tank effluent of low solids concentration is collected from the top of the clarification zone over overflow weirs into collection channels which convey the effluent to the tank outlet. The sludge collected at the bottom of the settling tank is removed for further treatment at the wastewater treatment plant’s solids handling facilities. The depth of the clarification zone is commonly referred to as a clear water zone (CWZ) depth, while the depth of the zone of sludge accumulation is named sludge blanket depth (SBD). The sum of the CWZ depth and the SBD is typically defined as a sidewater depth (SWD).

SETTLING TANK TYPES

Depending on their function settling tanks are categorized as primary and secondary. Primary settling tanks are located downstream of the wastewater treatment plant headworks and their main purpose is to remove the settleable suspended solids in the plant influent. Typically, primary settling tanks are also equipped with devices for removal of the floatable compounds (i.e., scum, oil and grease) in the wastewater influent which accumulate on the surface of the tanks during the sedimentation process. Secondary tanks are located downstream of the biological (secondary) treatment facilities of the wastewater treatment plant (such as activated sludge aeration basins or trickling filters) and are used to separate the biomass generated during the secondary treatment process from the treated plant effluent.

Depending on their geometrical shape, both primary and secondary clarifiers are classified in two main categories: rectangular and circular. Clarifier shape most suitable for a given application depends on a number of factors and has to be selected based on a cost-benefit analysis. Table 1 summarizes key advantages and disadvantages of rectangular and circular settling tanks.

Rectangular Settling Tanks

Rectangular settling tanks are long concrete structures which consist of individual basins (units) with common inner walls, and inlet and outlet channels (Fig. 1). Each individual tank basin is equipped with a separate sludge collection mechanism which transports the solids settled in the tank into a hopper for withdrawal or has a sludge suction collection mechanism which sweeps and removes solids accumulated at the tank's bottom. The length-to-width ratio of the individual tank basins is usually 3:1 to 15:1 (Fig. 1). The minimum settling tank length from inlet to outlet is typically 3 meters (10 ft). Tank depth is most frequently between 2 to 6 meters (6.6 to 20 ft). Rectangular tank unit width is usually selected based on available standard sizes of sludge collection mechanisms and varies between 2 to 6 meters (6.6 to 20 feet).

Circular Settling Tanks

Circular settling tanks are round facilities which consist of inlet structure, cylindrical clarification zone, conical sludge accumulation zone and effluent weirs (Fig. 2). The effluent weirs of these tanks are placed near the facility perimeter to create radially-directed flow pattern from the tank center towards the walls. The slope of the bottom

Table 1. Comparison of Rectangular and Circular Settling Tanks

Item	Rectangular Settling Tanks	Circular Settling Tanks
Advantages	Less land required for construction of multiple units. Potential construction cost savings because of use of common walls between individual tanks. Longer flow path minimizing short-circuiting. Higher effluent weir loading rates acceptable. Better sludge thickening.	Shorter detention time for settling sludge favoring use as secondary clarifiers. More simple sludge collection system. Easier to accommodate in-tank flocculation chamber—a benefit for activated sludge settling. Overall, lower maintenance requirements. Easier to remove heavy sludge.
Disadvantages	Longer detention time of the settled sludge—not favorable for plants with septic wastewater influent. Less effective for high solids loading conditions.	Higher short-circuiting potential. Higher flow distribution headlosses. Small circular tanks require more yard piping than do rectangular tanks of similar size.

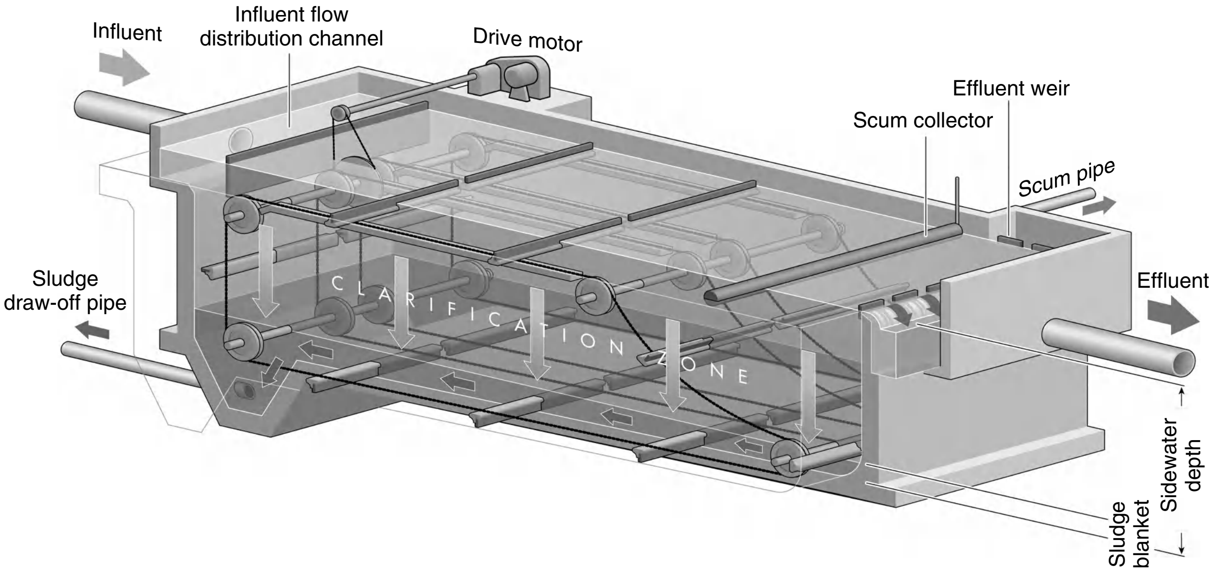

Figure 1. Rectangular settling tank.

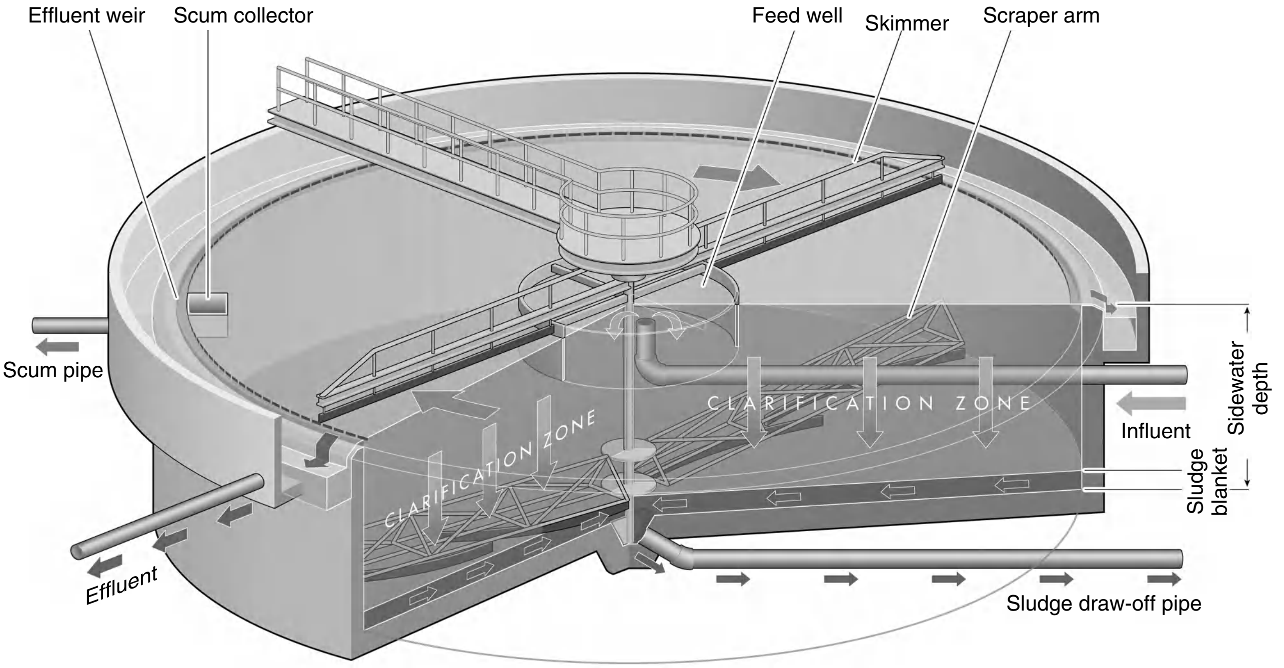

Figure 2. Circular settling tank.

conical floor is usually 1:10 to 1:12 and depends on the type of the sludge collection mechanism. Tank diameter ranges from 3 meters (10 ft) to over 100 meters (300 ft). Circular settling tanks are typically built in pairs of 2 or 4 to simplify the influent flow distribution between the individual units. Circular tank sidewater depth varies from 2.5 to 5 meters (8 to 16 feet).

Depending on the configuration of the tank inlet, circular settling thanks are classified as center feed and peripheral feed. Currently, the most widely used circular tanks are center feed type (see Fig. 2). In these tanks, influent flow enters though a feed pipe located in the center of the tank into a feedwell. The purpose of the feedwell is to provide uniform radial distribution of the tank influent and to dissipate the energy of the feed stream to a level adequate for efficient quiescent settling and uniform radial flow distribution. The conventional feedwells most widely used today are cylindrical metal structures with a diameter of 15 to 25% of the tank diameter which extend to 30 to 75% of the tank sidewater depth. Usually, conventional feedwells are designed for an average downflow velocity of 10 to 13 mm/s (2.0 to 2.5 ft/min) and maximum velocity of 25 to 30 mm/s (5.0 to 6.0 ft/min).

Settling Tank Enhancements

Inclined Plates and Ballasted Flocculation. Inclined plates and ballasted flocculation are used predominantly to enhance the performance of primary rectangular settling tanks. A typical inclined plate (lamella) system consists of bundles of parallel plastic tubes or metal plates inclined at 45 to 60° which are installed at the surface of the settling tank to a vertical depth of approximately 2 meters (6 feet). The distance between the individual plates is between 40 and 120 mm.

Ballasted flocculation combines the addition of coagulant and settling ballast (usually fine sand or sludge) to the tank influent with the installation of inclined plates in the tanks. A portion of the settled sludge or the recovered ballast is recycled to the primary clarifier influent to seed the influent. The addition of ballast increases the density of the influent floc particles by agglomeration. This enhancement typically yields three to five fold increase of the allowable clarifier surface overflow rate (SOR). Typically, conventional settling tanks are designed for SOR of 33 to 49 $m^3/m^2\cdot$ day (800 to 1,200 $gal/ft^2\cdot$ day). The use of high-rate ballasted solids separation technology allows increasing design clarifier SOR to at least 160 $m^3/m^2\cdot$ day (4,000 $gal/ft^2\cdot$ day). Because the ballast enhances solids removal, its use in primary clarification reduces the solids and organic loading of the downstream biological treatment processes.

Flocculating Center Feed Well. Flocculating center feed wells are used to enhance the performance of secondary settling tanks used for clarification of activated sludge. As compared to a conventional center feedwell which radius is approximately 10 to 13% of the tank radius, the flocculating feedwell's radius extends to 20 to 50% of the tank radius and the well size is designed to obtain a detention time of 20 to 30 minutes. The flocculating feedwell typically extends down to 40 to 50% of the tank depth. Some designs also include installation of mechanical mixers in the feedwell to enhance the flocculation process. The flocculating feedwell enhancement aims at creating optimum conditions for coagulation and flocculation of the incoming solids with the return activated sludge (RAS) recycled to the sedimentation tank. In the feedwell, the larger-size recycled RAS particles are given an ample time to attract and flocculate the smaller-size activated sludge particles conveyed form the aeration basins, thereby creating stronger and heavier solids particles that settle better and faster. More detailed design considerations for circular clarifiers with flocculating feedwells as well as a number of other available sedimentation tank process and equipment enhancements are presented elsewhere (1–3).

DESIGN CONSIDERATIONS FOR PRIMARY SETTLING TANKS

Performance efficiency of the primary settling tanks is affected by the upstream wastewater collection and treatment facilities and has a significant impact on downstream biological treatment and solids handling facilities. Primary settling tank performance is typically measured by tank's total suspended solids (TSS), biological oxygen demand (BOD), and phosphorus removal efficiencies and by the condition of the primary sludge (sludge septicity, concentration, and volume). Adequately designed and operated conventional primary settling tanks treating municipal wastewater typically remove 50 to 65% of the influent TSS; 25 to 35% of the influent BOD and 5 to 10% of the influent nitrogen and phosphorus. Clarifier TSS, BOD and nutrient removal efficiencies could be improved by chemical coagulation and flocculation of the influent wastewater solids prior to sedimentation (2–4).

Key design criteria used for sizing primary settling tanks are surface overflow rate and hydraulic detention time. Recommended values for these criteria according to various design guideline sources are presented in Table 2. Typically, primary sedimentation tanks are designed for effluent weir loading rates of less than 190 m^3/day per meter of length of the weir (5,000 gpd/ft) (Table 2).

Proper primary settling tank sludge collection, removal and withdrawal are of key importance for maintaining consistently high primary effluent quality and efficient and cost-effective solids handling. If primary settling tank sludge is retained for excessively long time in the tanks, the sludge could easily turn septic. Sludge septicity is accompanied with release of malodorous gases, which may disturb the normal sedimentation process as they travel from the tank bottom to the surface. Septic sludge is also more corrosive and more difficult to pump and dewater. Besides creating conditions for sludge septicity, maintaining relatively deep sludge blanket in the primary settling tanks may also make sludge collection and withdrawal more difficult and in extreme conditions, may cause damage of the sludge collection and withdrawal equipment (broken sludge collectors, plugged solids lines, and damaged pumps).

A widely accepted practice to prevent primary sludge septicity and its negative effect on settling tank performance is not to carry a sludge blanket, which is achieved by removing sludge continuously or very frequently from the settling tank's bottom. When not controlled appropriately, continuous sludge removal often results in pumping large quantities of diluted sludge or wastewater to the downstream solids handling facilities, which has a negative effect on their performance. In order to avoid over-pumping of diluted sludge to the downstream solids handling facilities and prevent the negative effects of excessively deep sludge blanket and associated sludge speticity, primary settling tank sludge blanket and concentration have to be maintained at optimum levels. The optimum primary sludge concentration is usually 3 to 5 percent and the most viable sludge blanket depth is typically between 1 and 3 feet. The optimum sludge blanket depth would vary seasonally and change during dry-weather and wet-weather conditions.

Table 2. Key Design Criteria for Primary Sedimentation Tanks

Design Guideline Source	Surface Overflow Rate (m^3/m^2/day)	Hydraulic Detention Time (hrs)
Metcalf and Eddy (5) (Primary Settling Followed by Secondary Treatment)	32–48 (at average flow) 80–120 (at peak hourly flow)	1.5–2.5
Randall et al. (4)	For SWD of 1.83–3.05 m: $\leq 2.184 \times \text{SWD}^2$ (at average flow) $\leq 4.368 \times \text{SWD}^2$ (at peak hourly flow). For SWD of 3.05–4.57 m: $\leq 6.672 \times \text{SWD}$ (at average flow) $\leq 13.344 \times \text{SWD}$ (at peak hourly flow)	NA
Great Lakes (6)	≤ 40 (at average flow) ≤ 60 (at peak hourly flow) Tank surface area is determined based on the larger of the two SORs. Minimum SWD = 2.1 m	NA
Qasim (7)	30–50 (at average flow) 40 (typical at average flow) 70–130 (at peak hourly flow) 100 (typical at peak hourly flow)	1.0–2.0

Note: SWD—Sidewater Depth; 1 m^3/m^2/day = 24.542 gpd/ft^2.

DESIGN CONSIDERATIONS FOR SECONDARY SETTLING TANKS

The performance of the secondary settling tanks has a significant effect on the wastewater plant's effluent water quality, on the operational efficiency of the biological treatment system and on the solids handling facilities. The secondary clarifiers have two key functions: clarification of the biologically treated wastewater; and thickening and storage of the sludge from the biological treatment process. Main factors that impact secondary settling tank performance are: (1) the amount of solids retained in the tanks, which is determined based on the concentration of the solids removed from these tanks (return activated sludge (RAS)/waste activated sludge (WAS) concentration) and the sludge blanket depth; (2) the amount of solids in the aeration basins, which is established by measuring the MLSS concentration and the RAS flowrate; (3) the activated sludge settleability; and (4) the plant influent flow and waste load, significant fluctuations of which may result in shifting solids between the settling tank and the aeration basin, and ultimately in solids loss with the secondary settling tank effluent. The two key secondary settling tank design criteria are: the SOR; and the solids loading rate (SLR). Table 3 presents recommendations for determining secondary clarifier design SOR and SLR. The tank effluent weir loading rates are typically designed not to exceed 124 m^3/day per meter of length of the weir (10,000 gpd/ft).

The maximum allowable SLR of settling tanks for clarification of activated sludge could be determined for using solids flux analysis (2,3,5,8). This method is based on the fact that for an activated sludge of given settleablity, these is a maximum amount of solids that can be processed through the clarifier (limiting solids flux), above which the clarifier will not be able to operate in a steady-state condition in terms of sludge blanket elevation and effluent water quality. One of the main benefits of the solids analysis concept is that it allows to link the design and operation of the secondary clarifier and the aeration basin and to optimize their performance as one system.

The amount of solids retained in the sedimentation basins can be effectively monitored by frequent manual or automated measurements of the settling tank sludge blanket depth and the concentration of the sludge removed from the settling tanks. While keeping track of the sludge blanket and plant influent flow changes allows gaining a general understanding of the settling tank performance, it is also very advantageous to monitor sludge settleability as well. The Water Environment Research Foundation and the Clarifier Research Committee of the American Society of Civil Engineers have developed protocols for evaluating sludge settleablity and analyzing secondary clarifier performance (9). These protocols are suitable for operational assessment of existing secondary sedimentation tanks and for planning of new facilities.

Table 3. Key Design Criteria for Secondary Sedimentation Tanks

Design Guideline Source	Surface Overflow Rate (m^3/m^2/day)	Solids Loading Rate (kg/m^2/h)
Metcalf and Eddy (5)		
Settling After Air-Activated Sludge (Excluding Extended Aeration).	16–32 (at average flow) 40–50 (at peak hourly flow)	4–6 (at average flow) ≤14 (at peak hourly flow)
Settling After Extended Aeration.	8–16 (at average flow) 24–32 (at peak hourly flow)	1–5 (at average flow) ≤7 (at peak hourly flow)
Settling After Trickling Filtration	16–24 (at average flow) 40–50 (at peak hourly flow)	3–5 (at average flow) ≤8 (at peak hourly flow)
Randall et al. (4)	For CWZ of 1.83–3.05 m: ≤2.184 × CWZ (at average flow) ≤6.672 × CWZ (at peak hourly flow). For CWZ of 3.05–4.57 m: ≤4.368 × CWZ (at average flow) ≤13.344 × CWZ (at peak hourly flow) Minimum SWD = 4.5 m	≤5(at average flow)
Great Lakes (6)		
Settling After Air-Activated Sludge (Excluding Extended Aeration).	≤49 (at peak hourly flow)	≤10 (at peak hourly flow)
Settling After Extended Aeration	≤41 (at peak hourly flow)	≤10 (at peak hourly flow)
	Minimum SWD = 3.7 m	
Qasim (7)	≤15 (at average flow) ≤40 (at peak hourly flow)	≤2 (at average flow) ≤6 (at peak hourly flow)

Note: CWZ—Clear Water Zone Depth; 1 m^3/m^2/day = 24.542 gpd/ft^2; 1 kg/m^2/h = 0.2048 lb/ft^2/h.

BIBLIOGRAPHY

1. Parker, D.S. (1983). Assessment of secondary clarifier design concepts. *J. Water Pollution Control Federation* **55**: 349–356.

2. Water Pollution Control Federation. (1985). *Manual of Practice FD-8, Clarifier Design*.
3. Water Environment Federation. (1998). *Manual of Practice 8, Design of Municipal Wastewater Treatment Plants*. Vol. 2, 4th Edn.
4. Randall, C.W., Barnard, J.L., and Stensel, H.D. (1992). *Design and Retrofit of Wastewater Treatment Plants for Biological Nutrient Removal, Water Quality Management Library*. Vol. 5, Technomic, Lancaster, PA.
5. Metcalf and Eddy. (1991). *Wastewater Engineering, Treatment Disposal and Reuse*. 3rd Edn. McGraw-Hill, New York.
6. Great Lakes—Upper Mississippi River Board of State Sanitary Engineering Health Education Services, Inc. (1978). *Recommended Standards for Sewage Works*. Albany ("Ten States Standards"), NY.
7. Qasim, S.R. (1985). *Wastewater Treatment Plants Planning, Design and Operation*. Holt, Rinehart and Wilson, New York.
8. Ekama, G.A., Barnard, J.L., Guntert, F.W., Krebs, P., McCorquodale, J.A., Parker, D.S., and Wahlberg, E.J. (1997). *Secondary Settling Tanks: Theory, Modeling, Design and Operation*. International Association on Water Quality. Scientific and Technical Report No. 6.
9. Wahlberg, E.J. (2001). *WERF/CRTC Protocols for Evaluating Secondary Clarifier Performance*. Water Environment Research Foundation.

TREATMENT FOR TECHNOLOGIES FOR SMALL DRINKING WATER SYSTEMS

National Drinking Water
Clearinghouse

INTRODUCTION

Small systems still face difficulties in meeting the requirements of the Safe Drinking Water Act (SDWA) because many technologies available to large systems may be too expensive or complicated for small systems to consider. Furthermore, trained operators and maintenance personnel may not always be available or affordable, leading to standards violations.

Overview of Some Treatment Technologies Used by Small Systems

When the SDWA was reauthorized in 1996, it addressed small system drinking water concerns and required the U.S. Environmental Protection Agency (EPA) to assess treatment technologies relevant to small systems serving fewer than 10,000 people. With this requirement, the SDWA also identified two classes of technologies:

- compliance technologies—which refer to affordable technologies or other treatment techniques (TT) that comply with the maximum contaminant level (MCL) and to technologies that satisfy a TT requirement. Options include package plants or modular systems, and point-of-entry (POE) or point-of-use (POU) treatment; and
- variance technologies—which refer to technologies that must reduce contaminants to levels that protect public health. These technologies may not achieve compliance with the MCL or TT requirement, but must achieve the maximum reduction or inactivation efficiency affordable to a system, considering its size and the quality of the source water.

With small systems' needs in mind, the National Research Council (NRC) recently published the results of a study—*Safe Water From Every Tap: Improving Water Service to Small Communities*—which found that continuous technical and financial assistance is still needed to help more than 54,000 small systems comply with changing regulations. In addition, the NRC study discussed some water treatment technologies that small systems may use to provide safe drinking water to their customers. These treatment technologies are also explained separately through Tech Briefs, four-page water treatment fact sheets, offered by the National Drinking Water Clearinghouse (NDWC). These fact sheets are available online at *www.ndwc.wvu.edu* or by calling (800) 624-8301.

DISINFECTION

The Surface Water Treatment Rule (SWTR) requires public water systems to disinfect water obtained from surface water supplies or groundwater sources under the influence of surface water. Primary methods of disinfection are chlorine gas, chloramines, ozone, ultraviolet light, chlorine dioxide, and hypochlorite.

Chlorine (Gas)

Chlorine gas removes almost all microbial pathogens and is appropriate as both a primary and secondary disinfectant. Chlorine is a dangerous gas that is lethal at concentrations as low as 0.1 percent air by volume. Adequate mixing and contact time must be provided after injection to ensure complete disinfection of pathogens.

Hypochlorites

Sodium Hypochlorite. is available as a solution in concentrations of five to 15 percent chlorine, but is more expensive than chlorine gas. Sodium hypochlorite is easier to handle than gaseous chlorine or calcium hypochlorite, but it is very corrosive and must be kept away from equipment that can be damaged by corrosion.

Calcium Hypochlorite. is a solid white substance, which is 65 percent available chlorine and dissolves easily in water. It is a corrosive material with a strong odor that must be kept away from organic materials, such as wood, cloth, and petroleum products because of the dangers of fire or explosion. Calcium hypochlorite readily absorbs moisture, forming chlorine gas so shipping containers must be emptied completely or carefully resealed.

Chloramines

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine. An effective bactericide that produces fewer disinfection byproducts, chloramine is generated onsite. It is a weak disinfectant and is much less effective against viruses or protozoa than free chlorine. Chloramine is appropriate for use as a secondary disinfectant to prevent bacterial regrowth in a distribution system. Nitrogen trichloride appears to be the only detrimental reaction. Adequate contact and mixing time must be provided.

Ozonation

Ozone is a powerful oxidizing and disinfecting agent formed by passing dry air through a system of high voltage electrodes. Requiring shorter contact time and a smaller dosage than chlorine, ozone is widely used as a primary disinfectant. Ozone does not directly produce halogenated organic materials unless a bromide ion is present. A secondary disinfectant, usually chlorine, is required because ozone does not maintain an adequate residual in water. The capital costs of ozonation systems may be high and operation and maintenance are relatively complex.

Ultraviolet Light

Ultraviolet (UV) radiation, which is generated by a special lamp, penetrates the cell wall of an organism, rendering it unable to reproduce. UV radiation effectively destroys bacteria and viruses. As with ozone, a secondary disinfectant must be used to prevent regrowth of microorganisms. UV radiation:

- is readily available,
- produces no known toxic residuals,
- requires short contact times, and
- is easy to operate and maintain.

Conventional UV radiation may not inactivate *Giardia lamblia* or *Cryptosporidium* cysts in a cost-effective way, and should be used only by groundwater systems not directly influenced by surface water and where there is virtually no risk of protozoan cyst contamination. UV radiation is unsuitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. However, microorganisms can be killed without generating byproducts of chemical oxidation or halogenation.

Chlorine Dioxide

Chlorine dioxide, although a powerful oxidant, may be more difficult to handle than other forms of chlorine. Chlorine dioxide requires trained staff to manage its use and is so reactive that it may not provide a residual disinfectant in the distribution system. Photochemical decomposition of chlorine dioxide in reservoirs may increase chlorate concentrations, and other factors, including the generation process used and water pH, can affect chlorate and chlorite levels.

FILTRATION

Federal and state laws require all surface water systems and systems under the influence of surface water to filter their water. Filtration methods include slow and rapid sand filtration, diatomaceous earth filtration, direct filtration, membrane filtration, and cartridge filtration.

Slow Sand Filtration

The filter consists of a bed of fine sand approximately three to four feet deep supported by a one-foot layer of gravel and an underdrain system. It is a low-cost, simple to operate, reliable technology, and it is able to achieve greater than 99.9 percent *Giardia* cyst removal. Slow sand filtration is not suitable for water with high turbidity. The filter surface requires maintenance. Extensive land is required due to low-flow operation. Biological processes and chemical/physical processes common to various types of filters occur on the surface of the filter bed. Slow sand filters do not require coagulation/flocculation and may not require sedimentation.

Diatomaceous Earth Filtration

Diatomaceous earth (DE) filtration, also known as precoat or diatomite filtration, relies on a layer of diatomaceous earth approximately 1/8-inch thick placed on a septum or filter element. Septums may be placed in pressure vessels or operated under a vacuum in open vessels. The filters are simple to operate and effective in removing cysts, algae, and asbestos. They have been chosen for projects with limited initial capital, and for emergency or standby capacity to service large seasonal increases in demand. This filter is most suitable for water with low bacterial counts and low turbidity. Coagulant and filter aids are required for effective virus removal. Since chemical coagulation is not required, small water systems have used DE filtration for many years.

Direct Filtration

Direct filtration systems are similar to conventional systems, but omit sedimentation. Effective direct filtration performance ranges from 90 to 99 percent for virus removal and from 10 to 99.99 percent for *Giardia* removal. Coagulation must be included for *Giardia* removal. Direct filtration is often used with steel pressure vessels to maintain the pressure in a water line to avoid repumping after filtration. Direct filtration is only applicable for systems with high quality and seasonally consistent influent supplies. Direct filtration requires advanced operator skill and has frequent monitoring requirements.

Membrane Filtration

More stringent water quality regulations and inadequate water resources are making membrane technology increasingly popular as an alternative treatment technology for drinking water. Capital, operation, and maintenance costs continue to decline, making membrane processes more viable.

Nanofiltration (NF). This membrane process employs pressures between 75 to 150 pounds per square inch (psi) for operation. While it provides removal of ions contributing to hardness (i.e., calcium and magnesium), the technology is also very effective for removing color and disinfection byproducts precursors.

Ultrafiltration (UF). Operational pressures range from 10 to 100 psi, depending upon the application. UF may be employed for removal of some organic materials from freshwater, and may be used for liquid/solid separation.

Microfiltration (MF). A major difference between MF and UF is membrane pore size. The primary applications for this membrane process are particulate and microbial removal.

Bag Filtration

Bag filtration systems are based on physical screening processes. If the pore size of the bag filter is small enough, parasite removal will occur. Unless the quality of the raw water precludes the need for pretreatment, EPA recommends pretreatment of the raw water using sand or multimedia filters, followed by preliminary bag or cartridge filtration, and the use of micron filters as final filters to increase particulate removal efficiencies and to extend the life of the filter.

Cartridge Filtration

Cartridge filters are an emerging technology suitable for removing microbes and turbidity. These filters are easy to operate and maintain, making them suitable for treating low-turbidity influent. They can become fouled relatively quickly and must be replaced with new units. Although these filter systems are operationally simple, they are not automated and can require relatively large operating budgets. A disinfectant is recommended to prevent surface-fouling microbial growth on the cartridge filters and to reduce microbial pass-through.

Backwashable Depth Filtration

Backwashable depth filters operate in part like cartridge filters. This method filters uncoagulated water and is designed to be backwashed when terminal head loss is attained or turbidity breakthrough occurs.

CORROSION CONTROL

Corrosion in a system can be reduced by adjusting pH and alkalinity, softening the water, and changing the level of dissolved oxygen. Any corrosion adjustment program should include monitoring as water characteristics change over time.

pH Adjustment. Operators can promote the formation of a protective calcium carbonate coating (scale) in water lines by adjusting pH, alkalinity, and calcium levels.

Lime Softening. Lime softening affects lead's solubility by changing the water's pH and carbonate levels. Hydroxide ions are then present, and they decrease metal solubility by promoting the formation of solids that protect the surface of the pipe.

Dissolved Oxygen Levels. The presence of excessive dissolved oxygen increases water's corrosive activity. However, removing oxygen from water is not practical because of the expense. The following strategies may be used to minimize the presence of oxygen:

- exclude the aeration process in groundwater treatment,
- increase lime softening,
- extend the detention periods for treated water in reservoirs, or
- use the correct size water pumps in the treatment plant to minimize the introduction of air during pumping.

ION EXCHANGE AND DEMINERALIZATION

Ion exchange and membrane processes are becoming used extensively in water and wastewater treatment. Ion exchange is primarily used to remove of hardness ions, such as magnesium and calcium, and for water demineralization. Reverse osmosis and electrodialysis, both membrane processes, remove dissolved solids from water using membranes.

Ion Exchange (IO)

IO units can be used to remove any charged (ionic) substance from water, but are usually used to remove hardness and nitrate from groundwater. Ion exchange effectively removes more than 90 percent of barium, cadmium, chromium, silver, radium, nitrites, selenium, arsenic, and nitrate. Ion exchange is usually the best choice for removing radionuclides.

Reverse Osmosis (RO)

RO systems are compact, simple to operate, and require minimal labor, making them suitable for small systems where there is a high degree of seasonal fluctuation in water demand. RO can effectively remove nearly all inorganic contaminants from water. Properly operated units will attain 96 percent removal rates. RO can also effectively remove radium, natural organic substances, pesticides, and microbiological contaminants. RO is particularly effective when used in series. Water passing through multiple units can achieve near zero effluent contaminant concentrations.

Electrodialysis

Electrodialysis is very effective in removing fluoride and nitrate and can also remove barium, cadmium, and selenium.

Some of the advantages are:

- all contaminant ions and most dissolved non-ions are removed,
- it is relatively insensitive to flow and total dissolved solids (TDS) level, and
- it may have low effluent concentration.

Some of the limitations are:

- high capital and operating costs,
- high level of pretreatment required,
- reject stream is 20 to 90 percent of feed flow, and
- electrodes require replacement.

Activated Alumina

Activated Alumina (AA) is a physical and chemical process in which ions in the feed water are sorbed to an oxidized AA surface. AA is used in packed beds to remove contaminants such as fluoride, arsenic, selenium, silica, and natural organic matter.

ORGANIC REMOVAL

The technologies most suitable for organic contaminant removal in drinking water systems are granular activated carbon (GAC) and aeration. GAC has been designated by the EPA as the best available technology (BAT) for synthetic organic chemical removal.

Granular Activated Carbon

Several operational and maintenance factors affect the performance of GAC. Contaminants in the water can occupy GAC adsorption sites, whether they are targeted for removal or not. Also, adsorbed contaminants can be replaced by other contaminants with which GAC has a greater affinity. Therefore, the presence of other contaminants might interfere with the removal of the contaminants of concern.

After a period of months or years, depending on the concentration of contaminants, the surface of the pores in the GAC can no longer adsorb contaminants. The carbon must then be replaced.

Aeration

Aeration, also known as air stripping, mixes air with water to volatilize contaminants (turn them to vapor), which are either released directly to the atmosphere or treated and released. Aeration is used to remove volatile organic chemicals (VOC) and can also remove radon. A small system might be able to use a simple aerator constructed from relatively common materials instead of a specially designed aerator system. Aerators include:

- a system that cascades the water or passes it through a slotted container,
- a system that runs water over a corrugated surface, or
- an airlift pump that introduces oxygen as water is drawn from a well.

Other Aeration Types

Packed Column Aeration (PCA). PCA or packed tower aeration (PTA) is a waterfall aeration process that drops water over a medium within a tower to mix the water with air. The medium is designed to break the water into tiny droplets and to maximize its contact with air bubbles for removal of the contaminant. Air is also blown in from underneath the medium to enhance this process. Packed columns usually operate automatically and need only daily visits to ensure that the equipment is running satisfactorily. Maintenance requirements include servicing pump and blower motors and replacing air filters on the blower.

Diffused Aeration. In a diffused aeration system, a diffuser bubbles air through a contact chamber for aeration. The diffuser is usually located near the bottom of the chamber where pressurized air is introduced. The main advantage of diffused aeration systems is that they can be created from existing structures, such as storage tanks. However, these systems are less effective than PCA and usually are employed only in systems with adaptable existing structures.

Multiple Tray Aeration. Multiple tray aeration directs water through a series of trays made of slats, perforations, or wire mesh. A blower introduces air from underneath the trays. Multiple tray aeration units have less surface area than PCA units and can experience clogging from iron and manganese, biological growth, and corrosion problems. Multiple tray aeration units are readily available from package plant manufacturers.

Shallow Tray Aeration (STA). STAs involve the use of shallow trays and are more efficient than multiple tray aerators. STAs increase the available area of mass transfer; thereby increasing the removal efficiency of most VOCs. However, because of the high air-to-water ratio, greater energy costs may be incurred.

Spray Aeration. Spray aeration is an accepted technology in which the contaminated water is sprayed through nozzles. The small droplets produced expose a large interfacial surface area through which VOCs can migrate from a liquid (water) phase to the gaseous (air) phase. Spray aerators have been used to effectively treat VOCs, but are not energy efficient and need a large operational area.

Mechanical Aeration. Mechanical aeration uses mechanical stirring mechanisms to mix air with the water. These systems can effectively remove VOCs. Mechanical aeration units need large amounts of space because they demand long detention times for effective treatment. As a result, they often require open-air designs, which can freeze in cold climates. However, mechanical aeration systems are easy to operate and are less susceptible to clogging from biological growth than PCA systems.

LIME SOFTENING

Lime softening is best suited to groundwater sources, which have relatively stable water quality. The combination of variable source water quality and the complexity of the chemistry of lime softening may make it too complicated for small systems that use surface water sources. Lime softening is unlikely to be suitable for treating

Surface Water Treatment Rule Compliance Technologies for Disinfection

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required	Raw Water Quality Range and Considerations[1]	Removals: Log *Giardia* & Log Virus w/CT's Indicated in ()[1]
Free Chlorine	(a, b)	Basic	Better with high quality. High iron or manganese may require sequestration or physical removal.	3 log(104) & 4 log(6).
Ozone	(c, d)	Intermediate	Better with high quality. High iron or manganese may require sequestration or physical removal.	3 log(1.43) & 4 log(1.0).
Chloramines	(e)	Intermediate	Better with high quality. Ammonia dose should be tempered by natural ammonia levels in water.	3 log(1850) & 4 log(1491).
Chlorine Dioxide	(f)	Intermediate	Better with high quality.	3 log(23) & 4 log(25).
Onsite Oxidant Generation	(g)	Basic	Better with high quality.	Research pending on CT values. Use free chlorine.
Ultraviolet (UV) Radiation	(h)	Basic	Relatively clean source water required. Iron, natural organic matter and turbidity affect UV dose.	1 log *Giardia* (80–120) & 4 log viruses (90–140) mWsec/cm2 doses in parentheses[2].

[1] CT (Concentration × Time), in mg-min/L, based upon 1989 Surface Water Treatment Rule Guidance Manual. Temp. 10 C, mid-pH range, unless otherwise indicated.

[2] UV dose is product of mW/cm2 (intensity) × sec (time); bases of viral inactivation ranges are rotavirus and MS−2 tests.

Limitations Footnotes

a. Providing adequate CT (contact time) may be a problem for some supplies.

b. Chlorine gas requires special caution in handling and storage, and operator training.

c. Ozone leaks represent hazard: air monitoring required.

d. Ozone used as primary disinfectant (i.e., no residual protection).

e. Long CT. Requires care in monitoring of ratio of added chlorine to ammonia.

f. Chlorine dioxide requires special storage and handling precautions.

g. Oxidants other than chlorine not detected in solution by significant research effort. CT should be based on free chlorine until new research determines appropriate CT values for electrolyzed salt brine.

h. No disinfectant residual protection for distributed water.

groundwater in systems serving 500 or fewer people unless those systems have access to a trained operator who can monitor the treatment process. Either hydrated lime or quicklime may be used in the softening process. The choice depends upon economic factors, such as the relative cost per ton of the two materials as well as the size and equipment of the softening plant.

What Are Other Softening Alternatives?

The selection of lime, lime-soda ash, or caustic soda softening is based on cost, TDS criteria, sludge production, carbonate and noncarbonate hardness, and chemical stability. Water containing little or no noncarbonate hardness can be softened with lime alone. Caustic soda softening increases the TDS of treated water, while lime and lime-soda ash softening often decrease TDS. Caustic soda softening produces less sludge than lime and lime-soda ash softening. Caustic soda does not deteriorate during storage, while hydrated lime may absorb carbon dioxide and water during storage, and quicklime may slake in storage causing feeding problems. The final selection is generally based on cost, water quality, and owner and operator preference.

FOR MORE INFORMATION

Small drinking water systems are more likely to violate SDWA regulations because when MCLs were set, they were based upon systems serving larger metropolitan areas. Thus, small systems must explore innovative technologies that they can afford. The NDWC's RESULTS (Registry of Equipment Suppliers of Treatment Technologies for Small Systems) database houses information related to small drinking water systems. The clearinghouse gathered this information from system operators, drinking water state offices, vendors, and others.

Database searches are available from the NDWC through combinations of site location, vendor name, type of technology, type of contaminant, and system size—and they include contact names and telephone numbers. Consulting engineers, local officials, private owners, and regulators may use RESULTS not only to understand technologies that small systems use, but

Surface Water Treatment Rule Compliance Technology for Filtration

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required	Raw Water Quality Range and Considerations[1]	Removals: Log *Giardia* & Log Virus
Conventional Filtration (includes dual-stage and dissolved air flotation)	(a)	Advanced	Wide range of water quality. Dissolved air flotation is more applicable for removing particulate matter that doesn't readily settle: algae, high color, low turbidity—up to 30–50 nephelometric turbidity units (NTU) and low-density turbidity.	2–3 log *Giardia* & 1 log viruses.
Direct Filtration (includes in-line filtration)	(a)	Advanced	High quality. Suggested limits: average turbidity 10 NTU; maximum turbidity 20 NTU; 40 color units; algae on a case-by-case basis.[1]	0.5 log *Giardia* & 1–2 log viruses (1.5–2 log *Giardia* w/coagulation).
Slow Sand Filtration	(b)	Basic	Very high quality or pretreatment. Pretreatment required if raw water is high in turbidity, color, and/or algae.	4 log *Giardia* & 1–6 log viruses.
Diatomaceous Earth Filtration	(c)	Intermediate	Very high quality or pretreatment. Pretreatment required if raw water is high in turbidity, color, and/or algae.	Very effective for *Giardia*; low bacteria and virus removal.
Reverse Osmosis	(d, e, f)	Advanced	Requires prefiltrations for surface water—may include removal of turbidity, iron, and/or manganese. Hardness and dissolved solids may also affect performance.	Very effective (cyst and viruses).
Nanofiltration	(e)	Intermediate	Very high quality of pretreatment. See reverse osmosis pretreatment.	Very effective (cyst and viruses).
Ultrafiltration	(g)	Basic	High quality or pretreatment.	Very effective *Giardia*, > 5–6.
Microfiltration	(g)	Basic	High quality or pretreatment required.	Very effective *Giardia*, > 5–6 log; Partial removal viruses.
Bag Filtration	(g, h, i)	Basic	Very high quality or pretreatment required, due to low particulate loading capacity. Pretreatment if high turbidity or algae.	Variable *Giardia* removals & disinfection required for virus credit.
Cartridge Filtration	(g, h, i)	Basic	Very high quality or pretreatment required, due to low particulate loading capacity. Pretreatment if high turbidity or algae.	Variable *Giardia* removals & disinfection required for virus credit.
Backwashable Depth Filtration	(g, h, i)	Basic	Very high quality or pretreatment required, due to low particulate loading capacity. Pretreatment if high turbidity or algae.	Variable *Giardia* removals & disinfection required for virus credit.

[1] National Research Council (NRC), Committee on Small Water Supply Systems. "Safe Water From Every Tap: Improving Water Service to Small Communities." National Academy Press, Washington, D.C. 1997.

[2] Adham, S.S., Jacangelo, J.G., and Laine, J.M. "Characteristics and Costs of MF and UF Plants." *Journal American Water Works Association*, May 1996.

Limitations Footnotes

a. Involves coagulation. Coagulation chemistry requires advanced operator skill and extensive monitoring. A system needs to have direct full-time access or full-time remote access to a skilled operator to use this technology properly.

b. Water service interruptions can occur during the periodic filter-to-waste cycle, which can last from six hours to two weeks.

c. Filter cake should be discarded if filtration is interrupted. For this reason, intermittent use is not practical. Recycling the filtered water can remove this potential problem.

d. Blending (combining treated water with untreated raw water) cannot be practiced at risk of increasing microbial concentration in finished water.

e. Post-disinfection recommended as a safety measure and for residual maintenance.

f. Post-treatment corrosion control will be needed prior to distribution.

g. Disinfection required for viral inactivation.

h. Site-specific pilot testing prior to installation likely to be needed to ensure adequate performance.

i. Technologies may be more applicable to system serving fewer than 3,300 people.

Compliance Technology for the Total Coliform Rule

40 CFR 141.63(d)−Best Technologies or Other Means to Comply (Complexity Level Indicated)	Comments/Water Quality Concerns
Protecting wells from contamination, i.e., placement and construction of well(s) (Basic).	Ten State Standards and other standards (AWWA A100−90) apply; interfacing with other programs essential (e.g., source water protection program).
Maintenance of a disinfection residual for distribution system protection (Intermediate).	Source water constituents may affect disinfection: iron, manganese, organics, ammonia, and other factors may affect dosage and water quality. Total Coliform Rule (TCR) remains unspecific on type/amount of disinfectant, as each type differs in concentration, time, temperature, pH, interaction with other constituents, etc.
Proper maintenance of distribution system: pipe repair/replacement, main flushing programs, storage/reservoir and operation and maintenance (O&M) programs (including cross-connection control/backflow prevention), and maintenance of positive pressure throughout (Intermediate).	O&M programs particularly important for smaller systems needing to maintain water purity. States may vary on distribution protection measures. See also EPA's Cross-Connection Control Manual (#EPA 570/9-89-077).
Filtration and/or disinfection of surface water or other groundwater under direct influence; or disinfection of groundwater (Basic thru Advanced).	Same issues as cited above under maintaining disinfection residual; pretreatment requirements affect complexity of operation. Refer to Surface Water Treatment Rule Compliance Technology List; and other regulations under development.
Groundwaters: Compliance with State Wellhead Protection Program (Intermediate).	EPA/State Wellhead Protection Program implementation (per §1428 SDWA): may be used to assess vulnerability to contamination, and in determination of sampling and sanitary survey frequencies.

Technologies for Inorganic Contaminants

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required	Raw Water Quality Range
1. Activated Alumina	(a)	Advanced	Groundwaters, competing anion concentrations will affect run length.
2. Ion Exchange (IO)		Intermediate	Groundwaters with low total dissolved solids, competing ion concentrations will affect run length.
3. Lime Softening	(b)	Advanced	Hard ground and surface waters.
4. Coagulation/Filtration	(c)	Advanced	Can treat wide range of water quality.
5. Reverse Osmosis (RO)	(d)	Advanced	Surface water usually require prefiltration.
6. Alkaline Chlorination	(e)	Basic	All groundwaters.
7. Ozone Oxidation		Intermediate	All groundwaters.
8. Direct Filtration		Advanced	Needs high raw water quality.
9. Diatomaceous earth filtration		Intermediate	Needs high raw water quality.
10. Granular Activated Carbon		Basic	Surface waters may require prefiltration.
11. Electrodialysis Reversal		Advanced	Requires prefiltration for surface water.
12. Point of Use (POU)-IO	(f)	Basic	Same as Technology #2.
13. POU-RO	(f)	Basic	Same as Technology #5.
14. Calcium Carbonate Precipitation	(g)	Basic	Waters with high levels of alkalinity and calcium.
15. pH and alkalinity adjustment (chemical feed)	(g)	Basic	All ranges.
16. pH and alkalinity adjustment (limestone contactor)	(h)	Basic	Waters that are low in iron and turbidity. Raw water should be soft and slightly acidic.
17. Inhibitors		Basic	All ranges.
18. Aeration	(i)	Basic	Waters with moderate to high carbon dioxide content.

Limitations Footnotes

a. Chemicals required during regeneration and pH adjustments may be difficult for small systems to handle.

b. Softening chemistry may be too complex for small systems.

c. It may not be advisable to install coagulation/filtration solely for inorganics removal.

d. If all of the influent water is treated, post-treatment corrosion control will be necessary.

e. pH must exceed pH 8.5 to ensure complete oxidation without build-up of cyanogen chloride.

f. When POU devices are used for compliance, programs for long-term operation, maintenance, and monitoring must be provided by water utility to ensure proper performance.

g. Some chemical feeds require high degree of operator attention to avoid plugging.

h. This technology is recommended primarily for the smallest size category.

i. Any of the first five aeration technologies listed for volatile organic contaminants can be used.

Technologies for Volatile Organic Contaminants

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required	Raw Water Quality Range[1]
1. Packed Tower Aeration (PTA)	(a)	Intermediate	All groundwaters.
2. Diffused Aeration	(a, b)	Basic	All groundwaters.
3. Multi-Stage Bubble Aerators	(a, c)	Basic	All groundwaters.
4. Tray Aeration	(a, d)	Basic	All groundwaters.
5. Shallow Tray Aeration	(a, e)	Basic	All groundwaters.
6. Spray Aeration	(a, f)	Basic	All groundwaters.
7. Mechanical Aeration	(a, g)	Basic	All groundwaters.
8. Granular Activated Carbon (GAC)	(h)	Basic	All groundwaters.

[1] National Research Council (NRC). "Safe Water from Every Tap: Improving Water Service to Small Communities." National Academy Press. Washington, DC. 1997.

Limitations Footnotes

a. Pretreatment for the removal of microorganisms, iron, manganese, and excessive particulate matter may be needed. Post-treatment disinfection may have to be used.

b. May not be as efficient as other aeration methods because it does not provide for convective movement of the water thus limiting air-water contact. It is generally used only to adapt existing plant equipment.

c. These units are highly efficient; however, the efficiency depends upon the air-to-water ratio.

d. Costs may increase if a forced draft is used. Slime and algae growth can be a problem but can be controlled with chemicals such as copper sulfate or chlorine.

e. These units require high air-to-water ratios (100–900 m3/m3).

f. For use only when low removal levels are needed to reach a maximum contaminant level (MCL) because these systems may not be as energy efficient as other aeration methods because of the contacting system.

g. For use only when low removal levels are needed to reach an MCL because these systems may not be as energy efficient as other aeration methods because of the contacting system. The units often require large basins, long residence times, and high energy inputs, which may increase costs.

h. See the Synthetic Organic Compounds (SOC) compliance technology table for limitation regarding these technologies.

Technologies for Synthetic Organic Compounds

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required[1]	Raw Water Quality Range and Considerations[1]
1. Granular Actived Carbon (GAC)		Basic	Surface water may require prefiltration.
2. Point of Use GAC	(a)	Basic	Surface water may require prefiltration.
3. Powdered Activated Carbon	(b)	Intermediate	All waters.
4. Chlorination	(c)	Basic	Better with high quality waters.
5. Ozonation	(c)	Basic	Better with high quality waters.
6. Packed Tower Aeration (PTA)	(d)	Intermediate	All groundwaters.
7. Diffused Aeration	(d, e)	Basic	All groundwaters.
8. Multi-Stage Bubble Aerators	(d, f)	Basic	All groundwaters.
9. Tray Aeration	(d, g)	Basic	All groundwaters.
10. Shallow Tray Aeration	(d, f)	Basic	All groundwaters.

[1] National Research Council (NRC). "Safe Water from Every Tap: Improving Water Service to Small Communities." National Academy Press. Washington, DC. 1997.

Limitations Footnotes

a. When POU devices are used for compliance, programs for long-term operation, maintenance, and monitoring must be provided by water utility to ensure proper performance.

b. Most applicable to small systems that already have a process train including basins mixing, precipitation or sedimentation, and filtration. Site specific design should be based on studies conducted on the system's particular water.

c. See the Surface Water Treatment Rule compliance technology tables for limitations associated with this technology.

d. Pretreatment for the removal of microorganisms, iron, manganese, and excessive particulate matter may be needed. Post-treatment disinfection may have to be used.

e. May not be as efficient as other aeration methods because it does not provide for convective movement of the water thus limiting air-water contact. It is generally used only to adapt existing plant equipment.

f. These units are highly efficient; however, the efficiency depends upon the air-to-water ratio.

g. Forces may increase if a forced draft is used.

technologies that are affordable, appropriate, and reliable. Information in RESULTS may be obtained three ways: access the database through the NDWC's Web site located at *www.ndwc.wvu.edu*; call the NDWC at (800) 624–8301 or (304) 293–4191 and ask a technical assistant to perform a search for you.

READING LIST

NDWC Report. 1998. *RESULTS Database: Small Water Systems Technologies*. Morgantown, WV, September.*

**NDWC* RESULTS Database: Small Water Systems Technologies *report and Tech Briefs are available online at www.ndwc.wvu.edu or by calling (800) 624-8301 or (304) 293-4191.*

Technologies for Radionuclides

Unit Technology	Limitations (see Footnotes)	Operator Skill Level Required[1]	Raw Water Quality Range and Considerations[1]
1. Ion Exchange (IO)	(a)	Intermediate	All groundwaters.
2. Point of Use (POU) IO	(b)	Basic	All groundwaters.
3. Reverse Osmosis (RO)	(c)	Advanced	Surface waters, usually require prefiltration.
4. POU RO	(b)	Basic	Surface waters, usually require prefiltration.
5. Lime Softening	(d)	Advanced	All waters.
6. Green Sand Filtration	(e)	Basic	
7. Co-precipitation with Barium Sulfate	(f)	Intermediate to Advanced	Groundwaters with suitable water quality.
8. Electrodialysis/Electrodialysis Reversal		Basic to Intermediate	All groundwaters
9. Pre-formed Hydrous Manganese Oxide Filtration	(g)	Intermediate	All groundwaters

[1] National Research Council (NRC). "Safe Water from Every Tap: Improving Water Service to Small Communities." National Academy Press. Washington, DC. 1997.

Limitations Footnotes

a. The regeneration solution contains high concentrations of the contaminant ions. Disposal options should be carefully considered before choosing this technology.

b. When POU devices are used for compliance, programs for long-term operation, maintenance, and monitoring must be provided by water utility to ensure proper performance.

c. Reject water disposal options should be carefully considered before choosing this technology. See other RO limitations described in the Surface Water Treatment Rule Compliance Technologies Table.

d. The combination of variable source water quality and the complexity of the chemistry involved in lime softening may make this technology too complex for small surface water systems.

e. Removal efficiencies can vary depending on water quality.

f. This technology may be very limited in application to small systems. Since the process requires static mixing, detention basins, and filtration; it is most applicable to systems with sufficiently high sulfate levels that already have a suitable filtration treatment train in place.

g. This technology is most applicable to small systems that already have filtration in place.

National Research Council. 1997. *Safe Water From Every Tap: Improving Water Service to Small Communities*. National Academy Press, Washington, DC.

NDWC Tech Brief: Disinfection, item #DWBLPE47.*

NDWC Tech Brief: Filtration, item #DWBLPE50.*

NDWC Tech Brief: Corrosion Control, item #DWBLPE52.*

NDWC Tech Brief: Ion Exchange and Demineralization, item #DWBLPE56.*

NDWC Tech Brief: Organics Removal, item #DWBLPE59.*

NDWC Tech Brief: Package Plants, item #DWBLPE63.*

NDWC Tech Brief: Lime Softening, item #DWBLPE67.*

NDWC Tech Brief: Iron and Manganese Removal, item #DWBLPE70.*

NDWC Tech Brief: Membrane Filtration, item #DWBLPE81.*

U.S. General Accounting Office. 1994. *Drinking Water: Stronger efforts Essential for Small Communities to Comply with Standards*. GAO/RCED-94-40. Washington, DC.

To ease many of the demands placed on small systems, the 1996 Safe Drinking Water Act amendments require the U.S. Environmental Protection Agency (EPA) to evaluate affordable technologies and address existing and future regulations, which establish a maximum contaminant level or treatment technique.

The following tables are taken from three EPA guidance documents: EPA-815-R-98-001, *Small System Compliance Technology List for the Surface Water Treatment Rule and Total Coliform Rule*; EPA-815-R-98-002, *Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996*; and EPA-815-R-98-003, *Variance Technology Findings for Contaminants Regulated Before 1996*.

For information about the availability of these guidance and support documents, please contact the Safe Drinking Water Hotline: phone (800) 426–4791, fax (703) 285–1101, or e-mail *hotline-sdwa@epamail.epa.gov*.

The National Drinking Water Clearinghouse assists small communities by collecting, developing, and providing timely information relevant to drinking water issues.

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ULTRAVIOLET DISINFECTION

National Drinking Water
Clearinghouse

Using ultraviolet (UV) light for drinking water disinfection dates back to 1916 in the U.S. Over the years, UV costs have declined as researchers develop and use new UV methods to disinfect water and wastewater. Currently, several states have developed regulations that allow systems to disinfect their drinking water supplies with UV light. Running a UV light system requires a basic level of operator skill and relatively clean source water. On the down side, however, UV offers no residual disinfection within the distribution system.

WHAT IS UV DISINFECTION?

UV light, which continues to be a reliable means of disinfection, involves exposing contaminated water to radiation from UV light. The treatment works because UV light penetrates an organism's cell walls and disrupts the cell's genetic material, making reproduction impossible.

A special lamp generates the radiation that creates UV light by striking an electric arc through low-pressure mercury vapor. This lamp emits a broad spectrum of radiation with intense peaks at UV wavelengths of 253.7 nanometers (nm) and a lesser peak at 184.9 nm. Research has shown that the optimum UV wavelength range to destroy bacteria is between 250 nm and 270 nm. At shorter wavelengths (e.g., 185 nm), UV light is powerful enough to produce ozone, hydroxyl, and other free radicals that destroy bacteria.

The U.S. Department of Health, Education, and Welfare set guidelines for UV light disinfection in 1966. These guidelines require a minimum dose of 16 mWs/cm^2 [milliwatt seconds per square centimeter] at all points throughout the water disinfection unit.

However, the American National Standards Institute and the National Sanitation Foundation International set the minimum UV light requirement at 38 mWs/cm2 for class A point of use (POU) and point of entry (POE) devices that treat visually clear water.

The U.S. Environmental Protection Agency (EPA) lists UV disinfection as an approved technology for small public water systems. In addition, EPA is considering the following variations of conventional UV treatment as "emerging" technologies: pulsed UV, medium-pressure UV, and UV oxidation (i.e., used in combination with peroxide or ozone).

ADVANTAGES

Generally, UV is simple to install and requires little supervision, maintenance, or space. Improved safety, minimum service time, low operation and maintenance costs, and the absence of a chemical smell or taste in finished water are primary factors for selecting UV technology rather than traditional disinfection technologies.

UV treatment breaks down or removes some organic contaminants. UV achieves 1-log reduction of *Giardia lamblia* at an intensity of 80–120 mWs/cm^2, and 4-log reduction of viruses at an intensity of 90–140 mWs/cm^2. Only recently has the scientific community begun to accept UV as a highly effective tool for *Cryptosporidium* control.

UV light disinfection does not form any significant disinfection byproducts, nor does it cause any significant increase in assimilable organic carbon (AOC).

Research has confirmed that UV effectiveness is relatively insensitive to temperature and pH differences. In addition, researchers found that UV application does not convert nitrates to nitrites, or bromide to bromines or bromates.

Recent pilot studies show that UV-treated drinking water inhibits bacterial growth and replication in the distribution system; however, conditions within distribution systems, such as leaks, still require additional residual disinfection (e.g., free chlorine).

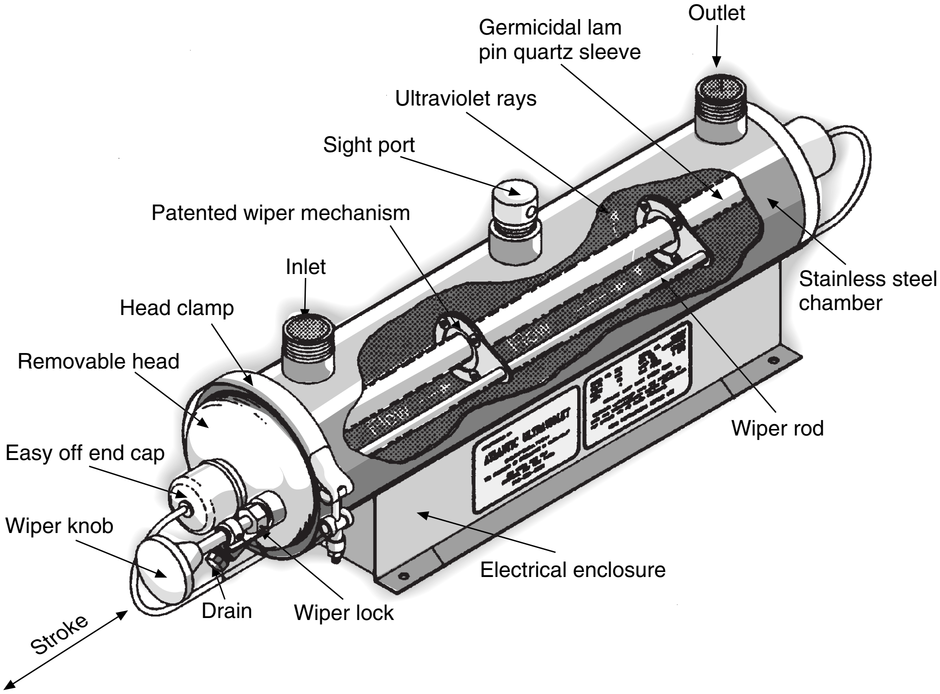
The advantages of using UV, rather than chemical disinfection, include:

- Has no known toxic or significant nontoxic byproducts;
- Has no danger of overdosing;
- Removes some organic contaminants;
- Has no volatile organic compound (VOC) emissions or toxic air emissions;
- Has no onsite smell and no smell in the final water product;
- Requires very little contact time (seconds versus minutes for chemical disinfection);
- Does not require storage of hazardous material;
- Requires minimal space for equipment and contact chamber;
- Improves the taste of water because of some organic contaminants and nuisance microorganisms are destroyed;
- Does not affect minerals in water; and
- Has little or no impact on the environment except for disposing of used lamps or obsolete equipment.

LIMITATIONS

Microbial and chemical characteristics are two major water quality factors that affect the UV unit performance. Microbial characteristics of water include type, source, age, and density. Chemical water characteristics include nitrites, sulfites, iron, hardness, and aromatic organic levels.

UV radiation is not suitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. These materials can react with UV radiation, and reduce disinfection performance. Turbidity makes it difficult for radiation to penetrate water.



Closed vessel ultraviolet reactor. *Reprinted with permission from the Atlantic Ultraviolet Corporation.*

Disadvantages of UV disinfection include:

- No disinfection residual;
- No technical database exists on how well UV systems perform for various water quality conditions; and
- No standardized mechanism measures, calibrates, or certifies how well equipment works before or after installation.

Systems also should consider using different kinds of microbial testing. Laboratories typically test for total coliform to judge microbiological activity in drinking water—but coliforms are sensitive to UV light. Because of this sensitivity, microbial tests for UV treated finished water should include a Heterotrophic Plate Count (HPC) test. HPC microorganisms may provide a better disinfection assessment than the UV sensitive coliforms.

PROCESS DESCRIPTION

UV light effectively destroys bacteria and viruses. However, how well the UV system works depends on the energy dose that the organism absorbs. If the energy dose is not high enough, the organism's genetic material may only be damaged rather than disrupted.

An effective dose is measured as a product of the lamp's intensity (the rate at which photons are delivered to the target), including radiation concentration, proper wavelength, exposure time, water quality, flow rate, and the microorganism's type, and source, as well as its distance from the light source.

At a minimum, drinking water systems should install two UV units, which are both capable of carrying the amount of water the system was designed to handle. Having two units in place assures continuous disinfection when one unit is being serviced. Two units also can ensure operation during low-flow demand periods.

Modular units designed for small drinking water systems are easy to install and operate (two plumbing connections per unit and one electrical hook-up). They should be equipped with automatic cleaners and remote alarm systems. For systems in isolated areas, operators should maintain and store a set of spare parts onsite, and consider a telemetry system for monitoring treatment.

Typical UV light components include:

- A stable high-voltage source of electricity because low-line voltage would result in a lower UV dose;
- A chamber made of stainless steel or any other material that is opaque and will not corrode;
- UV lamps that are properly secured inside quartz sleeves, easing installation, replacement, and maintenance;
- Quartz sleeves with sufficiently high transmission rates to deliver the UV energy produced by UV lamps;
- Mechanical wipers to maintain optimum transmission between scheduled cleaning and maintenance work;
- Sensors to monitor the UV intensity passing through the water. These sensors need to be connected to alarm systems to alert the operator in case of low UV intensity. The operator must have easy access to these sensors for necessary installation, replacement, calibration, and maintenance;
- Safety control to shut off UV lamps in case of low-flow levels and elevated lamp temperature;
- Arc and lamp-out monitors to alert the operator of system failure; and
- Electronic ballasts.

UV units are currently used as stand-alone treatment systems or as part of a series of other drinking water treatment processes or multiple barrier system. A common treatment that uses UV light to remove and disinfect contaminants from groundwater sources involves a combined ozone or hydrogen-peroxide process along with UV application. So, it is common to find that manufacturers of UV equipment also manufacture ozone equipment.

Furthermore, the drinking water treatment industry provides UV equipment (mainly closed chamber units) for short-term uses. Rental units are used in cleanup and emergency situations, such as if groundwater is contaminated by spilled toxic organic compounds.

MONITORING AND OPERATION REQUIREMENTS

Factors that affect UV light system performance are: lamp output, lamp aging, and plating or fouling of unit surfaces. To better control these factors, operators must ensure continuous dose measurement (i.e., accurate intensity and flow-rate measurement) and proper maintenance (cleaning as well as lamp and sleeve replacement regimes).

Technological advances have eliminated many of the operation and maintenance problems that were associated with earlier UV applications. Current systems are equipped with mechanical cleaners, ultrasonic cleaners, or some self-cleaning mechanism (mandatory if water fouling agents, such as iron, are present in the water entering the unit); lamps that are easy to install and replace; and alarm systems that indicate minor and major failure.

To ensure continued system operation, a maintenance schedule needs to be in place. This schedule should include periodic site inspections; changing lamps annually or when light transmission efficiency has decreased to 70 percent; inspecting and cleaning surfaces; inspecting or cleaning the UV chamber interior every six months; and inspecting and replacing ballasts, O-rings, valves, and switches.

Furthermore, the operator should monitor water turbidity and color since they are natural barriers to UV light transmission. And some dissolved minerals, such as calcium, have a tremendous negative effect on UV absorbance.

Since it may not be practical to provide instantaneous stand-by power during power outages, the system should be designed to automatically stop water flow or provide an alternate means of disinfection as a backup. Where the system is dependent on electrically powered pumps, this measure may not be necessary because the pumps will shut off when the power goes out. However, gravity flow systems may be vulnerable.

UV disinfection should have the following minimum operational controls and procedures:

- A central display indicating alarms for power failure, lamp failure, hours of lamp operation, low UV dosage, high lamp temperature, high ballast temperature, and high system flows;
- Methods that monitor lamp temperature, ballast temperature, and system water flows;
- A minimum of two photodiode sensors per unit to monitor UV dosage at 254 nm. These sensors must be calibrated using approved standards each time the lamps are cleaned or replaced or the UV chamber is serviced;
- Automatic UV system by-pass or shutoffs, which are activated whenever the system exceeds peak design flow rates, when UV dosage is low, or when lamp or ballast temperatures are high; and
- Two UV units should be installed so flow is not interrupted when one unit is out of service.

WHERE CAN I FIND MORE INFORMATION?

Hargy, T.M., J.L. Clancy, and Z. Bukhari. 2000. "Shedding UV Light on the *Cryptosporidium* Threat." In NSF Proceedings of the Small Drinking Water and Wastewater Systems. International Symposium and Technology Expo: Phoenix, Arizona.

Malley, J.P., G.A. Snicer, and A.M. Doucette. 1998. "Alternative Disinfection Strategies for Small Systems." In *Small Systems Water Treatment Technologies: State of the Art Workshop*. NEWWA Joint Regional Operations Conference and Exhibition: Marlborough, Massachusetts.

Parrotta, M.J. and F. Bekdash. 1998. "UV Disinfection of Small Groundwater Supplies." *Journal of the American Water Works* Association. AWWA: Denver.

U.S. Environmental Protection Agency. 1996. *Ultraviolet Light Disinfection Technology in Drinking Water Application—An Overview*. Office of Water: Washington, DC. EPA/811-R-96-002.

U.S. Environmental Protection Agency. 1998. *Small System Compliance Technology List for the Surface Water Treatment Rule and Total Coliform Rule*. Office of Water: Washington, DC. EPA/815/R/98/001.

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"Tech Briefs" drinking water treatment fact sheets have been a regular feature in the National Drinking Water Clearinghouse (NDWC) newsletter *On Tap* for more than four years. NDWC Technical Assistance Specialist Mohamed Lahlou, Ph.D., researches, compiles, and writes these very popular items.

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ULTRAVIOLET IRRADIATION

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Ultraviolet irradiation (UV) is a potential alternative to chlorination for drinking water disinfection. UV provides disinfection without producing the problematic disinfection by-products of chemical disinfectants such as chlorine. During retrofitting of UV to an existing potable water treatment process or during design of a new installation, there can be significant benefits in reexamining the overall disinfection strategy for the treatment plant and the water distribution system (1).

MECHANISM

Light whose wavelengths are longer than 700 nm is in the infrared and radio emission range. Light of wavelengths shorter than 400 nm is in the ultraviolet range. This range is subdivided into UVA (320–400 nm) light, which is responsible for sun tanning, UVB (280–320 nm) light, which causes sun burning and the danger of skin cancer, and UVC (200–280 nm), which is absorbed by DNA and causes genetic damage and inactivates bacteria and viruses (2). UVC light is often called “germicidal” radiation. Organic molecules absorb energy primarily in the 200 to 300 nm range, and this range evidences the most disinfectant or germicidal properties. Bacterial disinfection is greatest at 260 nm, although other wavelengths also affect cells. A given individual microorganism is almost transparent to UV; it absorbs only a small fraction of the incident UV irradiance. Thus, germicidal effectiveness is directly proportional to the absorbance of the organism, which often peaks around 260 nm and accounts for the maximum germicidal effectiveness at that wavelength.

DNA is a nucleic acid polymer in a double-stranded helix linked together by a sequence of four constituent bases (adenine, cytosine, guanine, and thymine), which constitute the genetic code (2). Of these four bases, thymine undergoes a unique photochemical reaction when exposed to germicidal wavelengths of UV light. If two thymine bases are located adjacent to each other, absorption of a UV photon by one of the thymines leads to formation of a chemical bond between the two thymines (called a thymine dimer). This disrupts the structure of the DNA, so that if enough thymine dimers are formed, the DNA cannot replicate in cell mitosis. This is the fundamental mechanism of UV disinfection or inactivation.

UV DOSAGE

The amount of damage created by UV radiation and hence, the effectiveness of the disinfection process are related to the intensity of light and the exposure time to that intensity. UV dose is defined as the product of the average intensity of light within the reactor and the duration of exposure to that intensity (UV dose = average UV intensity × exposure time). The units of intensity are milliwatts per square centimeter, and those of exposure time are seconds. Dose therefore has the units of milliwatt seconds per square centimeter ($\mathrm{mW{\cdot}s/cm^2}$). Typical UV doses for drinking water range between 16 and 40 $\mathrm{mW{\cdot}s/cm^2}$ depending on the application, water quality, target disinfection level, etc.

MEASUREMENT AND ESTIMATION OF UV DOSE

In a UV reactor, UV irradiance at a certain point can be measured with a radiometer; however, the UV irradiance detected is only measured at a specific point, and only those photons that enter the detector from a narrow acceptance angle can be detected (3,4). This makes it difficult to obtain a direct “measurement” of the UV dose in a reactor configuration (3). Actinometry is a direct method for estimating UV doses. Actinometry measures UV light through a photochemical reaction for which the quantum yield (molecules of product formed per photon absorbed) is well established. A chemical mixture sensitive to UV light at the wavelength of interest is exposed, and the resulting photochemical changes are determined analytically. A quartz cell containing the chemical mixture is inserted into the reactor and exposed to the UV light. The chemical change produces a product over the period of exposure. From the product yield and the quantum yield, one can obtain the total photons incident at that point (3).

Several manufacturers also recommend employing mathematical models such as a multiple point source summation (MPSS) model for estimating UV doses (3,5). Most UV light sources are long narrow lamps. The light output from such a lamp may be approximated by a large number (n) of “point sources” equally spaced along the lamp axis. The light from each point source is assumed to radiate equally in all directions, and the irradiance across a small volume element, a section of an area to be irradiated, in the reactor is then obtained by summing the irradiance at that volume element from all n point sources. Proper account has to be taken of reflection, refraction, and absorption of a beam as it propagates toward the target volume element (3). Once the irradiance is calculated for each volume element in a large three-dimensional grid filling the reactor, the average irradiance is obtained by averaging the irradiance of each volume element over the entire grid. If more than one lamp is in the reactor, the irradiance at a given point is the sum of the irradiance from each lamp.

EFFECTIVENESS

UV irradiation is effective against bacteria at UV doses of 3 to 30 $\mathrm{mW{\cdot}s/cm^2}$ and against viruses at 30 to 100 $\mathrm{mW{\cdot}s/cm^2}$ (2). However, it was thought that protozoa such as *Giardia* and *Cryptosporidium* were unsusceptible to this approach. This inaccurate perception was linked to assays that evaluated UV treatments based on the physical damage they caused to the organisms' outer surfaces. Studies measuring infectivity, however, confirm that UV radiation penetrates the outer walls of *Giardia* and *Cryptosporidium*, causing internal damage and eliminating their threat, even when they are exposed to doses of 30 mW·s/cm^2 or less.

Generally, it has been found that the more complex the microorganism, the more sensitive it is to UV inactivation. Thus, viruses are the least sensitive, then bacterial spores, and finally bacteria are very sensitive. Until recently, protozoa, such as *Cryptosporidium parvum* and *Giardia lamblia*, appeared to go against this trend as it was thought they were very insensitive to UV because of difficulty in penetrating the shell in their cyst or oocyst state.

TYPICAL TREATMENT SYSTEM

A typical UV treatment system consists of a reactor vessel, where a UV lamp irradiates the flowing water. Ideally, uneven distribution is prevented by radial mixing within the reactor, so that all objects moving through it receive equivalent irradiation.

UV SOURCES

Light sources can vary widely. They encompass high- and low-vapor- pressure lamps, broadband sources covering the germicidal region from 200 to 300 nm, and narrowband emitters targeting sensitive wavelengths. UV light is most commonly generated by low- and medium-pressure mercury vapor lamps. In low-pressure mercury lamps, the energy is emitted primarily at 254 nm. A 4-foot, 40 watt (W) fluorescent lamp is a low-pressure mercury lamp with a "fluorescing" pigment on the inner surface. In medium-pressure mercury lamps, the emission is more widely distributed across the 200 to 600 nm range, and the power density is much higher. For example, a 4-foot lamp can carry as much as 30 kilowatts (kW) of electrical power.

FACTORS AFFECTING UV

Dissolved substances in the water—especially organic carbon and nitrates—can absorb UV light. Turbidity also plays a role in the transmittance of light, but mostly due to scattering or reflecting properties. In water, the particles that make up turbidity can also block or hide microbes (some of which can attach to a particle) and then prevent exposure to UV irradiation. However, until the turbidity reaches 5 NTUs (nephelometric turbidity units) or greater, this effect is usually negligible. Other factors include average UV intensity within the reactor received by the microbes in the water, hydraulic behavior of the fluid as it flows through the reactor and the amount of turbulence created, short-circuiting and retention time distribution, pretreatment processes prior to UV disinfection, particulate count and size distribution, and the microbial characteristics of the water to be disinfected (1).

CONCLUSION

UV technology is just beginning to be applied on a large scale to drinking water. The cost of obtaining a total biological barrier with UV disinfection is estimated to be same or less than traditional disinfection methods such as chlorination or ozonation. Because of this, UV disinfection of drinking water could become the most significant advance in protecting drinking water sources since the introduction of chlorination.

BIBLIOGRAPHY

1. Cairns, W.L. (1994). Ultraviolet technology for water supply treatment. *20th Annu. Convention and Exhibition, Water Qual. Assoc.*, March 15–20, 1994, Phoenix, AZ.
2. Bolton, J.R., Dussert, B., Bukhari, Z., Hargy, T., and Clancy, J.L. (1998). Inactivation of *Cryptosporidium parvum* by ultraviolet light: Comparison of laboratory- and pilot-scale results on finished water. *AWWA Annu. Conf.*, Dallas, June 1998.
3. Bolton, J. (2000). Calculation of ultraviolet fluence rates distribution in an annular reactor: Significance of refraction and reflection. *Water Res.* **34**(13): 3315–3324.
4. Severin, B.F. and Roessler, P.F. (1998). Resolving UV photometer outputs with modeled intensity profiles. *Water Res.* **32**(5): 1718–1724.
5. Blatchley, E.R. (1997). Numerical modeling of UV intensity: Application to collimated beam reactors and continuous-flow systems. *Water Res.* **31**(9): 2205–2218.

READING LIST

American Public Health Association (APHA). (1995). *Standard Methods for the Examination of Water and Wastewater*. 19th Edn. AWWA, Denver, CO.

Anderson, W.B., Huck, P.M., Dixon, D.G., and Mayfield, C.I. (in press). Endotoxin inactivation in water using medium pressure UV lamps. *Appl. Environ. Microbiol.*

Hrudey, S.E., Payment, P., Huck, P.M., Gillham, R.W., and Hrudey, E.J. (2003). A fatal waterborne disease epidemic in Walkerton, Ontario: Comparison with other waterborne outbreaks in the developed world. *Water Sci. Technol.* **47**(3): 7–14.

Ollos, P.J., Huck, P.M., and Slawson, R.M. (2003). Factors affecting biofilm accumulation in model distribution systems. *JAWWA* **95**(1): 87–97.

Park, C.H. and Huck, P.M. (2003). A conceptual model for *Cryptosporidium* transport in watersheds. *Water Qual. Res. J. Can.* **38**(1): 77–113.

Parrotta, M.J. and Bekdash, F. (1998). UV disinfection of small Groundwater supplies. *JAWWA* **90**(2): 71–81.

US EPA. (1996). *Ultraviolet Light Disinfection Technology in Drinking Water Application—an Overview*. EPA 811-R-96-002.

Verkoeven, J.W. (1996). Glossary of terms used in photochemistry. *Pure Appl. Chem.* **68**(12): 2223–2286.

Zimmer, J.L., Slawson, R.M., and Huck, P.M. (2003). Inactivation and potential repair of *Cryptosporidium parvum* following low- and medium-pressure UV irradiation. Submitted to *Water Res.*

WATER DISINFECTION USING UV RADIATION—A SRI LANKAN EXPERIENCE

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BACKGROUND

Treated public water supplies are available in most urban areas in Sri Lanka. National Drinking Water Quality Standards have been established, based on WHO Guidelines for Drinking Water Quality, and usually the quality of water leaving the treatment plant is up to the Standards. However, for various reasons such as old pipelines, leaks in the distribution system, low pressure leading to back-siphonage and cross connections, the risk of subsequent contamination of the water is very high. In addition, many users depend on either overhead tanks, which are filled at night, or sump-pump-overhead tank arrangements to store the water, due to low pressure in the distribution system and unreliable supplies. Dual water supplies, where private surface or groundwater supplies are used to supplement the public water supply, are also common due to the inadequacy of the public water supply. Often, the same plumbing system is used for the two systems. The public water supply is treated, but the well water is usually untreated and is pumped directly into the sump or the overhead tank.

The risks of contaminating the drinking water in these situations are considerable. Residual chlorine doses applied at treatment plants are often insufficient to maintain the safety of the water, and many domestic consumers boil water before drinking it. Although boiling is a very reliable method of disinfection of small quantities of water, it is not practical for large-scale uses, such as hostels, canteens, hospitals, and factories. Even though bottled water is available in the market, it is expensive, and the reliability of the cheaper products is questionable. Therefore, it has become necessary to find an appropriate method for disinfecting such water supplies in the light of possible outbreaks of waterborne diseases among users, particularly where dual water supplies are used.

BREAK-POINT CHLORINATION

Chlorination is the most common disinfection method used in water treatment. Chlorine is used in the gaseous form, in solid form as calcium hypochlorite [$Ca(OCl)_2$], or in liquid form as sodium hypochlorite [$NaOCl$] solution.

Chlorine, a very strong oxidizing agent, reacts with many organic and inorganic substances in water, in addition to disinfecting water. The "chlorine demand" of these other substances has to be satisfied before excess free chlorine is available for disinfection.

Thus the total amount of chlorine added to water is not available for disinfection. Initially, the added chlorine is used immediately to oxidize inorganic and organic substances in reduced form. When this immediate chlorine demand is satisfied, the added chlorine combines with ammonia and similar compounds in the water to form chloramines. Chloramines in water are called "combined available chlorine," because they are also effective in disinfection, although not to the same extent as free chlorine. Further addition of chlorine has the effect of oxidizing the chloramines formed, thus reducing the available chlorine. When all chloramines are oxidized, further addition of chlorine produces "free available chlorine", which is the most effective form of chlorine for disinfection. The point at which all oxidation is completed and free available chlorine starts to appear is called the "break point," and chlorination beyond this point is called "break-point chlorination."

Thus, to produce a free chlorine residual which would be available to disinfect any contamination within the distribution system at the consumer's premises, such as in the household plumbing system, overhead tank, or sump, sufficient chlorine should be added to achieve break-point chlorination.

UV RADIATION TECHNOLOGY

UV radiation has been established as an effective bactericide and viricide. UV radiation penetrates the cell wall and is absorbed by cellular nucleic acids. Radiation absorption prevents replication, thus killing the cell. However, the effectiveness of UV radiation in killing spore forming bacteria such as *Giardia lamblia* has not yet been established. UV radiation is not a chemical agent, so it produces no toxic residuals.

A special lamp is used to transfer electromagnetic energy to the target organism's cells. Mercury arc lamps are the most commonly used type of lamp because about 85% of the energy output is of the 253.7 nm wavelength, which is within the optimum germicidal range of 250–270 nm.

The effectiveness of radiation is a direct function of the energy dose absorbed by the organism, which is measured as the product of the lamp's intensity and the time of exposure. Intensity is the rate at which photons are delivered to the target organism. It is governed by the lamp's power, the depth of water, and the presence of substances that absorb the energy, such as suspended solids, color, turbidity, and soluble organic matter. The radiation dose absorbed by the water is the water's UV demand (which is similar to the chlorine demand) and is quantified as the absorption of UV energy (wavelength 253.7 nm) in a given depth of water. The energy dose also depends on the exposure time of the water to the UV radiation, although the required time is only seconds, rather than minutes, for effective disinfection. However, water that has high concentrations of substances like suspended solids, color, turbidity, and soluble organic matter may not receive an adequate radiation dose for effective disinfection.

If the radiation dose is not sufficient to destroy the target organism's DNA macromolecules, but only damages them, disinfection would not be effective. Photoenzymatic repair, called "photoreactivation," occurs from exposure to sunlight, incandescent, or fluorescent light for certain types of bacteria. Therefore, as a rule of thumb, the UV dosage is increased to more than that required to achieve the specified percentage of kill.

MAIN ADVANTAGES AND DISADVANTAGES OF UV RADIATION OVER CHEMICAL METHODS OF DISINFECTION

The main advantages of UV radiation over chemical methods of disinfection are the simplicity of the system for installation and operation, minimal space requirement, absence of any changes in the characteristics of the water and any residual by-products due to reactions in the water, and very short required contact time (seconds rather than minutes) for effective disinfection.

On the other hand, chlorination requires chemical handling and dosing equipment, and ozone and chlorine dioxide need to be produced at the site due to their chemical instability. All chemical disinfectants produce disinfection by-products, by oxidation, reduction, or disproportionation of the disinfectant itself and by reaction of the disinfectant with substances that are already in the raw water. For example, chlorination adds chloride ions to the water and produces trihalomethanes (THMs) and other halogenated organics, which are known to have harmful health effects, when the water contains organic matter. Chlorine dioxide produces chlorite and chlorate ions, which have been identified as harmful, and ozone is also known to produce some harmful by-products if certain organic substances, such as the pesticide heptachlor, are present in the raw water.

The major disadvantage of UV disinfection is the absence of a residual disinfecting mechanism left in the water to be used downstream, as would occur in chlorination and ozonation to some extent. Therefore, it is very important that the UV radiation is carried out as close to the point of consumption as practically possible to prevent recontamination of the treated water. Other disadvantages are the necessity of pretreatment to avoid shielding of microbiological cells by solids and the high cost of the equipment.

CASE STUDY

A UV water purification system that had a maximum flow rate of 60 L/h was used in the laboratory as a case study. The system consisted of an activated carbon filter unit and a UV light unit, as shown in (Fig. 1). Observations were also made on a system whose capacity was 300 L/h; it was installed at the University canteen.

The study was carried out for a period of 2 years. The main objectives of the study were

1. to find the potential of the UV water purification system to destroy pathogens at various flow rates for various sources of water;
2. to study the time taken by the UV equipment to produce disinfected water at the point of consumption; and
3. to compare the performance and cost of disinfection using UV radiation with that of chlorination using bleaching powder.

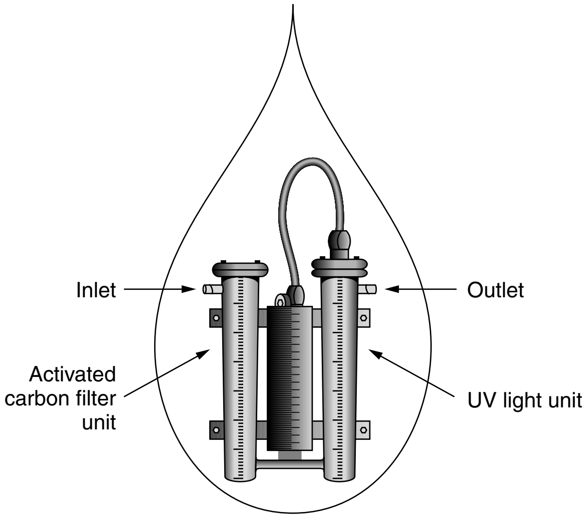

Figure 1. UV water purification system used in the case study.

Table 1. Typical Water Quality at the Water Sources Used in the Case Study

Water Quality Parameter	Location Boat Yard	Ranmal	San Michele	University Well
Total coliform, per mL	167	127	510	97
Fecal coliform, per mL	134	116	481	92
Turbidity, NTU	4.1	3.7	5.7	1.1
DO, mg/L	5.7	6.3	7.7	5.9
Alkalinity, mg/L $CaCO_3$)	0.4	0.4	0.25	0.3
Ammonia, mg/L	1.04	0.56	0.28	1.20
Conductivity	218	1678	925	168.6
pH	7.14	7.43	7.45	7.5
Color, Hazen	40	20	15	5
Temperature, °C	29	29	28.5	29

A simple apparatus was set up using a ground level tank, a pump, a constant head overhead tank to feed the water through the UV purification system at a constant head, and devices to control and measure the flow rate and collect samples of raw and treated water for analysis at various times. Surface water from three locations of a large lake called Bolgoda Lake, several kilometers away from each other, and ground water from a dug well in the University premises were used as raw water sources. A map showing the locations of raw water sources for the case study is given in (Fig. 2). The typical water quality parameters at these water sources are given in Table 1.

Studies on the performance of the UV purification system in the laboratory showed that the total and fecal coliform numbers in the treated effluent from samples of raw water from all four sources, which initially contained high total coliform and fecal coliform, as shown in Table 1, were all zero after passing through the system. The tests were carried out at several flow rates, from as low as

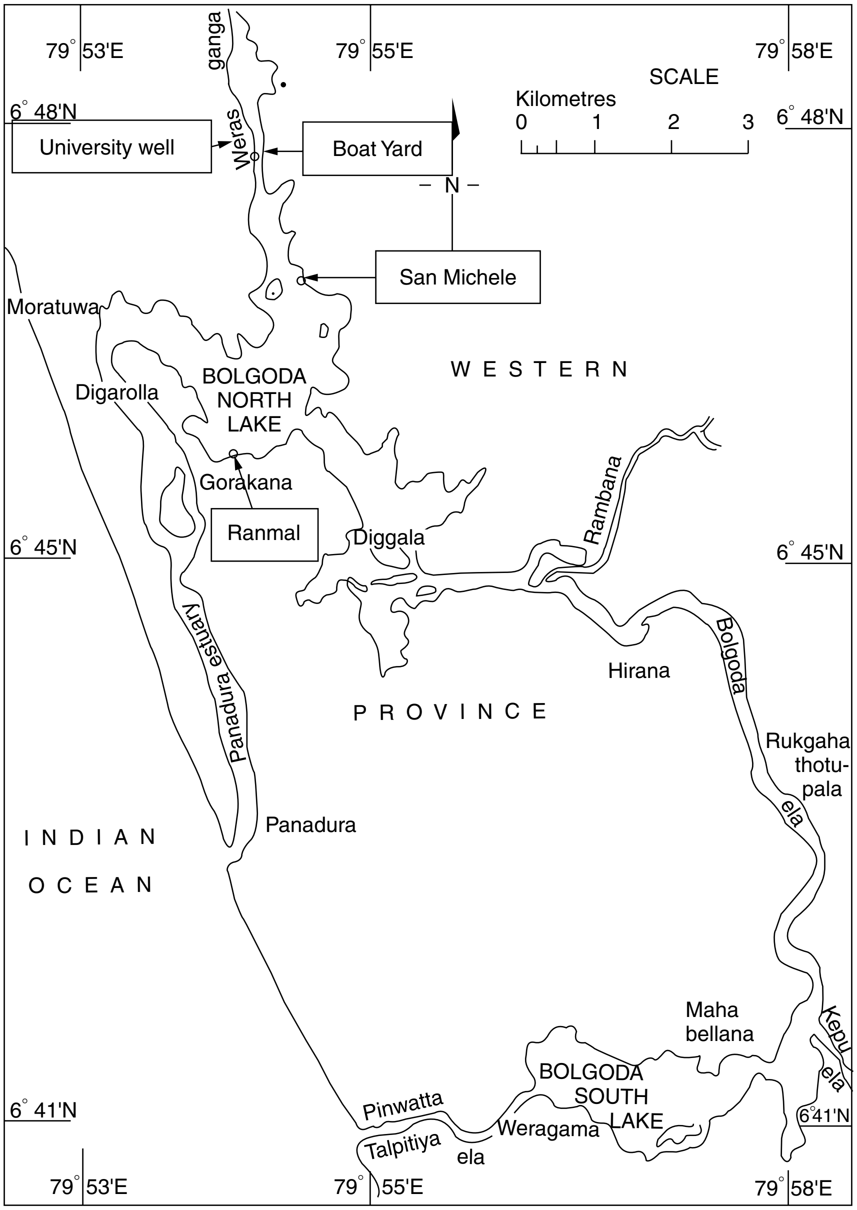

Figure 2. Map of locations of raw water sources taken for the case study.

10 liters per minute to 110 liters per minute, which is almost twice the maximum rate specified for the UV system. The resulting total and fecal coliform contents were always zero, when sampled after 5 minutes of UV lamp operation. The performance of the UV system when used for water from Bolgoda Lake at San Michele and Ranmal Hotel locations and the University well water are shown graphically in (Fig. 3). As can be observed, the total and fecal coliform counts were slightly reduced by the activated carbon filter, but the water cannot be considered safe because the coliforms were still present at all flow rates. However, when sampled 5 minutes after the UV lamp was switched on, none of the samples contained total or fecal bacteria. There is a slight improvement in the turbidity of the water after the activated carbon filter, but no significant change can be seen from the UV radiation.

During the first 5 minutes of system operation, initial studies showed that the coliform numbers do not immediately drop to zero but showed a gradual drop to zero, as shown in (Fig. 4). It was apparent that up to 4 minutes were needed to obtain water that was free from total and fecal coliform bacteria. However, further studies carried out using the same UV system showed that the total and fecal coliform numbers fall to zero when effluent samples are collected as early as after 30 seconds using the same water sources. Tests carried out using the larger UV system which is installed in the University canteen and has a design flow rate of 300 L/h, showed that the total and fecal coliform numbers in the water after passing through the system were zero when tested after 1, 2, 3, 4 and 5 minutes at the design flow rate, as well as double the design flow rate (600 L/h); this is the maximum flow rate possible from the tap. Thus, no

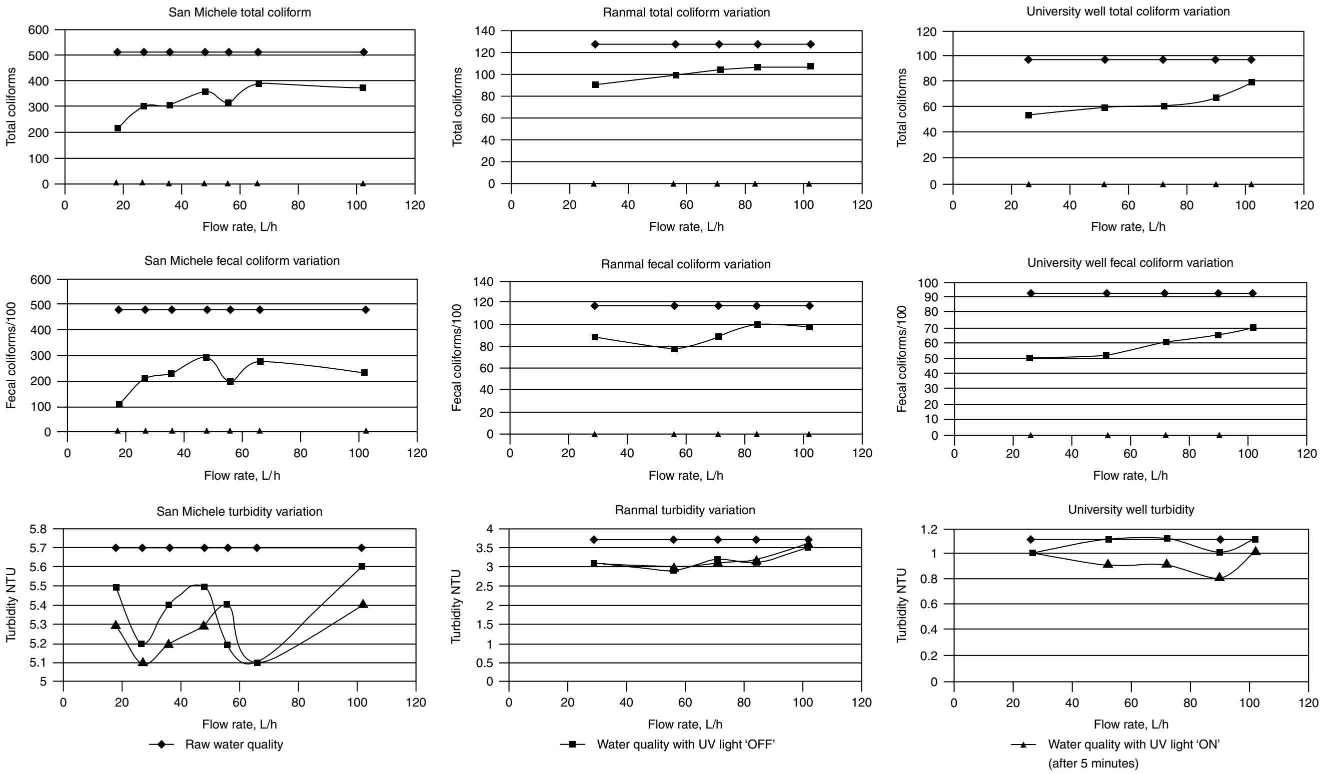

Figure 3. Performance of the UV system on water from different sources at different flow rates.

conclusive evidence could be gathered to determine the required lag time for the water. The time lag experienced earlier could be partly due to the time taken to replace the untreated water in the pipeline, particularly, at low flow rates.

When the system was used with the UV light in the "off" position, there was some improvement in the water quality, including a 20–40% reduction in the coliform content. However, this was not reduced to acceptable levels in any of the trials, and the reduction in total and fecal coliforms was lower at higher flow rates. Thus, it could be inferred that the 100% coliform removal obtained was due to UV radiation. Conversely, it is important to establish the fact that the water would not be safe from pathogenic organisms if the UV light were not turned "on." The function of the activated carbon filter is to remove turbidity, color, and organic matter in the raw water, so that the UV disinfection can be more effective.

A comparative study was done on the same source of raw water, to find the chlorine requirement of the water. It was attempted to find the "break point" for chlorination, but no clear break point was identified, presumably due to the low concentrations of ammonia that were present in the water sources. In raw water from the San Michele location of Bolgoda Lake, a slight depression of residual chlorine could be noticed (see Fig. 5) at an added chlorine concentration of 2.5 to 3.0 mg/L. However, at the Boat Yard location, there was no noticeable break point, but a high initial chlorine demand was noticed, probably due to the more polluted and stagnant status of the water at this location.

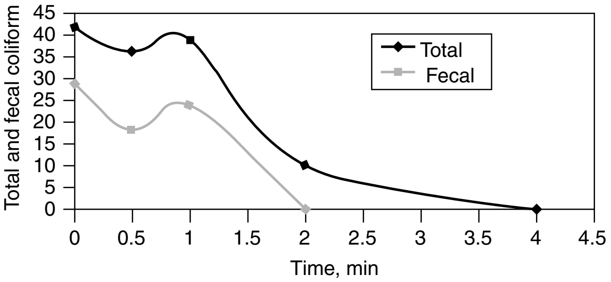

Figure 4. Variation of total and fecal coliform content in treated effluent within the first 5 minutes (initial trials).

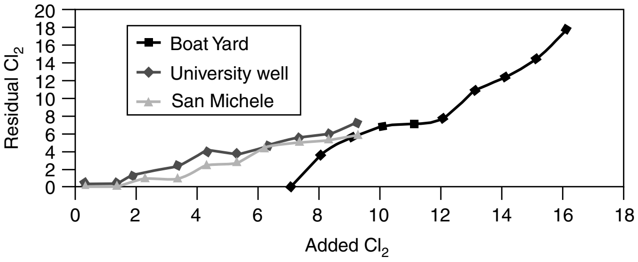

Figure 5. Chlorine demand of the source water.

The following example was used in comparing the cost of the UV treatment and chlorination using bleaching powder:

Water Source: Bolgoda Lake at San Michele location
Selected point of consumption: University canteen
Number of hours used per day: 16
Average flow rate: 300 L/h

— Annual consumption of water: 1,752,000 liters

UV treatment		
Cost of installation of the UV system	SLR 32344.00	US$ 359.38
Assumed lifetime of the unit	5 years	—
Price of a UV bulb	SLR 1200.00	US$ 13.33
Power of a UV bulb for 300 L/h unit	8 watts	—
Lifetime of a UV bulb	8000 hours operation	—
⇒ Number of bulbs required for 5 years	4	—
Cost of bulb per year	SLR 960.00 per annum	US$ 10.60
Annual cost of power for UV unit	SLR 280.00 per annum	US$ 3.11
At a discount rate of 15% per annum,	—	—
capital cost of UV unit as an annuity	SLR 9660.00 per annum	US$ 107.33
⇒ Total Annual Cost of UV unit	**SLR 10,900.00 per annum**	**US$ 121.11 per annum**

Chlorination using bleaching powder		
Required chlorine dosage at break point	2.5 mg/L	—
Required amount of chlorine per year	4.38 kg per annum	—
Percentage of chlorine in bleaching powder used	Approx. 8.9%	—
Required amount of bleaching powder,	44.88 kg per annum	—
	—	—
Total amount of bleaching powder required allowing 10% wastage	50 kg per annum	—
Cost of bleaching powder @Rs. 80 per kg	SLR 4000.00 per annum	US$ 44.44
Assumed annual O&M cost	SLR 12,000.00 per annum	US$ 133.33
⇒ Total Annual Cost of Chlorination	**SLR 16,000.00 per annum**	US$ 177.77

This example showed that the UV radiation equipment is more economical for this application than using bleaching powder for disinfection, considering the local conditions.

CONCLUSION

The case study showed that ultraviolet radiation preceded by activated carbon filtration was a very effective method of disinfecting water from surface as well as groundwater. Thus, it is a very useful method of disinfection when dual water supplies are used, and the treated public water supplies are supplemented by well or surface water, which does not require conventional treatment. The activated carbon unit reduces the color, turbidity, and dissolved organic substances that interfere with disinfection by ultraviolet radiation. However, if the water contains high amounts of the above substances, the filter unit will need frequent replacement. Therefore, it is most suitable for use with well water, rather than surface water. UV disinfection itself is more suitable for well water disinfection, as the disinfection effect of UV radiation on spore forming bacteria such as *Giardia lamblia* is not yet well established.

In comparing the cost of disinfection using UV radiation and chlorination, even though the UV equipment needs a rather high capital investment, the total annual cost of the UV system is lower than that of disinfection using bleaching powder. Considering the ease of operation and ability to have the unit on-line, it is a very attractive option for applications where a large number of users are expected to use water during short periods of time, such as in canteens and hostels.

However, care must be taken to maintain the system and to make sure that the UV lamp is turned on when the water is being used for consumption.

Acknowledgments
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BIBLIOGRAPHY

1. Black & Veach. (1995). EPRI's Community Environment Center December 1995, *UV Disinfection for Water and Waste Water Treatment*. Report CR—105252 www.energy.ca.gov/water/publication/public.
2. Cairns, W.L. *Comparing Disinfection by Ultraviolet Light and Chlorination—The Implications of Mechanism For Practice*. Trojan Technologies, London, Ontario, Canada.
3. Fahey, R.J. (1990). The UV effect on wastewater. *Water Engineering and Management* **137**(12): 1–4.
4. Grombach, P. (1983). *Disinfection in Water Treatment Plants*. Asian National Development. 32.
5. Harris, G.D. et al. (1987). The influence of photoreativation and water quality on UV disinfection of secondary municipal wastewater. *J. Water Pollution Control Federation* **59**: 781.
6. Metcalf & Eddy. (1990). *Waste Water Engineering Treatment, Disposal, Reuse*. New York, pp. 351–352.
7. Pontius Fedrick, W. (1990). *Water Quality and Treatment*. Washington, DC, p. 924.
8. Teresa, G. (1998). Canadian water and wastewater association. *A Technical & Socio-Economic Comparison of Options*, Chapter 5.
9. Thampi, M.V. (1990). Basic guidelines for specifying the design of UV disinfection systems. *J. Pollution Engineering*: 65.
10. US EPA. (1986). *Municipal Wastewater Disinfection Design Manual*. EPA/625/1861021, Washington, DC.
11. Water Pollution Control Federation. (1986). *Wastewater Disinfection*. Manual of Practice NO. FD-10, Washington, DC.
12. White, G.C. (1986). *Handbook of Chlorination*, 2nd Edn. Von Nostrand Reinhold Company, New York, p. 186.
13. World Health Organization. (1993–1998). Guidelines for drinking-water quality, 2nd Edn. Vol. 1: Recommendations (1993), pp. 122–130 & 114–121; Vol. 2: *Health criteria and other supporting information*, (1996) pp. 940–949 & 908–915; Addendum to Vol. 2 (1998) pp. 281–283.
14. *Survey of Effluent Disinfection Practices*. (1996). www.fuseinc.com/1996survey.htm - 95 k.
15. *Water disinfection methods*. www.pureflow.com/Artl.htm - 18 k.
16. *Comparing Disinfection by UV Light and Chlorination. www.trojanuv.com/papers/COMP_UY_CHL.htm - 54 k.*

DRINKING WATER QUALITY STANDARDS (DWQS)-UNITED STATES

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In 1974, the U.S. Congress, through the Safe Drinking Water Act (SDWA), created the first-ever mandatory national program to protect consumers from harmful contaminants in drinking water. There have been several amendments to the Act—the most recent in 1996. The SDWA requires the U.S. Environmental Protection Agency (EPA) to set national drinking water quality standards (DWQS). The EPA has set primary and secondary DWQS for chemical, physical, radiological, and microbiological contaminants listed in Tables 1 and 2. More Americans are now served by water systems without health risk violations since the EPA (2) began tracking violations around 1980.

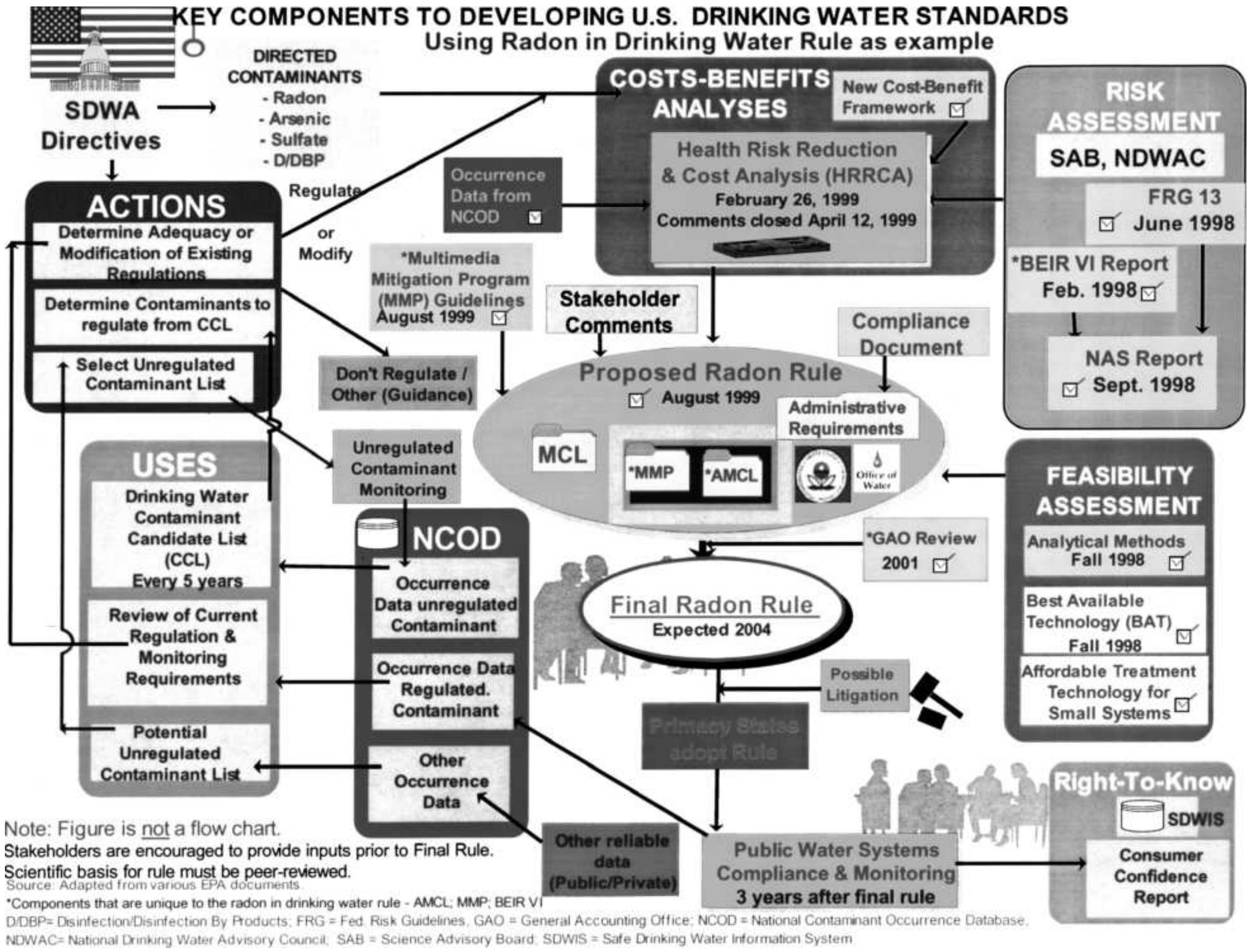
INTRODUCTION

Public Water Systems (PWS) are required to comply with the SDWA. A PWS, by definition, provides water to at least 15 connections or 25 persons for at least 60 days out of the year PUBLIC WATER SUPPLY—UNITED STATES. PWS provide domestic water to about 275 million Americans (3); about 42 million people, or 16% (4) depend on private sources, such as house wells. EPA does not regulate the quality of water in private wells, but many state and local governments have regulations to protect users of private wells.

Media coverage of waterborne disease outbreaks, such as the 1993 outbreak of cryptosporidiosis in Milwaukee, and popular culture movies, such as "A Civil Action" and "Erin Brockovich" increased public interest in the health risks of contaminated water. At least 50 people died and more than 400,000 people suffered from gastrointestinal illness during the 1993 incident in Milwaukee (7). Many consumers resorted to drinking bottled water. Bottled water is regulated by the U.S. Food and Drug Administration, and is required to meet DWQS. Some consumers rely on "Point of Use" or "Point of Entry" devices to improve the quality of domestic water.

EPA considers costs and health benefits when setting DWQS (see Fig. 1). The annual costs of operating U.S. PWS exceed \$3.5 billion (5). The EPA (6) estimated that it would cost about \$31 billion (Table 3) over a 20-year period to comply with existing and proposed SDWA regulations. The SDWA requires PWS to have the technical, financial, and managerial capability to provide safe drinking water (2). There are many programs to assist PWS in complying with DWQS, such as the drinking water State Revolving Funds that has a budget authority of \$9.6 billion for the fiscal period 1994–2003 [http://www.epa.gov/OW/regs/intro.html].

The SDWA includes a multiple-barrier protection framework against pollution—source water protection, treatment, distribution system integrity, and public information. PWS conduct Source Water Assessments to reduce the potential for contamination (WELL HEAD PROTECTION). The Underground Injection Control (UIC) program of the SDWA and other Federal environmental laws, such as the Clean Water Act (CWA), are important for source water protection (1). U.S. EPA is using source water protection [WELLHEAD PROTECTION], and water safety and security to leverage the linkages between the CWA and SDWA. The Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (SDWA Section 1433(a)) requires certain CWS to conduct Vulnerability Assessments (VAs), and prepare/revise Emergency Response Plans (ERPs) to protect the security ["quality"] of drinking water. Under the CWA, U.S.



Note: Figure is not a flow chart.
Stakeholders are encouraged to provide inputs prior to Final Rule.
Scientific basis for rule must be peer-reviewed.
Source: Adapted from various EPA documents.
*Components that are unique to the radon in drinking water rule - AMCL; MMP; BEIR VI
D/DBP= Disinfection/Disinfection By Products; FRG = Fed. Risk Guidelines, GAO = General Accounting Office; NCOD = National Contaminant Occurrence Database, NDWAC= National Drinking Water Advisory Council; SAB = Science Advisory Board; SDWIS = Safe Drinking Water Information System

Figure 1. Key components to developing and monitoring drinking water standards.

EPA established the Human Health Water quality criteria [http://epa.gov.waterscience/humanhealth/15table-fs.htm], which though not DWQS are numeric values that protect human health from the harmful effects of pollutants in ambient water based solely on science without considering socio-economic impacts. DWQS standards are often regarded as "Applicable or Relevant and Appropriate Requirements" (ARARs) in cleanup decisions affecting polluted water. Water conservation programs may reduce the need to use poorer quality sources for drinking water.

DEFINITIONS

Many terms are used to describe the numerical and/or narrative qualities of drinking water. Such terms include regulations, standards, goals, levels, limits, advisories, etc. (8). Terms used by the EPA (9,10) in published drinking water regulations include

Maximum Contaminant Level Goal (MCLG): The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow a margin of safety and are nonenforceable public health goals. Table 1 is a list of the MCLGs.

Maximum Contaminant Level (MCL): The highest level of a contaminant that is allowed in drinking water. EPA sets the MCL as close to the MCLG as feasible, using the best available treatment technology (BAT) and considering cost. MCLs are enforceable standards and are listed in Table 1.

Maximum Residual Disinfectant Level Goal (MRDLG): The level of a drinking water disinfectant below which there is no known or expected risk to health (Table 1). MRDLGs do not reflect the benefits of using disinfectants to control microbial contaminants.

Maximum Residual Disinfectant Level (MRDL): The highest level of a disinfectant allowed in drinking water (Table 1).

Secondary MCLs or "SMCLs" are established for nuisance chemicals only as guidelines for aesthetic considerations, such as taste, color, and odor and are not considered to present a risk to human health at the SMCL. SMCLs (Table 2) are unenforceable at the federal level. Some states enforce SMCLs at the state level (1).

Treatment Technique (TT): A required process to reduce the level of a contaminant in drinking water. EPA

Table 1. United States Environmental Protection Agency National Primary Drinking Water Standards[1]

Microorganisms	MCLG, mg/L	MCL or TT, mg/L	Organic Chemicals	MCLG, mg/L	MCL or TT, mg/L
Cryptosporidium	zero	TT	Acrylamide	zero	TT
Giardia lamblia	zero	TT	Alachlor	zero	0.002
Heterotrophic plate count	n/a	TT	Atrazine	0.003	0.003
Legionella	zero	TT	Benzene	zero	0.005
Total coliforms[2]	zero	5.00%	Benzo(a)pyrene (PAHs)	zero	0.0002
Turbidity	n/a	TT	Carbofuran	0.04	0.04
Viruses (enteric)	zero	TT	Carbon tetrachloride	zero	0.005
	–	–	Chlordane	zero	0.002
Inorganic chemicals	–	–	Chlorobenzene	0.1	0.1
Antimony	0.006	0.006	2,4-D	0.07	0.07
Arsenic (01/01/06)	0	0.01	Dalapon	0.2	0.2
Asbestos (fiber > 10 micrometers)	7 MFL	7 MFL	1,2-Dibromo-3-chloropropane (DBCP)	zero	0.0002
Barium	2	2	*o*-Dichlorobenzene	0.6	0.6
Beryllium	0.004	0.004	*p*-Dichlorobenzene	0.075	0.075
Cadmium	0.005	0.005	1,2-Dichloroethane	zero	0.005
Chromium (total)	0.1	0.1	1,1-Dichloroethylene	0.007	0.007
Copper (action level = 1.3)	1.3	TT	*cis*-1,2-Dichloroethylene	0.07	0.07
Cyanide (as free cyanide)	0.2	0.2	*trans*-1,2-Dichloroethylene	0.1	0.1
Fluoride	4	4	Dichloromethane	zero	0.005
Lead action level = 0.015	zero	TT	1,2-Dichloropropane	zero	0.005
Mercury (inorganic)	0.002	0.002	Di(2-ethylhexyl) adipate	0.4	0.4
Nitrate (measured as nitrogen)	10	10	Di(2-ethylhexyl) phthalate	zero	0.006
Nitrite (measured as nitrogen)	1	1	Dinoseb	0.007	0.007
Selenium	0.05	0.05	Dioxin (2,3,7,8-TCDD)	zero	3E-08
Thallium	0.0005	0.002	Diquat	0.02	0.02
	–	–	Endothall	0.1	0.1
Radionuclides[3]	–	–	Endrin	0.002	0.002
Alpha particles	zero	15 pCi/L	Epichlorohydrin	zero	TT
Beta particles and photon emitters	zero	4 mrem/yr	Ethylbenzene	0.7	0.7
Radium-226 and Radium-228 (combined) as of 12/08/03	zero	5 pCi/L	Ethylene dibromide	zero	0.00005
Uranium (12/08/03)	zero	30 μg/L	Glyphosate	0.7	0.7
	–	–	Heptachlor	zero	0.0004
Disinfectants & DBP	MRDLG	MRDL	Heptachlor epoxide	zero	0.0002
Bromate	zero	0.01	Hexachlorobenzene	zero	0.001
Chloramines (as Cl_2)	4	4	Hexachlorocyclopentadiene	0.05	0.05
Chlorine (as Cl_2)	4	4	Lindane	0.0002	0.0002
Chlorine dioxide (as ClO_2)	0.8	0.8	Methoxychlor	0.04	0.04
Chlorite	0.8	1	Oxamyl (Vydate)	0.2	0.2
Haloacetic acids (HAA5)	n/a	0.06	PCBs	zero	0.0005
Total trihalomethanes (TTHMs)	n/a	0.08	Pentachlorophenol	zero	0.001
	–	–	Picloram	0.5	0.5
	–	–	Simazine	0.004	0.004
	–	–	Styrene	0.1	0.1
	–	–	Tetrachloroethylene	zero	0.005
	–	–	Toluene	1	1
	–	–	Toxaphene	zero	0.003
	–	–	2,4,5-TP (Silvex)	0.05	0.05
	–	–	1,2,4-Trichlorobenzene	0.07	0.07
	–	–	1,1,1-Trichloroethane	0.2	0.2
	–	–	1,1,2-Trichloroethane	0.003	0.005
	–	–	Trichloroethylene	zero	0.005
	–	–	Vinyl chloride	zero	0.002
	–	–	Xylenes (total)	10	10

Notes: TT: Treatment Technique; pCi/L: picocuries per Liter MFL:million fibers per liter; PCBs: Polychlorinated biphenyls; mrem/yr: millirems per year; DBP: Disinfection by-products; MCL: Maximum Contaminant Level; MCLG: Maximum Contaminant Level Goal; MRDL: Maximum Residual Disinfectant Level; MRDLG: Maximum Residual Disinfectant Level Goal.

[1] There are many footnotes, not reproduced here.

[2] Including fecal coliform and *E. coli*

[3] Proposed radon rule: MCLG = 0, MCL = 300 pCi/L; Alternate MCL = 4,000 pCi/L + an approved Multimedia Mitigation Program.

Log on to URL of source for full details.

Primacy states may have more stringent standards.

Adapted from: http://www.epa.gov/safewater/mcl.html specifies a TT only if it is not “economically or technologically feasible” to ascertain the concentration of a contaminant (2,8).

Action Level: “The concentration of a contaminant which, if exceeded, triggers treatment or other requirements which a water system must follow. For lead or copper, it is the level which, if exceeded in more than 10% of the homes tested, triggers treatment (9).

Alternative Maximum Contaminant Level (AMCL): Unique to radon in drinking water, it is the level of radon in drinking water that would not increase the level of radon in indoor air beyond the natural level of radon in outdoor air Radon in Water.

Health Risk Reduction and Cost Analysis (HRRCA): The goal of the HRRCA is to provide a neutral and factual analysis of the incremental costs, benefits, and other impacts of controlling contaminant levels in drinking water based on system size.

Best available technology (BAT): The field-proven feasible treatment technique for removing contaminants from drinking water below the MCL. Historically, the EPA has based feasibility on technologies appropriate for large PWS, but the 1996 SDWA requires EPA to specify compliance technologies that can be feasibly implemented by small water systems.

Health Advisories [http://www.epa.gov/ost/drinking/standards] describe the levels of a contaminant at which adverse health effects would not be anticipated for different durations of exposure (10).

Some states have additional standards. The Office of Environmental Health Hazard Assessment (OEHHA) within the California EPA sets a Public Health Goal (PHG) based exclusively on health risk assessment. A PHG [http://www.oehha.org/water/phg/allphgs.html] is set at the level at which no known or anticipated adverse effect on health will occur with an adequate margin of safety; considering possible synergistic effects resulting from exposure to two or more contaminants; and the existence of groups in the population that are more susceptible to adverse effects of the contaminant. PHG is nonregulatory, but another state agency, the California Department of Health Services (DHS), is required to use the PHG as the basis for setting MCL.

Action Level (AL): In California, an AL is a health-based advisory level for a contaminant for which an MCL has not been adopted. DHS sets an AL when one of the following occurs: (1) a chemical is found in an actual or proposed drinking water source; or (2) a chemical is in proximity to a drinking water source, and guidance is needed, should it reach the source. DHS set the AL at 4 μg/L for perchlorate, the main active explosive ingredient in rocket fuel [http://www.dhs.ca.gov/ps/ddwem/chemicals/AL/actionlevels.htm].

Table 2. Secondary Maximum Contaminant Levels

Parameter	SMCL	Noticeable Effects Above the Secondary MCL
Aluminum	0.05 to 0.2 mg/L*	Colored water
Chloride	250 mg/L	Salty taste
Color	15 color units	Visible tint
Copper	1.0 mg/L	Metallic taste; blue-green staining
Corrosivity	Non-corrosive	Metallic taste; corroded pipes/fixtures staining
Fluoride	2.0 mg/L	Tooth discoloration
Foaming agents (MBAS)	0.5 mg/L	Frothy, cloudy; bitter taste; odor
Iron	0.3 mg/L	Rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	Black to brown color; black staining; bitter metallic taste
Odor	3 TON	“Rotten-egg,” musty or chemical smell
pH	6.5–8.5	Low pH: bitter metallic taste; corrosion high pH: slippery feel; soda taste; deposits
Silver	0.1 mg/L	Skin discoloration; graying of the white part of the eye
Sulfate	250 mg/L	Salty taste
TDS	500 mg/L	Hardness; deposits; colored water; staining; salty taste
Zinc	5 mg/L	Metallic taste
Bolero[1,2]	0.001 mg/L	Odor is detected at a lower concentration than its taste
MtBE[1]	0.005 mg/L	–

Notes: MtBE: Methyl tertiary-butyl ether
TON: Threshold Odor Number
TDS: Total Dissolved Solids
[1] California SMCL
[2] Also known as Thiobencarb
Adapted from: http://www.epa.gov/safewater/consumer/2ndstandards.html
http://www.dhs.ca.gov/ps/ddwem/chemicals/MCL/secondarymcls.htm
*MCL for Aluminum in California is 1 mg/L

HISTORY OF U.S. DWQS AND SDWA

Clean drinking water used to mean clear, palatable, nonodorous water. It was not until the early 1900s that DWQS other than for general clarity existed (2), even though the first U.S. community water system (CWS) began in 1799 (8). By 1900, many of the more than 3000 CWSs then contributed to major disease outbreaks because they “provided an efficient vehicle for the delivery of pathogenic bacteria” (8).

Federal authority to regulate drinking water began with the Interstate Quarantine Act of 1893 (1). In 1914, the U.S. Public Health Services (USPHS) set bacteriological DWQS for water systems that provided drinking water to interstate carriers such as ships and trains, as directed by the Act. Those standards were commonly referred to as “Treasury Standards” (1). In 1915, the federal government committed to reviewing DWQS on a regular basis (8). USPHS revised and expanded the standards in 1925, 1946, and 1962 (1). All 50 states adopted the USPHS

Table 3. 20-Year Regulatory Need (in Millions of January 1999 Dollars)

Regulations	Current Need	Future Need	Total Need
Existing SDWA regulations	–	–	–
Surface Water Treatment Rule[1]	$14,492.1	$4,873.3	$19,365.4
Total Coliform Rule[1]	$358.1	$112.8	$470.9
Nitrate/Nitrite Standard[1]	$197.1	$31.9	$229.0
Lead and Copper Rule	$1,039.6	$186.5	$1,226.2
Total Trihalomethanes Standard	$39.1	$60.6	$99.7
Other Regulations[2]	$430.8	$85.4	$516.2
Subtotal National Need	$16,556.9	$5,350.4	$21,907.4
Costs Associated with Proposed and Recently Promulgated Regulations (Taken From EPA Economic Analyses)[3]	–	$9,324.3	$9,324.3
Total National Needs	$16,556.9	$14,674.8	$31,231.7

Note: Numbers may not total due to rounding.

[1] Regulations for contaminants that cause acute health effects.

[2] Includes regulated VOCs, SOCs, IOCs, and Radionuclides

[3] Includes regulations for contaminants that cause acute and/or chronic health effects. In the Economic Analyses, the compliance costs for some regulations are given as a range. In calculating the $9.3 billion need, the survey used EPA's lead option, unless one was not available in which case the survey used the more conservative estimate.

Source: U.S. EPA. Drinking Water Infrastructure Needs Survey: 2nd Report to Congress. Office of Water, Washington, D.C. EPA 816-R-01-004, February 2001. http://www.epa.gov/safewater/dwsrf.html

standards with minor modifications either as regulations or as guidelines even though the federal government did not mandate them (11).

In the late 1960s, several studies found that many man-made chemicals from sources, such as intensive agriculture and manufacturing plants, were contaminating water supplies. One of the environmental laws passed to protect public health is the SDWA in 1974. The 1974 SDWA required EPA to establish legally enforceable DWQS for all PWS in the United States and a surveillance system for PWS. The 1974 law also included a schedule and procedures for developing new drinking water standards, which are to be reviewed at least every 3 years. In 1975, the EPA promulgated interim regulations based on the 1962 USPHS standards, with some additional health-effects information (1). The SDWA was amended and/or reauthorized in 1977, 1979, 1980, 1986, 1988, and 1996 (2).

The SDWA amendments of 1986 declared that the interim standards promulgated in 1975 are final and required EPA to regulate 83 contaminants within 3 years after enactment (2). EPA was required to regulate an additional 25 contaminants every 3 years and to designate the best available treatment technology (BAT) for each regulated contaminant. EPA was directed to require all PWS to disinfect. Filtration was mandated for surface water systems.

The SDWA Amendments of 1996 [http://www.epa.gov/safewater/sdwa/sdwa.html] modified the regulatory schedule and included new sections such as criteria and procedures for variance, operator certification requirements, and provisions for capacity development (1). The EPA published guidelines for certifying and recertifying operators of PWS [http://www.epa.gov/safewater/opcert/plan.html].

STANDARDS SETTING

EPA promulgates two types of drinking water regulations—the National Primary Drinking Water Regulations (NPDWRs) and the National Secondary Drinking Water Regulations (NSDWRs). NPDWRs address health risks/effects that may be acute or chronic and include enforceable maximum limits for drinking water contaminants (MCL) and disinfectants. A NPDWR also includes BAT, monitoring, reporting, recordkeeping provisions, and Regulatory Impact Analyses (Fig. 1). NSDWRs address drinking water aesthetics such as taste and odor that render drinking water unpalatable or undesirable to use. NSDWRs (SMCL) are not enforceable at the federal level. Regulating aesthetic standards deters consumers from seeking more pleasant but less safe sources of water (12). In California, the SMCL for methyl tertiary-butyl ether (MtBE) (5 μg/L) is lower than its MCL (13 μg/L).

The EPA (13) usually follows these steps when setting DWQS (Fig. 1): Determine whether to regulate a contaminant based on peer-reviewed science; set an MCLG DRINKING WATER QUALITY—STANDARDS AND CRITERIA, DRINKING WATER QUALITY—STANDARDS, REGULATIONS AND GOALS; propose an MCL or treatment technique (TT); finalize by, setting an enforceable MCL or TT; and authorize states to grant variances for PWS that serve up to 3300 people based on affordability criteria. Stakeholders can participate in the process.

The EPA selects from the Contaminant Candidate List (CCL) that contains the names of unregulated contaminants. The EPA is to revise the CCL [http://www.epa.gov/safewater/ccl/ccl_fr.pdf], every 5 years. The EPA has developed and maintains a publicly available database known as the National Contaminant Occurrence Database (NCOD), which contains information on regulated and unregulated contaminants that can be found in drinking water [http://www.epa.gov/ncod/].

COMPLIANCE AND SUPERVISION

The EPA administers the SDWA through primacy states. The SDWA allows the EPA Administrator to treat

Tribes, District of Columbia, Guam, Puerto Rico, the Northern Mariana Islands, the Virgin Islands, American Samoa, and the Trust Territory of the Pacific Islands as states for purposes of primacy. Primacy states usually adopt EPA DWQS, but some states set standards that are more stringent than those of the EPA. Nothing precludes a state from establishing DWQS for any water constituent not regulated by the EPA. The EPA, the states, the PWS, and the public cooperatively implement the SDWA.

The EPA provides grants to primacy states to assist states in developing and implementing drinking water programs and provides oversight in enforcing the standards. The EPA (2) has granted primacy to all states but Wyoming. None of the tribal governments has yet been granted primacy. The EPA has primary enforcement authority in states without primacy. States must adopt newly promulgated EPA regulations to maintain primacy status.

PWS are required to collect and analyze water samples at designated intervals and locations. Water samples must be analyzed in approved laboratories and the results reported to the state, which determines compliance. The three main types of violations (2) are

- MCL violation: occurs when contaminant level in treated water exceeds the MCL.
- TT violation: occurs when a PWS fails to treat water as prescribed by the EPA.
- Monitoring and reporting violation: occurs when a PWS either fails to test its water for certain contaminants or fails to report test results in a timely fashion.

An MCL or TT violation indicates a potential health risk. The EPA (2) estimated that in 1994, 89% of the population was served by CWS with neither MCL nor TT violations. The EPA plans to achieve a 95% level by 2005 (2). PWS in violation must notify the public. The EPA maintains a Federal database of violations known as Safe Drinking Water Information (SDWIS) [http://www.epa.gov/enviro/html/water.html#SDWIS].

The EPA, some water-related national associations, and more than 200 surface water utilities throughout the United States established a voluntary cooperative effort known as the Partnership for Safe Water [http://www.awwa.org/partner/partner2.htm?]. Utility members of the Partnership implement preventive programs to increase safety where legislation or regulation does not exist. The preventive measures are based around optimizing treatment plant performance and thus increasing protection against microbial contamination in the drinking water supply. PWS must provide their customers with "Consumer Confidence Reports" (CCR) CONSUMER CONFIDENCE REPORTS.

FUTURE TREND

In the 1980s and 1990s, the EPA set DWQS using the "Risk Assessment/Risk Management" (RA/RM) paradigm based on targeted mandates that prioritize and manage environmental risks, pollutant by pollutant and medium by medium. The proposed radon rule allowed the EPA to address health risk reduction within a multimedia framework. The EPA Science Advisory Board (14) proposed a conceptual framework for integrated environmental decision-making to "guide the Agency in the continuing evolution of environmental decision-making."

BIBLIOGRAPHY

1. American Water Works Association (AWWA). (2001). *Safe Drinking Water Advisor: A Compliance Assistance Resource*. AWWA, May 2001 CD-ROM Edition.
2. EPA. (1999). *25 Years of the Safe Drinking Water Act: History and Trends*. EPA 816-R-99-007.
3. EPA. (2000). Providing Safe Drinking Water in America. Office of Enforcement and Compliance Assurance, Washington, DC. EPA 305-R-00-002. http://www.es.epa.gov/ncepihom/index.html.
4. Solley, W.B., Pierce, R.R., and Perlman, H.A. (1998). Estimated Use of Water in the United States in 1995. U.S. Geological Survey Circular 1200. Denver, CO. http://water.usgs.gov/watuse/pdf1995/html/.
5. EPA. (1999). *Water Facts*. EPA 810-F-99-020.
6. EPA. (2001). Drinking Water Infrastructure Needs Survey: 2nd Report to Congress. Office of Water, Washington, DC. EPA 816-R-01-004. http://www.epa.gov/safewater/dwsrf.html.
7. Davis, J.P. et al. (1996). *Cryptosporidiosis-Associated Mortality Following a Massive Waterborne Outbreak in Milwaukee, Wisconsin*. Bureau of Public Health, Madison, WI.
8. Cotruvo, J.A. and Vogt, C.D. (1990). Chapter 1, Rationale for Water Quality Standards and Goals. *Water Quality and Treatment: A Handbook of Community Water Supplies*. 4th Edn. F.W. Pontius (Ed.). American Water Works Association, McGraw Hill, New York, pp. 1–62.
9. EPA. (2000). *Drinking Water Standards and Health Advisories*. Office of Water, Washington, DC. EPA 822-B-00-001.
10. EPA. (2001). *National Primary Drinking Water Standards*. Office of Water, Washington, DC. EPA 816-F-01-007.
11. Pontius, F.W. and Clark, S.W. (1999). Chapter 1, Drinking Water Quality Standards, Regulations and Goals. Water Quality and Treatment. 5th Edn. *American Water Works Association*. R.D. Letterman (Ed.). McGraw Hill, New York.
12. Tate, C.H. and Arnold, K.F. (1990). Chapter 2, Health and aesthetic aspects of water quality. *Water Quality and Treatment: A Handbook of Community Water Supplies*. 4th Edn. F.W. Pontius (Ed.). American Water Works Association, McGraw Hill, New York, pp. 63–156.
13. EPA. (1999). *Drinking Water Standards & Health Effects*. EPA 810-F-99-017.
14. EPA Science Advisory Board. (2000). *Toward Integrated Environmental Decision-Making*. EPA-SAB-EC-00-011.

See also CONSUMER CONFIDENCE REPORTS; DRINKING WATER QUALITY—STANDARDS AND CRITERIA; DRINKING WATER QUALITY—STANDARDS, REGULATIONS AND GOALS; PUBLIC WATER SUPPLY—UNITED STATES; RADON IN WATER; and WELL HEAD PROTECTION.

VALVES

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Valves direct, start, stop, mix, or regulate the flow, pressure, or temperature of a fluid. Valves range from simple water faucets to control valves equipped with microprocessors. Many different valve types exist; however, the most common types include gate, plug, ball, butterfly, check, pressure relief, and globe valves.

WHAT ARE THE VALVE FUNCTIONS?

Valve functions vary based on the position of the closure element in the valve. The closure position can be adjusted manually or automatically. Valves usually fall into one of three classes:

1. shut-off valves block the flow or allow it to pass;
2. anti-reversal valves allow flow to travel in one direction; and
3. throttling valves regulate flow at a point between fully open to fully closed.

However, specific valve-body designs may fit into one, two, or all three classifications.

WHAT ARE THE BASIC VALVES?

Manual Valves (See Figure 1)

Manual valves require manual operation, such as a hand wheel or lever, which are primarily used to stop and start flow (shut-off valves), although some designs can be used for basic throttling. A manual valve operator is any device that requires the presence of a human being to operate the valve, as well as to determine the proper action (open, closed, or a throttling position). Manual valves are also used to divert or combine flow through a three- or four-way design configuration. Four types of manual valves exist:

1. rotating valves, such as plug, ball, and butterfly valves;
2. stopper valves, such as globe and piston valves;
3. sliding valves, such as gate and piston valves; and
4. flexible valves, such as pinch and diaphragm valves.

Check Valves (See Figure 2)

Check valves are automatic valves that open with forward flow and close against reverse flow. Check valves, also known as non-return valves, prevent return or reverse flow and maintain pressure. Check valves do not require an outside power supply or a signal to operate. In fact, a check valve's operation depends upon the direction in which the water is flowing. A pump or a pressure drop may determine water flow. If the flow stops or if pressure conditions change so that flow begins to move backward, the check valve's closure element moves with the reverse

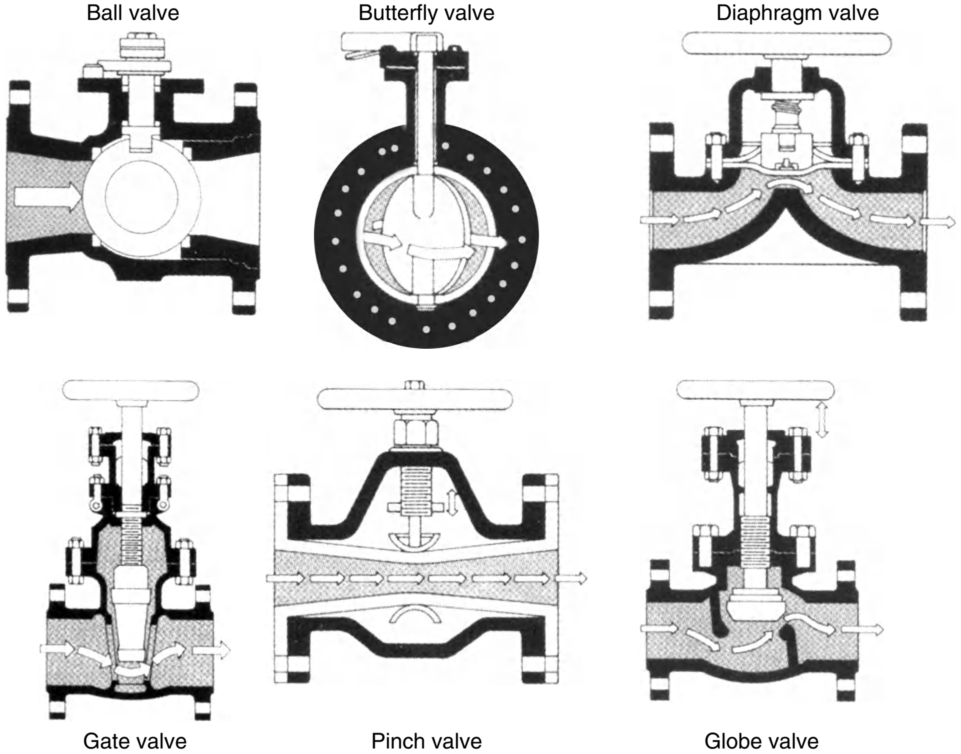

Figure 1. Manual valves.

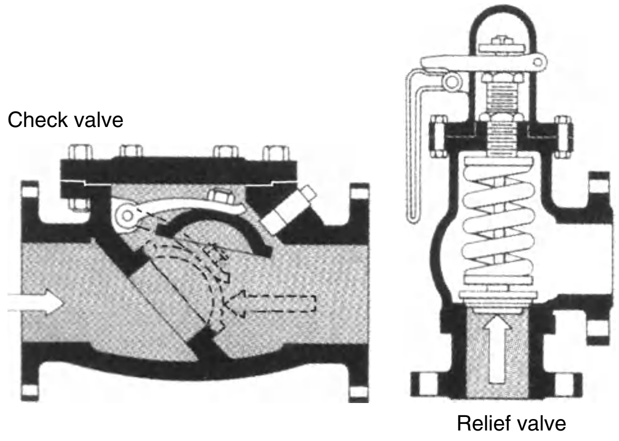

Figure 2. Check valves.

flow until it is seated, preventing any backward flow. There are different types of check valves, but they all have the same operating principle. Check valves include lift-check valves, swing-check valves, tilting-disk valves, split-disk valves, and diaphragm-check valves.

Pressure Relief Valves

A pressure-relief valve is used to protect against overpressurization of the system. When excess line pressure is detected, the pressure-relief valve automatically opens and relieves the excess pressure. A pressure-relief valve is installed where excess pressure constitutes safety concerns, such as pipes or equipment bursting. Following the depressurization of the water line to safe or normal limits, the pressure-relief valve automatically closes again to allow for normal system operation.

Control Valves (See Figure 3)

Control valves, also known as automatic control valves, are used to regulate flow anywhere from fully open to fully closed. Control valves are a fast growing segment of the valve industry because of the quickening pace of water-industry automation. Control valves are almost always equipped with some sort of actuator or actuation system (See definition under Manual Operators and Actuators below.) Manually operated valves and pressure regulators can stand alone in a throttling application, while a control valve cannot. Hence the difference: a control valve is a throttling valve, but not all throttling valves are control valves.

MANUAL OPERATORS AND ACTUATORS

With most valves, some mechanical device or external system must be devised to open or close the valve or to change the position of the valve. Manual operators, actuators, and actuation systems are those mechanisms that are installed on valves to allow this action to take place. Automatic valve control requires an actuator, which is defined as any device mounted on a valve that, in a response to a signal, automatically moves the valve to the required position using an outside power source.

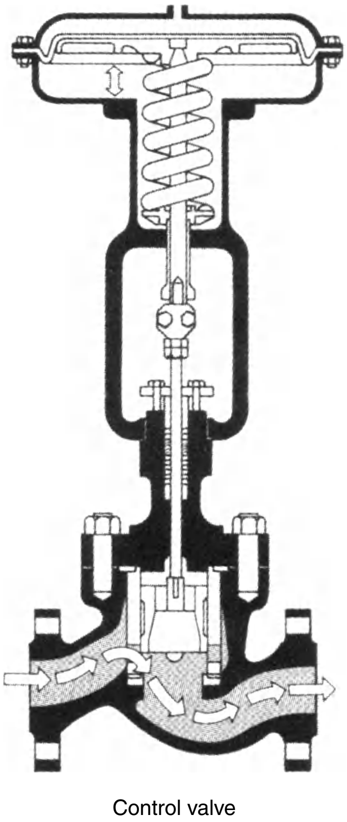

Figure 3. Control valves.

WHAT ARE COMMON VALVE PROBLEMS?

Pressure drop or pressure differential, which is the difference between the upstream and downstream pressures, makes water flow move through a valve. If the piping size is identical both upstream and downstream from the valve and the velocity is consistent, the valve will use frictional losses to reduce the fluid pressure and create flow. Because the pressure drop that a valve generates absorbs energy through frictional losses, an ideal pressure drop allows the full flow to pass through the valve's body without excessive velocity, absorbing less energy.

However, some systems may need to take a larger pressure drop through the valve. A high-pressure drop through a valve creates a number of problems, such as cavitation, flashing, choked flow, high noise levels, and vibration. Such problems present a number of immediate consequences: erosion or cavitation damage to the body and trim, malfunction or poor performance of the valve itself, attached instruments will not remain calibrated, piping fatigue, or hearing damage to nearby workers. In these instances, valves in high-pressure-drop applications require expensive trims, more frequent maintenance, large spare-part inventories, and piping supports. Such measures drive up maintenance and engineering costs.

Although users typically concentrate on the immediate consequences of high-pressure drops, the greatest threat a high-pressure drop presents is lost system efficiency. Usually, a pump adds pressure and, thus, energy to the system. As the system absorbs more energy, including the energy that valves with high-pressure drops lose, it must use larger pumps. Consequently, if the system is designed with few valves with high-pressure drops, the system is more efficient and able to use smaller pumps.

Cavitation

Cavitation happens when low-pressure bubbles suddenly form and then collapse within a small area of the valve within microseconds. Minor cavitation damage may be considered normal for some applications, which can be dealt with during routine maintenance. If unnoticed or unattended, severe cavitation damage can limit the life expectancy of the valve. It can also create excessive leakage, distort flow characteristics, or cause the eventual failure of the valve body and piping. In some severe high-pressure drop applications, cavitation can destroy valve parts within minutes.

One of three basic actions can control or eliminate cavitation. Operators can:

- modify the system;
- make certain internal body parts out of hard or hardened materials; or
- install special devices in the valve that are designed to keep cavitation away from valve surfaces or prevent the formation of the cavitation itself.

Flashing

When the downstream pressure is equal to or less than the vapor pressure, the vapor bubbles generated stay intact and do not collapse. This phenomenon is known as flashing. When flashing occurs, the fluid downstream is a mixture of vapor and liquid moving at a very high velocity, which results in erosion in the valve and in the downstream piping.

Unfortunately, eliminating flashing completely involves modifying the system itself, in particular the downstream pressure or the vapor pressure. However, not all systems are easily modified and this may not be an option. When flashing occurs, no solution can be designed into the valve, except possibly using hardened trim materials.

Choked Flow

The presence of vapor bubbles that cavitation or flashing cause significantly increase the specific volume of the fluid. This increase rises at a faster rate than the increase that the pressure differential generates. If upstream pressure remains constant, decreasing the downstream pressure will not increase the flow rate. Choked flow must be considered when sizing a valve.

HIGH VELOCITIES

Large pressure differentials create high velocities through a valve and in downstream piping. This in return creates turbulence and vibration if the velocities are not lowered. Lower velocities will reduce problems associated with flashing and erosion.

WATER HAMMER EFFECTS

A valve that is opened too quickly or slammed shut when the closure element is suddenly sucked into the seat (“bathtub stopper effect”) as the valve nears shutoff may cause water-hammer effect. Although water hammer generates considerable noise, the real damage occurs through mechanical failure. Water hammer can burst or damage piping supports and connections. In valves, water hammer can create severe shock through trim, gasket, or packing failure.

With valves, the best defense against water hammer is to prevent any sudden pressure changes to the system. For example, one solution may involve slowing the closure of the valve itself. Adding some type of surge protection to the piping system can also reduce water hammer.

WHAT ARE THE OPERATION AND MAINTENANCE REQUIREMENTS?

To avoid mechanical failure, design a practical valve maintenance program, which can result in cost savings for the water system. A job that appears to be mammoth becomes less daunting if the operator implements a systematic maintenance schedule. Operation and maintenance procedures for various types of valves are included in the manufacturer’s operation manuals and in the appropriate product standards. Valve records are essential for planning, operating, and verifying the system’s integrity. The valve record should contain information about valve condition, testing, and maintenance required.

WHAT ABOUT SAFETY/TERRORISM?

Recent events have understandably heightened concern that water supplies may be vulnerable to terrorist attacks—biological, chemical, and structural. Relief from this concern can come via knowledge, planning, and preparedness. It is crucial now to regularly inspect the location, accessibility, and operation of all the valves in the distribution system. This inspection will reveal the condition of the valve box and chamber.

It also is imperative to update the location of the valves on the map. E. H. Wachs Companies for example, offer “Valvecard” software that allows water utilities to manage their valve distribution system from a desktop computer. The software can be used to create valve inventory databases that require a secure user-friendly system to input, store, and analyze valve data or to collect valve information directly from each valve in a system. The software also can be used to operate and exercise valves in the system and record this information or monitor the system and keep it operational at all times. It can perform queries regarding valve properties, location, activities, and conditions as well as interface with Geographic Information Systems and map files.

After having complete and accurate information about all the valves in the system, the utility manager can run through a large number of “what if” scenarios to determine where a contaminant is likely to move and how valves or other utility operations can control its movement. To do this, the utility needs a calibrated, extendedperiod simulation model. There are a few types of software on the market for water distribution modeling and engineering that allow system managers to view scenarios graphically. Some of this software, such as WaterCad by Haestad Methods, can give a clear picture of what is occurring or will occur in the system in response to any operational measures that management proposes.

U.S. Environmental Protection Agency and the American Water Works Association in collaboration with Sandia National Laboratories continue to develop a risk- and consequence-based vulnerability assessment technique to improve the safety and security of water supply and distribution systems against emerging physical, chemical, and biological threats.

WHERE CAN I FIND MORE INFORMATION?

American Water Works Association. 1996. *Distribution Valves: Selection, Installation, Field Testing, and Maintenance (M44)*. AWWA: Denver, CO.

Haestad Methods. 2002. Proceedings from Water Security Summit. Haestad: Waterbury, CT.

National Environmental Services Center. 2002. *Small Drinking Water System Security*. NESC: Morgantown, WV.

Skousen, P. L. 1998. *Valve Handbook*. McGraw-Hill: New York, NY.

Zappe, R.W. 1999. *Valve Selection Handbook*. Fourth Edition. Gulf Publishing Company: Houston, TX.

Walski, T., D. Chase, and D. Savic. 2001. *Water Distribution Modeling*. Haestad Methods: Waterbury, CT.

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REMOVAL OF PATHOGENIC BACTERIA, VIRUSES, AND PROTOZOA

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INTRODUCTION

Pathogenic bacteria, viruses, and protozoa can be removed from potable water by various processes. These removal processes can be categorized into three groups: (1) *initial*, (2) *principal*, and (3) *alternative/supplemental. Initial removal processes* are used to remove microbial pathogens before they enter or as they enter a treatment plant. The main objective of these processes is to reduce the particulate loadings, including microbial loadings, to the subsequent treatment processes of a treatment plant. Examples of initial removal processes are roughing filters, microstrainers, off-stream storage, bank filtration, and presedimentation with coagulation. *Principal removal processes* are those most frequently used to remove the majority of the microbes in the water being treated. These processes are sedimentation, flotation, and high-rate granular media filtration. They are often used in conjunction with coagulation and flocculation. *Alternative/supplemental removal processes* are used either as (1) alternatives to principal removal processes or (2) supplemental processes to enhance drinking water quality. These processes include slow sand filtration, precoat filtration, membrane filtration, bag filtration, and cartridge filtration.

The performance of removal processes is often quantified in terms of the log removal of pathogens, which is defined as log C_0/C, where C_0 and C are the pathogen concentrations in the water entering and leaving a process, respectively. A 1-log removal is equivalent to 90% removal, and a 2-log removal is equivalent to 99% removal. Drinking water regulations in the United States typically target log removals of pathogens. However, the performance of a removal process can also be quantified by the turbidity level in the outlet flow of the process or the removal of turbidity by the process. Turbidity is a measure of water clarity. A low turbidity level in the water leaving a treatment process is considered an indication that the process effectively removes pathogens.

INITIAL REMOVAL PROCESSES

Roughing Filters

Roughing filters are coarse granular media filters used to remove large particles from high turbidity waters prior to downstream processes. Although the term filter is used, roughing filters act more as a series of sedimentation boxes filled with media of decreasing size in the direction of flow. The media effectively reduce the settling distance of particles to the order of a few millimeters. The direction of flow through a roughing filter can be either horizontal or vertical. Typical roughing filter media are gravel, rock, crushed coconut, or other locally available materials.

According to a pilot study (1), a roughing filter can achieve average log removals of 0.28 for total bacteria and 0.20 for algal cells. It was also found that the removal of clay particles is improved when the filter has been ripened with algae. Another pilot study indicates a log removal of 0.64 to 0.96 for fecal coliforms, depending on filtration rate (2).

Roughing filters are often used in developing countries to serve as an initial process for slow sand filtration. Important design parameters for roughing filters are hydraulic filtration rate, filter depth (for vertical filters) or length (for horizontal filters), and media size. A review of design variables for roughing filters is available (2).

Microstrainers

Microstrainers are filtration units that use a thin medium, usually fabrics woven of stainless steel or polyester wires. The mesh sizes of microstrainer fabrics are less than 100 μm and typically from 15 to 45 μm. Microstrainers can be used to remove fine suspended particles and algal cells from surface waters. They are very effective for certain types of green algae, diatoms, and cyanophyta. A major application of microstrainers in potable water treatment is as an initial removal process for downstream membrane processes. They reduce particle loading to the membrane processes and also protect the membranes from debris.

The removal efficiencies of algae by microstrainers can vary from 0.22 to 0.52 logs, depending on the type of algae present (3). Large protozoa such as *Balantidium coli* cysts (whose diameter is about 60 μm) can also be removed by microstrainers. However, due to their small size, the removal of bacteria and viruses by microstrainers is usually insignificant.

Off-Stream Storage

Off-stream storage refers to reservoirs or basins whose locations in the treatment flow path are between the raw water source and treatment processes of a water treatment plant. Off-stream storage can improve microbial water quality through a combination of mechanisms. The major mechanisms are settling and die-off of pathogens and equalization of water quality spikes. The critical factors for the performance of off-stream storage are the storage's hydraulic residence time, flow patterns within the storage, and water temperature. Control of algal growth within the storage is important because algae can cause taste and odor problems in water. It is also very critical to avoid fecal contamination from animals and runoff from surrounding areas. Otherwise, the storage may actually deteriorate the quality of the water leaving it.

Settling is the primary mechanism by which pathogens are removed by off-stream storage. The longer the hydraulic residence time of off-site storage, the greater the amount of settling that takes place in it. The removal of coliform bacteria in off-stream reservoirs with hydraulic residence times greater than 40 days is from 0.7 to 2 logs (4). A 1.5 log reduction of enteroviruses was reported for an off-stream reservoir with a hydraulic residence time of about 100 days (5). In two studies, reductions of 1.4 to 2.0 logs for *Cryptosporidium*, 2.3 to 2.6 logs for *Giardia*, 2.2 logs for *Escherichia coli*, and 1.7 logs for fecal streptococci were found for storage reservoirs with residence times of 24 weeks or greater (6),(7). These results indicate that, for settling to be an effective method of removing microbes in off-stream storage, a long residence time and, therefore, a large land area are required.

Although not a removal process, the die-off of pathogens within off-site storage can improve microbial water quality. The die-off of pathogens is a kinetic process and may be considered a first-order reaction (8). Based on bench scale studies, the die-off rate constants found for *Cryptosporidium* are 0.01/day at 5 °C and 0.024/day at 15 °C (9). These are equivalent to a 0.5 log reduction in 50 days at 5 °C and in 21 days at 15 °C, indicating the significance of temperature in the die-off process.

Off-stream storage can also reduce the peak values of pathogen concentration spikes through the management of the source water pumping schedule. The peak levels of microbial contaminants are often associated with the turbidity spikes that follow rainfalls. By not using source water from the watercourse during these peaks and using the stored water instead, pathogen spikes of microbial contaminants can be avoided.

Bank Filtration

Bank filtration is a process by which surface water from a watercourse infiltrates into a groundwater aquifer and is later brought to ground level by well pumps. As the water passes through the ground, the aquifer acts as a natural filter and reduces the concentration of viable pathogens by two major mechanisms: deposition of the pathogens on porous aquifer materials and die-off of pathogens due to the long residence time within the aquifer. This process is also termed riverbank infiltration. It has been widely used as a water treatment process in European countries and, in the past few years, has received increased interest in the United States.

In a full-scale bank filtration study, no *Giardia* or *Cryptosporidium* were detected in wells, even though they were frequently detected in river water, and total coliform bacteria were never detected in wells (10). In a study of three different infiltration sites, the removals of bacteriophage were 3.1 logs and 4.0 logs when water passed through 2 m and 4 m of very fine dune sand, respectively (11).

Bank filtration can be highly effective in removing microbial pathogens. Aquifers suitable for bank filtration are composed of unconsolidated, granular, fine-grained materials and have open, interconnected pores that allow groundwater to flow (12). Other important factors affecting the treatment efficiency of bank filtration are the time of travel from the watercourse to the well (thus, the residence time of the water in the aquifer), the quality of the source surface water (e.g., turbidity), and the water temperature. USEPA proposes a treatment credit for *Cryptosporidium* of either 0.5 or 1.0 logs for bank filtration systems that meet some specific criteria. These criteria include aquifer compositions, distance from the pumping wells to surface water, and turbidity level in the well effluent (12).

Presedimentation with Coagulation

Presedimentation is used to remove gravel, sand, and other relatively large suspended materials from source water prior to principal treatment processes. It is often used for source waters that have highly variable raw water quality to reduce occasionally high solid loadings on the principal treatment processes. Microbial pathogens can be removed by this process if they are attached to or trapped inside larger particles. Adding coagulants can enhance the removal of pathogens by presedimentation.

According to a full-scale study of four presedimentation basins using surface loading rates of from 0.3 to 1.6 gpm/ft^2 and polymer and ferric sulfate as coagulants, the removal of *Bacillus subtilis* averaged 1.1 logs (12). The results of a full-scale study of inclined-plate presedimentation basins using a surface loading rate of 0.52 gpm/ft^2 and alum and polymer as coagulants indicated that the median removal of total aerobic spores and *Giardia* were 0.5 logs and 1.5 logs, respectively (12).

PRINCIPAL REMOVAL PROCESSES

Sedimentation

Sedimentation is a solid–liquid separation process that removes particles and pathogens from water by providing conditions that will cause them to settle under the force of gravity. The hydraulic loading per unit of surface area, hydraulic detention time, inlet/outlet conditions, and internal flow patterns are considered important design parameters for sedimentation basins, but the most important factor in removing microbial pathogens from sedimentation basins is the use of coagulation and flocculation processes upstream of the basins.

Due to their small size and low mass density, individual microbes have a very low settling velocity. In the absence of proper coagulation and flocculation, sedimentation does not achieve significant removals of microbial pathogens. Coagulation involves adding coagulants that either have or can form positively electrically charged species to neutralize negatively charged microbial particles. Because microbial particles are of like electrical charges, they repel each other. Neutralizing these charges facilitates contact between particles. When two or more particles come in contact, they form larger particles that settle more readily. The coagulant can also form precipitates or floc particles that attach to the naturally occurring particles in the water and form larger, heavier agglomerates. The flocculation process establishes conditions that increase the number of opportunities for particles and agglomerates to contact one another and result in large particles that have sufficient settling velocities to be removed in the sedimentation basins that follow.

To achieve good removal of pathogens by sedimentation, the type and dose of coagulant and the coagulation chemistry must be optimized. Also important in coagulation are rapid, thorough mixing, and gentle, relatively slow mixing and sufficient contact time in the flocculation process.

Based on pilot studies, it was reported that sedimentation achieved an average removal of 0.2 logs for *Cryptosporidium* under suboptimal coagulation conditions and the removal increased to 1.3 logs under optimal coagulation conditions (13). This indicates the importance of coagulation, as mentioned above.

Based on full-scale observations at treatment plants in various countries, sedimentation preceded by coagulation and flocculation achieved average removals of 0.14 to 0.59 logs for viruses, 0.17 to 0.89 logs for bacteria (total coliforms or fecal streptococci), and 0 to 1.22 logs for algae (14).

Flotation

Unlike sedimentation which removes materials whose mass densities are greater than that of water, flotation removes materials whose mass densities are less than that of water. In potable water treatment, the flotation of materials is induced and is termed dissolved air flotation (DAF). In DAF, dissolved air is injected into the process stream under high pressure. Then, the process stream is exposed to atmosphere pressure, and the dissolved air forms air bubbles. The bubbles form around and attach to particles in the process stream. This causes particle/air bubble agglomerates to have a mass density that is less than that of water and, thus, to float to the surface of the liquid where they are skimmed off. DAF is most applicable to waters with heavy algal blooms or waters with low turbidity, low alkalinity, and high color. These waters are difficult to treat using sedimentation because the coagulant floc particles produced typically have a low settling velocity.

The performance of DAF for *Cryptosporidium* oocyst removal depended on the pH, coagulant dose, flocculation time, and the ratio of the air-saturated water stream to process stream. According to several full-scale studies, DAF removes 1.4 to 2.0 logs of the algae *Aphanizomenon* and *Microcystis* (3). Study also shows that DAF achieved between 2 and 2.6 logs removal of *Cryptosporidium* oocysts, whereas conventional sedimentation resulted only in 0.6 to 0.8 log removals (15). Based on bench-scale testing, it was reported that DAF averaged 0.5 logs higher removal of *Cryptosporidium* than sedimentation (16).

High Rate Granular Filtration

High-rate granular filtration is the most widely used potable water treatment process for removing pathogens. This process is described separately in GRANULAR BED AND PRECOAT FILTRATION.

ALTERNATIVE/SUPPLEMENTAL REMOVAL PROCESSES

Slow Sand Filtration

Slow sand filtration is described separately in Granular Bed and Precoat Filtration.

Precoat Filtration

Precoat filtration is described separately in Granular Bed and Precoat Filtration.

Membrane Filtration

Membrane filtration is a separation process in which a thin, semipermeable membrane is used to remove contaminants from water. A differential hydraulic pressure across the membrane causes the water to pass through it. This differential pressure can be created by applying a higher pressure on one side of the membrane than the other and pushing the water through the membrane or by applying a negative pressure on one side and pulling the water through.

The most commonly used membrane processes in drinking water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). They differ from each other by their pore sizes. MF membranes have the largest pore size (of the order of 0.1 μm), followed by UF membranes (of the order of 0.01 μm) and NF membranes (of the order of 0.001 μm). RO membranes have the smallest pore size of the order of 0.0001 μm.

The pore size of the membrane is the key factor in determining which contaminants are removed by the membrane. Contaminants large than the membrane's pore size are retained and removed by the membrane. The pore size of the membrane also affects the operating hydraulic of the membrane process. Membranes that have smaller pore sizes require higher differential hydraulic pressures. The operating pressure of MF and UF is similar and from 30 to 50 kPa. It increases to 500 to 1000 kPa for NF and to 1000 to 5000 kPa for RO.

The sizes of protozoa and most bacteria are of the order of a micron or larger and can therefore be removed very effectively by MF. Removal of bacteria may sometimes be poor, if bacteria grow in the membrane system. Viruses have sizes from 0.01 to 0.1 μm and are likely to pass through MF membranes, unless coagulation pretreatment is provided. According to a pilot study using three MF membranes with pore sizes from 0.08 to 0.22 μm, log removals of greater than 4.6 to greater than 7.0 for *Giardia* and greater than 4.2 to greater than 6.9 for *Cryptosporidium* were achieved (17). Removals of MS2 bacteriophage were, however, less than 1 log. This was expected due to the small size of MS2, which is 0.025 μm. In a pilot study using MF with coagulation pretreatment, virus removals were more than 7 logs, even though the tested virus has a size of 23 nm and the membrane pore size is 100 nm (0.1 μm) (18).

In addition to bacteria and protozoa, UF can remove some viruses. In a study using UF membranes with pore sizes of 0.01 to 0.05 μm, neither *Giardia* nor *Cryptosporidium* were detected in the filtered water (17). The log removals were greater than 4.7 to greater than 7.0 for *Giardia* and greater than 4.4 to greater than 7.0 for *Cryptosporidium*. The membrane having the smallest pore size achieved MS2 bacteriophage removals of 6 logs and greater.

Because of their high costs, NF and RO are seldom used to remove microbial pathogens alone. NF is primarily used for softening because it can remove divalent, hardness-causing cations such as Ca^{++} and Mg^{++} and for removals of disinfection by-product precursors (dissolved organic carbon compounds). RO is primarily used for desalination because it can remove monovalent, salinity-causing ions such as Na^{+} and Cl^{-}. However, the ability of NF and RO to remove pathogens enhances their cost-effectiveness when they are used for these other treatment objectives.

During a bench-scale study using five different RO membranes, virus reductions of 2.7 logs to greater than 6.5 logs were achieved (19). A pilot study was conducted to investigate the efficiency of sequential membrane systems, using two different NF membranes with two different MF membranes as pretreatment (20). The removal of *Bacillus subtilis* endospores, a surrogate for *Cryptosporidium* oocysts and *Giardia* systs, varied from 8.0 to 11.0 logs.

Detailed descriptions of their design and operation are available in the literature (21). Maintenance of membrane integrity was very critical to process efficiency. The loss of membrane integrity (e.g., fiber breakage) certainly permits passage of pathogens into finished water.

Bag Filters and Cartridge Filters

A differential pressure is used to push the water through both bag filters and cartridge filters. Bag filters use nonrigid, fabric filter media bags housed in a pressure vessel. Water flows from inside the bags to outside the bags. Cartridge filters are quite the opposite. They use a rigid or semirigid, fabric filter media housed in a pressure vessel, and water flows from outside the cartridges to the inside of the cartridges.

These types of filters are often used for small systems and for point-of-use filtration applications. They can also be applied as an additional filtration process following the principle filtration processes such as high-rate granular filtration to improve water quality. High turbidity and algae cells can easily clog bag and cartridge filters, so they are appropriate only for high quality water. Addition of disinfectant prior to the filters should also be considered to minimize biofilm growth within filter media.

The typical pore size range for bag and cartridge filters is from 0.2 to about 10 μm. This is usually small enough to remove protozoa such as *Cryptosporidium* oocysts and *Giardia* cysts. Submicron-sized microbes, such as viruses and most bacteria, can pass through these filters. As water passes through a bag or cartridge filter, particles accumulated within the filter material increase the hydraulic pressure drop through the filter. When this pressure drop increases to a level that it is impractical for further operation, the bag or cartridge is replaced with a clean one.

Microbial removal by bag and cartridge filters can vary significantly. A range of 0.5 to 3.6 logs *Cryptosporidium* removal has been reported for bag and cartridge filters (12). Interestingly, there was not a correlation between nominal pore size and removal because the nominal pore size of a bag or cartridge filter medium, as reported by the manufacturer, represents only an average size. A pore size distribution exists, which means that some pores are of sizes greater than the nominal size and the pore size distribution values vary from one filter medium to another.

BIBLIOGRAPHY

1. Collins, M.D., Westersund, C.M., Cole, J.O., and Roccaro, J.V. (1994). *Evaluation of Roughing Filtration Design Variables*. American Water Works Association Research Foundation, Denver, CO.
2. Wegelin, M. (1988). Roughing gravel filters for suspended solids removal. In: *Slow Sand Filtration: Recent Developments in Water Treatment Technology*. N.J.D. Graham (Ed.). Ellis Horwood Ltd., Chichester, UK, pp. 103–122.
3. Mouchet, P. and Bonnelye, V. (1998). Solving algae problems: French expertise and world-wide applications. *Aqua* **47**: 125–141.
4. Bernhardt, H. (1995). Reservoirs and drinking water supply—a global perspective. *Aqua* **44**: 2–17.
5. Kors, L.J. and Bosch, A.D. (1995). Catchment protection of a multi-functional reservoir. *Aqua* **44**: 80–84.
6. Ketelaars, H. et al. (1995). Occurrence of *Cryptosporidium* oocysts and *Giardia* cysts in the river meuse and removal in the biesbosch reservoirs. *Aqua* **44**: 108–111.
7. van Breemen, L.W.C.A. and Waals, J.M.J. (1998). Storage of surface water in the Netherlands: Challenges of the future. *Water Supply* **16**: 375–381.
8. Oskam, G. (1995). Main principles of water quality improvement in reservoirs. *Aqua* **44**: 23–29.
9. Medema, G., Bahar, M., and Schets, F. (1997). Survival of *Cryptosporidium parvum, Escherichia coli, faecal Enterococci,* and *Clostridium perfringens* in river water: Influence of temperature and autochthonous microorganisms. *Water Sci. Technol.* **35**: 249–252.
10. Gollnitz, W.D., Clancy, J.L., Whitteberry, B.L., and Vogt, J.A. (2003). RBF as a microbial treatment process. *J. Am. Water Works Assoc.* **95**(12): 56–66.
11. Schijven, J.F. and Rietveld, L.C. (1997). *How Do Field Observations Compare with Models of Microbial Removal? Under the Microscope—Examining Microbes in Groundwater*. American Water Works Association Research Foundation, Denver, CO.
12. US EPA. (2003). *Long Term 2 Enhanced Surface Water Treatment Rule: Proposed Rule*. United States Environmental Protection Agency, Washington, DC.
13. Dugan, N.R., Fox, K.R., Owens, J.H., and Miltner, R.J. (2001). Controlling *Cryptosporidium* oocysts using conventional treatment. *J. Am. Water Works Assoc.* **93**(12): 64–76.
14. Gimble, R. and Clasen, J. (1998). International report: Removal of micro-organisms by clarification and filtration processes. *Water Supply* **16**: 203–208.
15. Plummer, J.D., Edzwald, J.K., and Kelley, M.B. (1995). Removing *Cryptosporidium* by dissolved-air flotation. *J. Am. Water Works Assoc.* **87**: 85–95.
16. Harrington, G., Chen, H., Harris, A., Xagoraraki, I., Battigelli, D., and Standridge, J. (2001). *Removal of Emerging Waterborne Pathogens*. American Water Works Association Research Foundation, Denver, CO.
17. Jacangelo, J.G., Adham, S.S., and Laîné, J-M. (1995). Mechanism of *Cryptosporidium, Giardia*, and MS2 virus removal by MF and UF. *J. Am. Water Works Assoc.* **87**(9): 107–121.
18. Matsui, Y. et al. (2003). Virus removal by ceramic membrane microfiltration with coagulation pretreatment. *Water Sci. Technol.* **3**(5–6): 93–99.
19. Adham, S.S., Trussell, R.S., Gagliardo, P.F., and Trussell, R.R. (1998). Rejection of MS-2 virus by RO membranes. *J. Am. Water Works Assoc.* **90**(9): 130–135.
20. Owen, C., Taylor, J.S., Robert, C., and Reiss, C.R. (1999). Microbial Challenge of Integrated Membrane System Large Scale Pilot Plants Treating a Highly Organic Surface Water. *Proc. AWWA Water Qual. Technol. Conf.*, American Water Works Association, Denver, CO.
21. Taylor, J.S. and Wiesner, M. (1999). Membranes. In: *Water Quality & Treatment*. R.D. Letterman (Ed.). McGraw Hill, New York, pp. 11.1–11.71.

WATER METER

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HISTORY OF WATER METERS

A water meter is a device for measuring and registering the amount of water that passes through a pipe or other outlet, usually for billing purposes. Water meters have various synonyms, used in different cities, countries, or circumstances. Some of these equivalent terms are volume counter, flow-gauging device, water totalizator, flowmeter, and accumulator.

The physical device used to measure the water consumed in a house or industry, or the water extracted from a well or similar supply source, is relatively simple compared to other quotidian instruments. It gauges and adds up the water volumes as they flow in the intake pipe (flow rate is the volume during a certain time span).

In cities when consumers must pay their water bills according to the volumes used, meters must be massively installed, so the logistics to assure their timely reading, quality, precision, repair, replacement, and several other aspects require thorough technical assessment and planning. Many cities of the world depend on them nowadays, although they are relatively modern (no more than 150 years) and are having a rapid evolution. Let us review a little of this evolution.

Humans have always liked to count and measure things ("Man is the measure of all things," Protagoras). Our troglodyte father counted his trophies, wives, possessions, or days passed with his fingers. Later, some other measuring units and quantifying devices were invented, although counting a shapeless and moving liquid was not so easy for some centuries.

Some indirect and ancient ancestors of our modern water meters were the water clocks or "clepsydra" (from Greek "water thieves") used since about 325 B.C., which were stone vessels with sloping sides that allowed water to drip at a nearly constant rate from a small hole near the bottom. Afterward, more sophisticated and artistic water clocks were used (as the huge Su-Sung water clock from China). These in a sense had the inverse purpose of water meters nowadays: first, it was measuring time from a known volume of water; now we want to measure a variable flow of liquid during a known span of time.

Flow, or water volume, must always be referred to a time unit and we must express it as liters per minute, m^3 per month, cubic kilometers per year, etc.

Time is measured with a calendar and/or a wristwatch. Volume can be counted (or estimated by calculus and assumptions) in many ways. One method is using a bucket or container of known dimensions; another procedure is measuring its velocity of travel in a pipe of known cross section (flow = velocity × area).

Most modern water-meters act on the principle of counting the number of turns made by a small reaction turbine moved by the water as it flows through it. This is the basis of Sir William Siemens' invention, who patented his water meter ('fluid meter') in April 1852 (1). Until that time, water metering was not possible; several attempts had been made to devise a suitable device, but all had failed. W. Siemens also invented meters for other applications (bathometer for the depth of the sea, electric pyrometer, etc.).

Ironically, England, where meters were invented, remains until now one of the few countries where almost no houses have water meters installed. This gives an idea of the complexity and expense of installing and reading them, particularly when they are not really indispensable (the United Kingdom has a relatively good quantity of rain and water to waste, but it is not the same in other countries).

Nowadays, water meters, instead of mechanical transmission of movements and signals (as in old clock gearing), send magnetic, electric, or digital pulses which can be stored (remote dial counter or display, data-logger, etc.).

Besides volume, there are multiple water parameters requiring measurement or pondering, for instance, temperature, color, chlorine or salt content, velocity, pressure, and environmental value. Each feature is useful for a given purpose. In leak detection, or billing consumption, and general management of a water utility, water volumes (referred to specific time spans) are key topics.

WATER SUPPLY MANAGEMENT AND CHARGING PRACTICES

Urban utilities use and need water meters as tools for the proper management of a valuable resource, which is water. Numerous water meter types exist that differ in design, material, size, precision, operating principle, reading display, purpose, and site where installed (Fig. 1 shows a brief sample of them). Before entering in any technical detail about how meters work, it is important to review why meters are required. This will give insight into the convenient meter type for a given task.

Water meters can be used either to measure the volumes supplied by the utility through different sources and aqueducts (macrometering), or to know the volumes consumed by clients (micrometering). There usually are differences among the volumes supplied and those consumed. Logically in this comparison, supply should be greater than real consumption, and their difference represents water losses, which must be studied to keep them within reasonable limits.

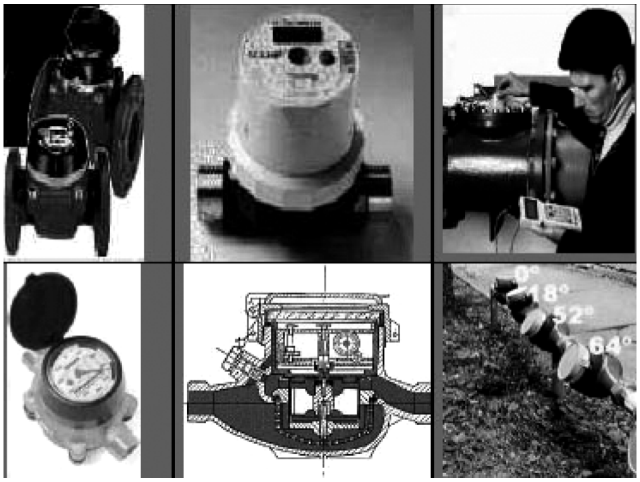


Figure 1. A variety of meters, installation and reading styles.

Metering is an important element to attain *water conservation* (*efficient water use*) in places where water availability is below potential demand. In fast growing cities with limited water resources, household water metering is primarily seen as an approach to control consumption (demand management). It avoids unrestricted use, so water supply and water demand can be balanced. Metering also leads the water undertaker into efficient use of other resources (money, energy, infrastructure, etc.) and good service. In some cases, "nonmetering" options can attain equivalent conservation results, but they must be evaluated carefully before any decision is made.

To be effective, water metering must be linked to appropriate tariffs and prices, together with ways to enforce them, for example, applying surcharges to consumers using more water than the average citizen or cancelling service to people who do not pay their water bills. This is particularly true when water conservation is a prime goal. The role of tariffs is to give a fair chance to everyone to use a reasonable quantity of water and to recover the operating and investment costs of the service. Tariff fixing is quite difficult and subjective when social fairness to consumers, historical privileges, and provisions for the future are involved.

Figure 2 illustrates different rate structure styles in a sample of 827 U.S. water utilities during 1996 (2). The most convenient style for conservation purposes is the "*increasing block rate*," where the price per each cubic meter is higher as total volume consumed grows.

REASONS AND PRIORITIES FOR HOUSEHOLD METERING

Water metering may have different approaches and purposes. Its most frequent bases are either slowing the growth of water demands via volumetric charges to consumers or improving the water utility's revenue through a fair pricing system. There may be other objectives, and any metering project obeys a combination of several of them.

Metering is not an exclusive way to obtain appropriate financial resources; other ways to get payments from consumers can be set up. Nevertheless, for *"consumptive" or "Western" mentalities*, billing water consumed through metering is a clear and fair charging system. The drawbacks are that meter installation, upkeep, and reading demand good organization and represent significant costs, particularly when massive radical changes are required in existing practices. It is relatively cheap when metering is done systematically in all new constructions and regular improvements in equipment and procedures take place.

The reasons and priorities to improve or adopt household metering may vary with place and time. For example in poor arid countries with fast growing urban populations, the priorities, in decreasing importance, may be:

1. Water conservation. Compel people to consume less water through volumetric charges. The water saved may allow extending the system, improving service standards, or protecting the environment.
2. Cost recovery and financial soundness of the water company. Appropriate revenue for all expenses (water supply, sewerage, pluvial drainage, or other services) and provision for future investments.
3. Individual household equity. Avoid discriminatory practices associated with fixed rate tariffs, and charge according to volume used.
4. Unaccounted for water reduction (*clandestine connections and leakages*) through better information on consumption.
5. Peak demand abatement. Cut down nonindispensable uses, or even provide the possibility of seasonal or hourly tariffs.
6. Social equity. Favor poor consumers, who use less water, with lower tariffs or through subsidies.
7. Better data about demand and variations to improve operation and planning of the water system.

Figure 3. Facets invovled in water meter planning.

Deciding the convenience of metering for a previously unmetered place, or upgrading it where it exists partially, requires careful evaluation of a broad spectrum of elements, ranging from local economy and politics to the family budget. It also involves family habits, health, institutional organization, and water service standards. Figure 3 represents the different elements that must be taken in account. Water metering planning requires a clear and careful bond of all technical, administrative, legal, and social aspects involved.

PRECISION TESTS FOR METERS

Various types of flow meters have mobile parts subject to wear, alteration, and clogging with debris or scaling (incrustation), so it is necessary to make periodic tests or replacements to assure their accuracy and proper performance. They could also have manufacturing defects or disarrangement during transport.

New and recently acquired meters usually are randomly tested at the utility's laboratory, on a testing bench, against the accepted standard (for example ISO 4064-1). Later, once installed, at intervals of some years, when

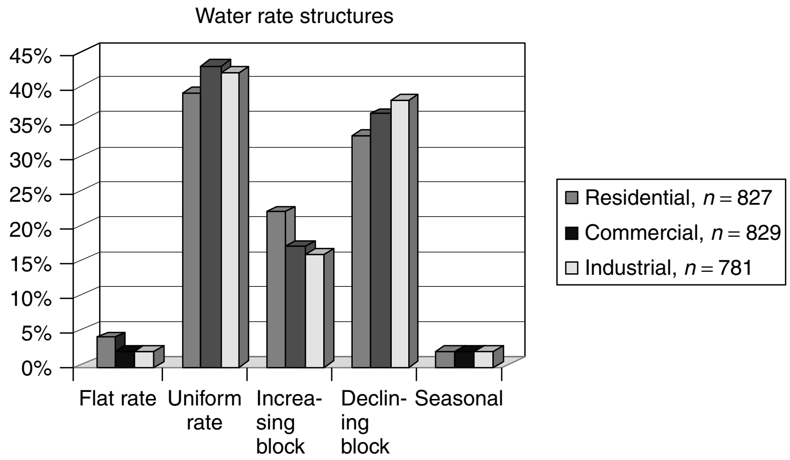


Figure 2. Water rate styles in various USA water utilities (year 1996).

a client complains about excessive charges, or there is a report of underregistration, the apparatus can be dismounted and taken to the lab to test its performance and to be repaired, although it is preferable to perform field tests (*in situ*, *without dismounting the house meter*) with a portable meter test kit. There is commercial equipment that provides everything needed to test domestic water meters accurately, contained in an easy-to-handle case. For more elaborate field assessment as in the case of intermittent service, where the main pipe could be empty, the utility may send a vehicle with all required elements for the test.

Water meters, like most gauging devices, even when new, are not always exact and reliable. Most meters do not perform well at very low flows, and at high flows, they also have errors. They have an appropriate working range where precision is high; out of it, errors increase exponentially. Meters of "*class D*" solve the underregistration presented by other types of meters when used in houses with frequently low inflow rates, for instance, those dwellings having a general storage tank with an admitting float ball-valve. These meters may be about 10% more expensive than "*class C*," but their impact on revenue (water sales) may be worth it. Even though they are more precise, they still cannot detect very low flows, for example, a leak through a dripping tap. Meters of "*class C*" are not precise for flows below 25 L/hour, and "*class D*" below 11 L/hour.

Meters by themselves, as any hydraulic fitting in a pipe, generate additional head losses and are obstacles that reduce the flow rate. It is important to know their potential effect because these losses may be reflected in additional pumping and energy costs for the undertaker in supplying appropriate pressure to some neighborhoods. Obviously meters that produce the lowest head losses are preferable. Figure 4 presents a typical precision graph and a head loss curve.

METER SELECTION AND SIZING

Many issues must be taken into account for the proper selection and sizing of a meter. The previous graph illustrates the need to select an apparatus yielding satisfactory precision without too much head loss. This evidently must be judged and compromised against purchasing and installation costs. Other factors to consider are house characteristics where meters will be installed; especial protection required against weather, vandalism, and tampering; or particular provisions for reading. When selecting a meter, it is necessary to assess the probable consumers demand (average flow, maximum flow), diameter and materials of the existing pipe, impact of water quality (corrosion, presence of sand or other suspended solids, scaling, dissolved air, temperature), effects of soil and environmental

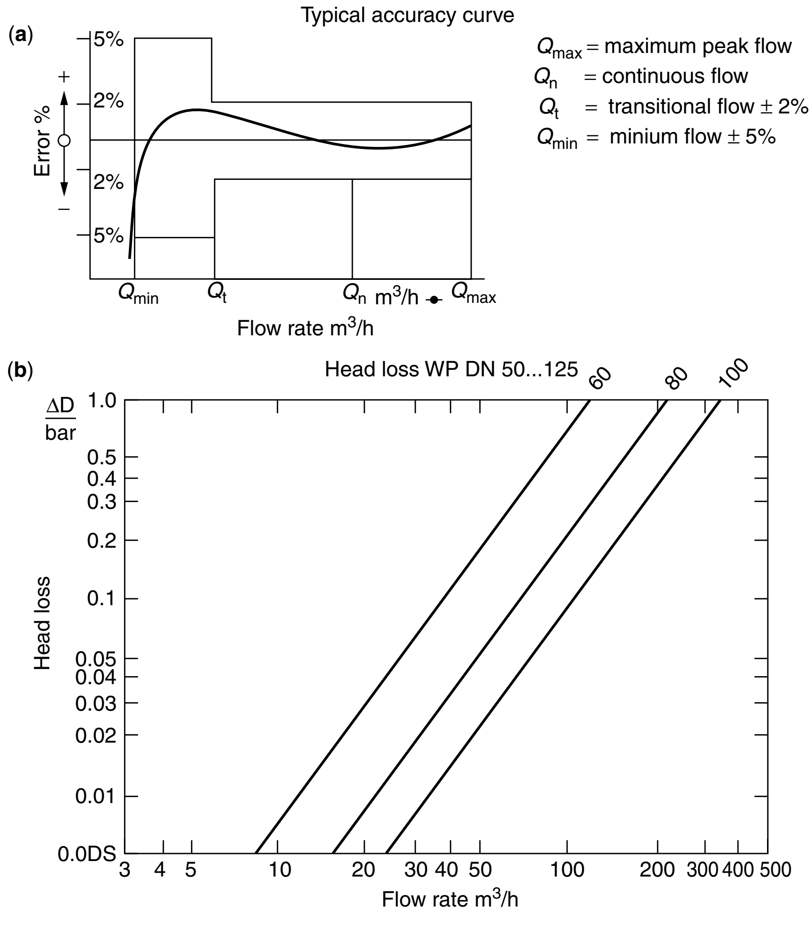


Figure 4. Examples of precision and pressure loss graphs for water meters.

aggression (temperatures, humidity, snow), tariff system and frequency for reading, inspection or replacement routines, risks of transport or from installation and bad practices (wrong position, inverted flow, tampering).

Still other issues affecting decisions are convenient stock for replacements (number of meters, models and their spare parts to be kept in reserve); available budget (acquisition, certification, storage, transport, installation, inspection, tests, visits, contracts and invoices to the consumer), financing sources, and legal and contractual adjustments (bylaws and codes to be modified or completed, inspections and enforcement required, renewal of contracts to customers).

Modern technology allows remote readings via radio, cable, or telephone, when the meter has the appropriate provisions for this, apart from the traditional direct display of its readings.

The installation of a macrometer (as for the study of a DMA, district-metering area) may require attaching some graphing or electronic recording device (data-logger) to it to monitor flow rates during different time spans.

In a consumer line with a rather big diameter, it is possible to save some money, sacrificing a little precision, by installing a “proportional meter.” This is placing a parallel detour (bypass) line with a smaller meter on it. Sometimes is possible to place “batteries of meters,” by means of parallel pipes with different meter diameters on each one.

Multirate meters and water charges through variable tariffs according to the time of day are quite feasible with modern electronics, although may be still expensive. Probably, in the next years, costs will drop and several cities will be using them (power companies in many parts of the world already use meters for electricity with such capability).

It is always important to select the appropriate meter in accord with consumer characteristics and their expected consumption patterns. The utility must have specific guidelines for different types of industries, commerce, service facilities, public offices housing, etc.

Meters can have a provision to restrict flow or pressure. Besides the billing effect of the meter in discouraging waste and high consumption, these adjustable restrictors associated with the counter, may lower peak demand during critical hours of the day. They can also reduce risks of leakage inside the house, or give equal chances to deliver fair and similar amounts of water to consumers in neighborhoods or streets too steep or long (with great differences in potential water pressure).

There can be approaches where nonpermanent installation of meters (random or temporary metering) or communal meters can be useful and economical. In old neighborhoods and in apartment buildings, the supply pipe is common to various dwellings, where installing individual meters, as well as periodic reading, may be extremely expensive and difficult.

TECHNICAL ASPECTS OF METERS

Flow meters work using basic physical and hydraulic principles of mass conservation or continuity, energy conservation (head losses due to flow and velocity energy converted to position energy), momentum, or inertia.

There is no space to describe the operating characteristics of the various measuring systems and instruments available and used nowadays. Figure 5 lists some of them (more details can be found in chapter 4 of Ref. 3).

Meters can be of various kinds, for example, volumetric, propeller, and remote sensing. All have different precision

Type of flow meter	Type of measurement
Venturi tube	Volumetric
Flow mazzle	Volumetric
Orifice plate	Volumetric
Magnetic	Velocity
Nutating disk	Volumetric
Oscillating piston	Volumetric
Bellows gas	Volumetric
Label impeller	Volumetric
Slide sense rotary	Volumetric
Retracting vane rotary	Volumetric
Helical gear	Volumetric
Turbine	Volumetric
Vortex shedding	Velocity
Vortex procession	Velocity
Fluidic oscillating	Velocity
TOF ultrasonic	Velocity
Doppler ultrasonic	Velocity
Thermo-anemometer	Velocity (mass)
Calorimetric	Velocity (mass)
Corrolis mass	Mass flow
Relameter	Velocity

Figure 5. Physics operating principles of some meters.

and manufacturing standards, distinct installation and operating costs, and, of course, will render distinct benefits to the water company.

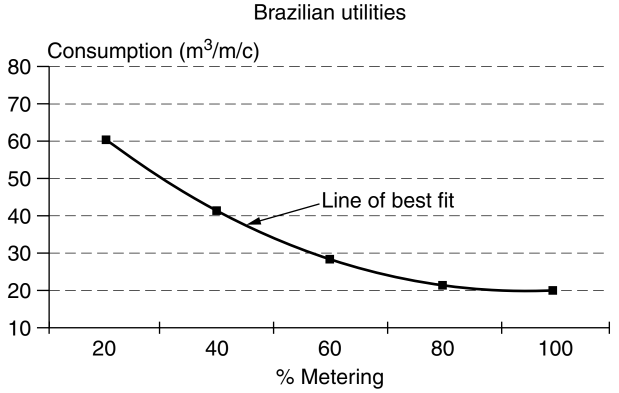
METERING DENSITIES, COSTS, AND IMPACTS

The following figures will give a rough idea of the costs, *per meter installed and working*, for the main concepts of a metering scheme: census, planning, and preliminary work $2 US; device purchase $30 US; installation $15 US; operating costs (meter reading, billing, error correction, tests, etc.) as additional cost compared to fixed tariff system $0.25 US/year, and meter reposition (in average every 15 years) $38 US/15 years.

The most important impact of water counters is in reducing consumption, compared to a situation where meters do not exist. Several references report consumption reductions ranging from 5% to 54% when water price increases and there is a volumetric system. This is known as "*price elasticity of demand*". Figure 6 is an example, taken from a report by the World Bank, illustrating the consumption behavior (cubic meters per month per connection) in Brazilian utilities according to the percentage of meter coverage in each city (4). Reductions are on the water supply side and also on the volume of waste production and the required size of sewerage and treatment infrastructure.

"Universal metering" (all houses and industries in the city have a counter) is adequate only for rich cities, where the possibility of uncontrolled demand may occur randomly from any consumer. It is easy to finance when a meter is always installed in every new construction. Its cost can be recovered as part of the connection fee.

"Voluntary metering," "random metering," "selective metering," temporary metering, or neighborhood or hydrometric district control are ways to avoid expensive universal metering. These, if well planned, can lead to better budgetary results for the institution and to nearly the same water conservation results as universal metering.



Source: Catalogo Brasileiro de Engenharia Sanitaria e Ambiental. CABES. 1990.

Figure 6. Impact of metering coverage on water consumption.

METER READING AND INFORMATION PROCESSING

Medium to big cities have thousands of meters to be read and accounts to be monthly billed and followed. This represents a basic regular task, requiring managerial ability from the water utility. Its success depends on good quality and reliability of the information handled and perfect synchronization among different departments and people.

Here, any gain to save time or money during reading and billing is desirable, and this is why new techniques are being tested and adopted continuously. Some utilities use contact rods to enter digital readings directly into a computer, instead of traditional visual reading and writing. Others use, reading through radio reception on a van circulating through the city streets. Reading through modems (telephone) is practiced as well.

In cities where traditional meters still exist, one important engineering task is optimizing the reading routes to save distance and time. These routes should be frequently reviewed and enhanced according to new customer contracts and technical improvements in metering and reading.

BIBLIOGRAPHY

1. Columbia Encyclopedia, 6th Edn. article on Siemens, Sir William, Infoplease learning network http://www.infoplease.com/ce6/people/A0845159.html.
2. AWWA. (1996). *Water Statistics*. American Water Works Association. http://www.awwa.org/h20stats/h20stats.htm http://www.awwa.org/h20stats/ratebar.htm.
3. EPA. (1998). *Compliance Assurance Monitoring (CAM). Technical Reference for Monitoring Equipment and Instruments. 4.4 Flow Rate Measurement Systems*. Environmental Protection Agency. http://www.epa.gov/ttn/emc/cam/sec4-5.pdf.
4. World Bank (Yepes, G. and Dianderas, A.). (1996). *Water and Waste Water Utilities Indicators*, 2nd Edn. Water and Sanitation Division, TWUWS, The World Bank. http://www.worldbank.org/html/fpd/water/pdf/indicators.pdf.

READING LIST

Aguas de Sevilla, Reglamento del suministro domiciliario, an example of specifications for water meter installation http://www.aguasdesevilla.com/Normativa/reglamento03.htm#art35.

AWWA. (1975). *Sizing Water Service Lines and Meters*. American Water Works Association.

Buenfil, R.M. (1992). *Water Metering Planning and Practices*. M.Sc. Thesis, Loughborough University.

Buenfil, R.M. (1993). *Needs and Illusions About Household Water Metering*. Management of Water Resources in North America, Arizona University & ASCE.

Buenfil, R.M. (1993). *Household Water Metering and Tariffs*. **Conserv-93**, AWWA-ASCE-AWRA Congr.

Buenfil, R.M. (2000). *Estrategia para la toma de lecturas en medidores*. CNA, IMTA.

Buenfil, R.M. (2002). *Clase 3, Medición, curso de uso eficiente del agua en ciudades*. DEPFI, UNAM (Universidad Nacional Autónoma de México). http://www.geocities.com/mario_buenfil/depfi/clase_3.htm.

Encyclopedia Britannica. article about Sir William Siemens, inventor of the water meter. http://34.1911encyclopedia.org/S/SI/SIEMENS_SIR_WILLIAM.htm.

Edwards, K. The fluid flow calculations website. LMNO Engineering, Research, and Software, Ltd. http://www.lmnoeng.com/index.shtml.

Hansen, R.P. (2001). *Elementos Secundarios de Medición de gasto Serie autodidáctica de medición*, IMTA.

ISO. (1993). *Measurement of water flow in closed conduits—Meters for cold potable water—Part 1: Specifications*, ISO 4064-1. International Standards Organization, http://www.dfmg.com.tw/dasp/standard/iso/d9772.html.

Lienhard, J. *Engines of our ingenuity. Episodes: 260 units of measure, 1363 man the measure, 1580 water clock*. University of Houston, College of Engineering http://search.uh.edu/engines_search.html http://www.uh.edu/engines/epi260.htm.

Mello, E.J. (2001). Conservação e Medição da Água various links and articles related to metering and water conservation. http://www.geocities.com/hidrometro/.

Nielse, M.J. Seleção e Dimensionamento de Medidores de Água. (principais critérios e fatores), http://www.geocities.com/hidrometro/dim_resum.htm.

NIST, International System of Units (SI), National Institute of Standards and Technology (USA), http://physics.nist.gov/cuu/Units/units.html.

Osaka Water Service. (2000). *How to Read Your Meter. How to Calculate Your Water Bill*. Water Service Handbook Osaka Water Service. http://www1k.mesh.ne.jp/osaka-water/english/benri/benri_5.html.

USBR. (1997). *Water Measurement Manual. Chapter 14—Measurements in Pressure Conduits*. United States Bureau of Reclamation. 3rd Edn. http://www.usbr.gov/wrrl/fmt/wmm/http://www.usbr.gov/wrrl/fmt/wmm/chap14_01.html.

MUNICIPAL WATERSHEDS

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INTRODUCTION

The Sustainable Development Summit in Rio de Janeiro in 1992 showed clearly that building and running more sustainable human settlements is one of the core challenges (1). Developed countries are characterized by having the majority of their population in urban settings, concentrations of relatively large numbers of people in a relatively small physical area. Transitional countries show a demographic shift from rural to urban settlement. In 2001, more than 54% of the world's 6 billion people lived in municipal centers (towns and cities); some countries have more than 90% (2). Developing and transitional countries often have megacities—Mexico City, Cairo, Sao Paulo, Jakarta, Bangkok—that completely dominate the watersheds they occupy. This form of municipal watershed lies at the least sustainable end of the scale because satisfying voracious demand is a priority, and water-producing zones of the watershed become either consumed by urban sprawl or cannot influence water policy.

In a humid environment, as a society moves from a preindustrial economy to an industrial economy, its watersheds experience three main stages of development (3): (1) few encroachments on water resources; more than enough water for everyone; water is free; (2) transitional infrastructure, including dams for energy and irrigation and interbasin transfers between water-rich and water-scarce watersheds; and (3) maximum streamflow regulation achieved, and aquifers are at maximum sustainable yield, so further development is both expensive and threatens to be unsustainable. Unfortunately, in the case of several megacity watersheds, a fourth stage of overexploitation by intensifying exploitive infrastructure and interbasin transfers is testing the functional viability of municipal watersheds.

TYPES OF MUNICIPAL WATERSHEDS

Megacities lie at one end of the municipal watershed scale (e.g., Mexico City); watersheds that have relatively equal-sized, similar economies and evenly distributed small towns form the other (e.g., Nashua River Watershed, Massachusetts, USA). In between, are watersheds that have a few large towns, a city or two, and several small towns; they have differing economies, needs, and priorities (Fig. 1).

As we move along the scale, the probability of achieving more integrated, sustainable watershed management declines primarily because of the rising conflicts of interest, increasingly significant cultural differences between municipalities, and growing pressure to overexploit natural resources that degrade the watershed ecosystem. In its most dramatic form, a megacity will also draw water resources from neighboring or external watersheds (e.g., Mexico City, Los Angeles), thereby becoming a regional 'sink' that has very significant ecological, sociopolitical, economic, and cultural impacts.

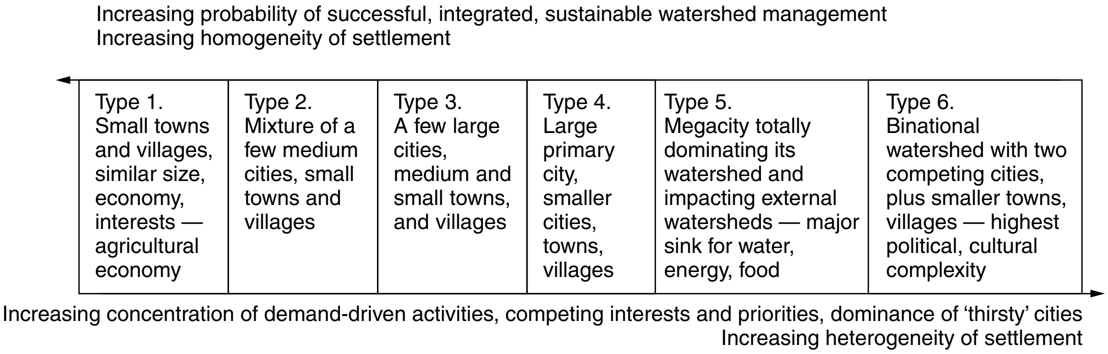
IMPACTS OF MUNICIPAL CENTERS ON WATERSHEDS

Water Quantity Impacts

Figure 2 shows a schematic of a typical municipal water cycle, which may also be considered to represent a composite of the water supply and wastewater sanitation infrastructure for all towns and cities of a municipal watershed. Humans perturb the stocks and flows of water in the watershed through withdrawals for water supply (4):

1. domestic (in-house and out-of-house);
2. industrial (e.g., factories, power stations), commercial (e.g., shops and hotels), and institutional (e.g., hospitals, schools);
3. agricultural (e.g., farms, crops, livestock);
4. public—for example, parks, fire fighting, sewer flushing;
5. Losses—distribution losses, consumer wastage, metering errors, and/or unrecorded consumption.

Domestic, industrial, and public demand tend to dominate municipal watersheds; agricultural demand dominates rural watersheds.



Increasing probability of successful, integrated, sustainable watershed management
Increasing homogeneity of settlement

Type 1.	Type 2.	Type 3.	Type 4.	Type 5.	Type 6.
Small towns and villages, similar size, economy, interests — agricultural economy	Mixture of a few medium cities, small towns and villages	A few large cities, medium and small towns, and villages	Large primary city, smaller cities, towns, villages	Megacity totally dominating its watershed and impacting external watersheds — major sink for water, energy, food	Binational watershed with two competing cities, plus smaller towns, villages — highest political, cultural complexity

Increasing concentration of demand-driven activities, competing interests and priorities, dominance of 'thirsty' cities
Increasing heterogeneity of settlement

Figure 1. A simple typology of municipal watersheds.

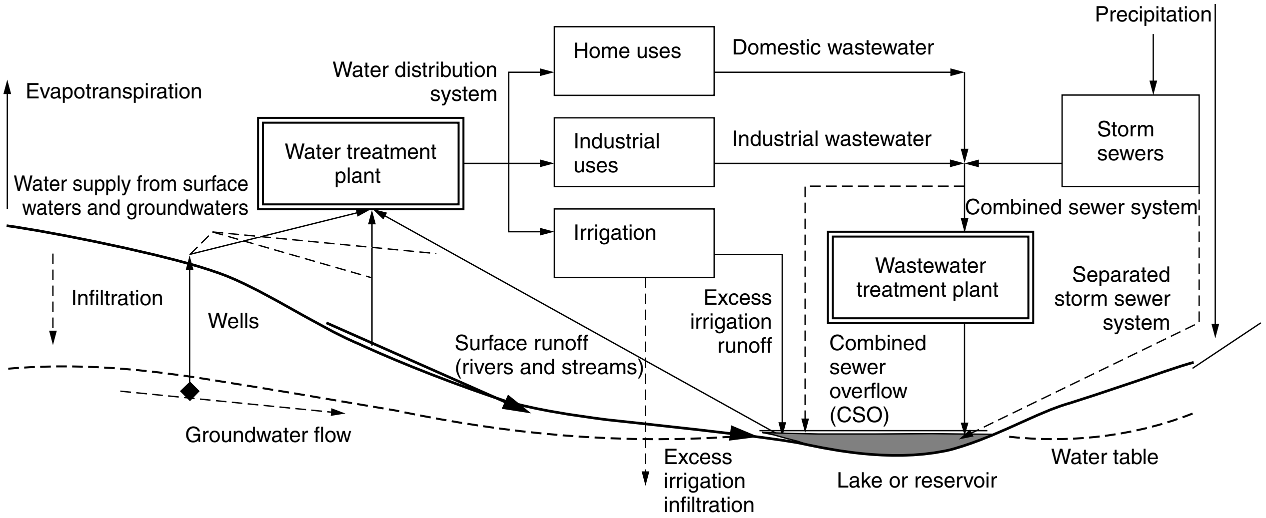


Figure 2. The water supply and wastewater sanitation cycle of a municipal center. The cycle also serves as a composite for the infrastructure serving a municipal watershed.

The estimation of water demand involves (4)

1. plotting the watershed population trend for the past 10–20 years and estimating the proportion likely to be due to immigration and that due to natural increase (births minus deaths);
2. dividing the supply area into different socioeconomic classes of domestic use and estimating the typical domestic consumption per capita in each class;
3. seeking values of future immigration and natural increase for the different classes of housing;
4. estimating distribution pipe loss rates, consumer wastage, and unsatisfied demand;
5. estimating the growth in industrial, commercial, and service demands (a function of population growth);
6. estimating growth in agricultural demand, hydroelectric demand, and public and ecosystem maintenance demand.

Water Quality Impacts

If the water supply–wastewater sanitation cycle is incomplete (usually the case in developing and transitional countries) and wastewater is untreated, it returns to the environment and pollutes receiving waters. The pollution by municipal wastewater also contaminates sediment and soil, air and biota; the distribution of contaminants is a function of their physicochemical properties and the biophysicochemical properties and processes of the environment. Even in a 'closed cycle' like (Fig. 2), municipal wastewater comprises stormwater runoff, combined sewer overflow (CSOs), and effluent from wastewater treatment plants (WWTPs), as well as industrial point source discharges. The location of the pollution sources, their magnitude, composition, frequency, and duration, plus the surface and groundwater hydrology of the receiving areas, will determine the impact. Specifically, it determines whether or not the assimilative capacity has been exceeded, causing pollutant accumulation. The temporal and spatial scales of impacts vary (after 2): (1) local scale for less than a day—acute toxic impacts, sediment resuspension, coarse material sedimentation; (2) subwatershed scale for days to weeks—BOD and DO changes, algal blooms; (3) watershed scale for months to decades—accumulation of pollutants in fish and sediments, cultural eutrophication, composition of aquatic species changes. As well as pollution potential, large municipal centers may affect microclimate by altering the energy regime, air quality, and circulation (2). Urban heat islands increase evaporation, whereas impervious surfaces reduce infiltration and increase runoff.

In developed countries, because of stricter laws, urban wastewater impacts mainly the recreational use of lakes and rivers, may contaminate shellfish, but rarely pollutes water supplies. Pathogens enter surface receiving waters from untreated CSOs, WWTP effluent, and stormwater runoff, posing risks to bathers, and leaking septic tanks can contaminate surface water and groundwater. In stark contrast, in developing countries, a polluted water supply, poor sanitation, and poor drainage cause a range of devastating impacts on public health (5,6): Vector-borne diseases like malaria and dengue fever (the former has an estimated annual global mortality of 1–2 million, morbidity 200 million, and more than 2 billion at risk); water-based diseases such as schistosomiasis (bilharziasis) and dracunculiasis (guinea worm); water-washed disease such as trachoma and scabia; and waterborne diseases such as cholera, bacillary dysentery, amebic dysentery, and typhoid (estimated annual mortality 4 million, morbidity more than 1.5 billion, 2 billion at risk).

In a municipal watershed, unregulated human activities produce a combination of ecological stressors: habitat destruction, flow modification, thermal pollution, invasive species, and toxic pollution from wastewater and solid waste. When these stressors act together, the possibility exists that degradation becomes synergistic, where one stressor magnifies the impacts of others. Clearly, from (Fig. 1), the municipal watershed ecosystems (including human populations) most at risk from such large-scale impacts are types 4, 5, and 6 because of the potential number, frequency, duration, and magnitude of stressors associated with large cities and megacities.

INTEGRATED MUNICIPAL WATERSHED MANAGEMENT (IMWM)—NEEDS

Municipal watershed management becomes *integrated* when actions on the local municipal scale are carried out in the context of connections with other settlements and the wider watershed. The integration can happen across dimensions described in terms of different kinds of capital. Scoones (7) identifies five categories of capital assets that sustain human livelihoods:

1. natural capital—land, water, wildlife, biodiversity—integration across types of natural resources because all are interrelated in the watershed ecosystem;
2. social capital—groups, networks, laws, regulations, institutions of people—integration across social groups (multistakeholder planning and management), and networking between communities, between government agencies, and between water users and government regulators;
3. human capital—skills, knowledge, healthy people—the integration of different disciplines, professions, interests, and abilities;
4. physical capital—basic infrastructure that supports shelter, transportation, energy, water supply and sanitation, health care, education, communications—the most obvious form of watershed integration, connecting water sources, supply and sanitation infrastructure serving different users;
5. financial capital—income, savings, credit—pooling of financial assets for investment in watershed management goals, including service charges, pollution taxes, and appropriate subsidies.

The last two are the most familiar; the first three require changes in thought, feeling, and action and are beginning to take place. It is notable that in the relatively few cases of 'successful' IMWM, integration has occurred, at some level or other, across each capital dimension. The goal of integrated water management has been described as: "the sustainable, coordinated management of water resources within a region, with the objectives of controlling and conserving water, minimizing adverse effects and achieving specified and agreed water management and social objectives" (8). The cycle of (Fig. 2) is made more sustainable as follows:

- optimizing the design of the engineered cycle to exploit sources responsibly and more sustainably and to minimize wastage, pipe leaks, unaccounted for losses, cross-contamination of supply and sanitation lines, and pollution of the receiving environment;
- reuse of wastewater for nondrinking uses (and drinking water if state-of-the-art tertiary treatment is economical, for example, in Windhoek, Namibia);
- water conservation measures by substituting more water efficient technologies (less water use), cleaner technologies (less wastewater production), and demand management through metering, pricing, and regulation.

Water Supply Enhancement

The World Health Organization (WHO) and the World Bank's basic water requirement for meeting survival needs is 20–40 liters/person/day (2). Many municipalities, especially in type 4, 5, 6 watersheds (Fig. 1), continue to develop new water supply projects and intra- and interbasin water transfer schemes to try to meet growing demand. New approaches emphasize conservation practices to regulate withdrawals (e.g., at or less than replacement levels for aquifers), enhance aquifer recharge, and exploit the economies of scale of conjunctive use of several water sources (2). Dual water supply systems—one for potable water, one for other uses—may be economical in areas of water scarcity, though retrofitting old water cycles is costly. Many new devices save water, like low-volume flushing toilets, shower heads, sprinklers, and washing machines. Considerable saving may be had from recycling rainwater or graywater (less polluted or partially treated wastewater). In a typical municipality, 20% of water use may be industrial, so improving process efficiency and reuse is an attractive option, especially for cooling waters that are polluted thermally. For dirty wastewaters, pretreatment options include ultrafiltration, activated carbon filtration, or reverse osmosis (2). Design of the treatment process depends on the effluent water quality, the required reuse quality, and the flow volume. Agricultural uses, though less important in a municipal watershed, may still account for 25%. Most water is used for crop irrigation and for cleaning dairy sheds (manure flushing), so reuse of graywater and rainwater is attractive. New hydroponic (soil-less) agriculture treats and recycles the water medium, using simple filtration (sand filters or biofilters) and ultraviolet disinfection (2). Xeriscaping—the planting of low water use plants for landscaping —is gaining popularity.

Wastewater Sanitation Enhancement

Development practitioners consider that ‘environmental sanitation’ encompasses wastewater, stormwater, and solid waste collection, handling, treatment and disposal, as well as personal, domestic, and communal hygiene practice. WHO considers that ‘improved’ sanitation consists of connection to sewers or septic tanks, pour-flush latrines, pit latrines and ventilated improved pit latrines; ‘not-improved’ devices include manually serviced bucket latrines and open latrines. The adoption of sanitation practices is heavily influenced by hygiene education and cultural norms. Black industrial wastewaters can undergo cheap pretreatment using unit processes like simple bioreactors (e.g., upflow anaerobic sludge bed technology) (2). The primary goal of wastewater treatment is to reduce total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia, and pathogens. Separation of wastewater streams at the source allows treating graywaters by simple primary filtration and settling processes (e.g., wetlands, sand filters) and then reuse; blackwaters are treated by primary (screening and settling) and secondary (aeration, bioreactors) unit processes (9). Urine may be collected, stored, and used as fertilizer; feces can be stored in a composting tank for later use as compost (10). In some places, biogas from biowaste decomposition is used for energy. Any agricultural reuse of wastewater and its sludge residue (biosolids) after treatment is carefully regulated so that food crops are not contaminated. Sludge processing can be costly, but the material can be used as a fertilizer.

Flood Protection and Drainage

By connecting land use/land cover planning with water flow management, the twin goals of flood defense and

Table 1. Key Aspects of Integrated Municipal Watershed Planning and Management

Information for Problem Definition[a]	Typical Priority Problems	Implementation Steps[b]
• Characterization of water resource capacities • Characterization of water quality • Inventory of aquatic life in the surface waters • Estimation of impacts of polluted water on humans and other species • Inventory of pollution sources (stormwater, CSOs, municipal, agricultural, and industrial point and nonpoint sources) • Inventory of existing water supply and sanitation infrastructure (treatment plant types, capacities) • Inventory of industrial and commercial wastewater discharges to municipal sewers • Land use/land cover inventory • Inventory of sensitive habitats • Soil contamination maps • Flood plain maps for various return periods • Groundwater hydrology and sustainable yield • Population data on numbers, growth, consumption	• Degraded habitats • Degraded water quality • Fisheries management • Supply deficits • Sanitation deficits • Leaky supply systems • User wastage	• Identify who the stakeholders are and their interests • Establish goals that are attainable, endorsed by stakeholders, and economically responsible • Develop a strategic plan on the appropriate (problem-determined) scale (local, subwatershed, watershed) • Develop the funding mechanism • Lobby politicians to gain support • Involve politicians in promoting the plan • Revise institutional roles and responsibilities to support the plan • Implement the plan • Monitor performance (postaudit)

[a] After (11).

[b] After (2).

habitat maintenance can be addressed. The former relies on educating people not to build in the floodplain, nonstructural measures such as laws and regulations, and structural measures such as reservoirs, levees, and revegetation. The considerable impervious surfaces in a municipal watershed reduce groundwater infiltration and increase rates of polluted runoff during precipitation. Stormwater management consists of three types (2):

1. policies and source controls—education, laws, regulations, including land-use zoning;
2. best management practices (BMPs) and community-level BMPs for the site—for example, rooftop detentions, ponding to increase infiltration, reducing slopes;
3. watershed-wide efforts—habitat conservation (especially wetlands), reducing soil erosion.

It has been shown that the total impervious area (TIA) of a watershed—a good development indicator—correlates with the biological integrity (BI—abundance and diversity of aquatic species) of streams (2): high BI—low TIA (<5–10%); moderate BI—moderate TIA (5–10% < TIA <35–45%); and low BI—high TIA (>35–45%). Stream restoration employs BMPs to provide sufficient, not excessive flows, and to mitigate pollution. In many cities of the developing world, periurban areas contribute highly polluted stormwater because of open sewers, open garbage dumps, and soil erosion from degraded slopes.

IMWM—Planning and Implementation

Not surprisingly, planning on a watershed scale requires a systems approach: (1) problem definition (needs and priorities); (2) description of alternative solutions; (3) evaluation of alternatives and selection of preferred option; (4) implementation of the preferred option; and (5) maintenance and monitoring of performance. Table 1 provides an overview of some key operational aspects.

CASE STUDY

The Nashua River Watershed (Fig. 3) and the Blackstone River Watershed are neighboring examples of municipal watersheds in New England, United States. Their management approaches illustrate many of the challenges for IMWM, and useful lessons can be drawn. Both rivers have similar industrial histories that caused severe pollution, equal areas (540 square miles), and both set out to clean up their rivers at the same time in 1969. Later, they set similar goals of meeting the 1972

Figure 3. Nashua River Watershed, a type 2 municipal watershed. Its integrated management has benefited from strong community leadership and a focus on water quality (12) (permission of Nashua River Watershed Association).

(and 1977 amendments) Clean Water Act standards of being 'fishable and swimmable' (Class B). Neither river has yet met this goal, originally set by the U.S. Environmental Protection Agency for *all* rivers in the country by 1983. But noticeable improvements in water quality have taken considerably longer in the Blackstone River than in the Nashua River. Why? Mailloux (13) found that Nashua's watershed management has been more successful compared to Blackstone's because of the strong community leadership that lobbied politicians and secured funding for paid positions in the Nashua River Watershed Association (NRWA). This community-based organization formed a cohesive, focused, highly motivated environmental movement devoted explicitly to improving water quality and able to take advantage of information resources and legislation. NRWA also formed strategic partnerships with industrial interests and government, significantly strengthening the social capital of their watershed. This process was aided by the relative homogeneity of the watershed settlements and constituent economies (type 2, (Fig. 1)). Blackstone did not enjoy the same homogeneity (type 3), complicated by bistate administration (Massachusetts and Rhode Island), and did not strengthen its social capital cohesively. Nor did it focus on the core issue of stemming water pollution; it was concerned primarily with recreational use and aesthetics.

CLOSING REMARKS

Municipal watersheds are complex socioecological systems that have many conflicting needs, interests, and priorities for the sustainable development of natural watershed resources: water, air, soil, energy, food, forests, and biodiversity. Without a watershed approach to stewardship, human needs sharply conflict with the needs of other species. With the rise of urbanization worldwide, municipal watersheds of different types are becoming geopolitically dominant in the landscape, placing strong demands on their water supply and wastewater sanitation systems and on their rural agricultural counterparts to produce food for them and often transfer water to them. In most developing countries, the problems are acute; few municipal watersheds have adequate systems; many have almost no sanitation. Unless major changes in policies and practices occur—those emphasizing integrated approaches, supply/sanitation optimization, cleaner production and efficiency—ever more settlements and habitats will be at risk from water stress, either from insufficient water quantity, degraded water quality, or both. Municipal watershed stewardship challenges our ingenuity and our political will, our core values, and the capacity of our institutions to respond. It is important, as always, to learn what works, and why, and draw on experience worldwide. Although the magnitudes of watershed problems differ from country to country, the underlying sociocultural obstacles to sustainable solutions are remarkably similar.

BIBLIOGRAPHY

1. UNCED (United Nations Conference on Environment and Development). (1992). *Earth Summit 1992—the United Nations Conference on Environment and Development*. The Regency Press, London.
2. Marsalek, J., Rochfort, Q., and Savic, D. (2001). Urban water as part of integrated catchment management. In: *Frontiers in Urban Water Management*. C. Maksimovic and J.A. Tejada-Guibert (Eds.). UNESCO and IWA, London, pp. 38–83.
3. Falkenmark, M. and Lindh, G. (1993). Water and economic development. In: *Water in Crisis, a Guide to the World's Fresh Water Resources*. P. Gleik (Ed.). Oxford University Press, New York, p. 80.
4. Twort, A.C., Ratnayaka, D.D., and Brandt, M.J. (2000). *Water Supply*, 5th Edn. Arnold and IWA, London, pp. 1–35.
5. Masters, G. (1998). *Introduction to Environmental Engineering and Science*, 2nd Edn. Prentice-Hall, Upper Saddle River, NJ, p. 174.
6. UNEP (United Nations Environment Programme). (1993). *Environmental Data Report 1993–94*. Blackwell, Oxford.
7. Scoones, I. (1998). *Sustainable Rural Livelihoods: A Framework for Analysis*. Working Paper 72, Institute of Development Studies, Brighton, UK.
8. ASCE (American Society of Civil Engineers, Water resources planning and management division) and UNESCO (International hydrological programme IV). (1998). *Sustainability Criteria for Water Resource Systems*. Task committee on sustainability criteria, Project M-4.3, ASCE, Reston, VA.
9. Skjelhaugen, O.J. (1999). Closed system for local reuse of blackwater and food waste integrated with agriculture. *Water Sci. Technol.* **39**(5): 161–168.
10. Otterpohl, R. (2001). Options for Alternative Types of Sewerage and Treatment Systems Directed to Improve the overall performance. *Proc Interurba II, 2nd Int Conf on Interactions Between Sewers, Treatment Plants and Receiving Waters in Urban Areas*. Lisbon, Portugal, Feb. 19–22.
11. Geiger, W.F. and Hofius, K. (1995). Integrated water management in urban and surrounding areas—findings of the International Workshops in Essen 1992 and Gelsenkirchen 1994 by the German-Dutch IHP Committee to UNESCO, Project M3-3a. In: *Preprints of the Int. Symp. Integrated Water Manage in Urban Areas*. J. Niemczynowicz and K. Krahner (Eds.). Lund, Sweden, Sept. 26–30, pp. 127–151.
12. NRWA (Nashua River Watershed Association). (1995). *1995–2020 Vision for the Nashua River Watershed*. a guide for the next quarter century, NRWA Inc., Groton, MA.
13. Mailloux, J. (2003). *A Tale of Two Rivers, Environmental Science and Policy Honors Thesis*. Clark University, May.

PUBLIC WATER SUPPLY WORLD

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VALUE OF A WATER SUPPLY

A good, dependable water supply promotes health, productivity, beauty, arts, safety, recreation, and most of the desirable goals of life and society. Probably, the first ancient human settlements simply occurred in places granted by nature with fruits, animals, and other food, and with enough and easily reachable water. People used to move or travel when conditions changed (*drought, flooding, climate change*) or simply because they wanted to explore new horizons. Later, the discovery of agriculture made sedentary groups larger, and towns grew. Water had a prime role in the possibility of producing food and having a stable place to live. Production and living depended on reliable, good quality water, requiring as little effort as possible in its conveyance, storage, and use. The best water sources were, and still are, regular rains, the stable flow of a river, or the constant level of a lake.

Growing Complexity

Meeting one or more of the previous conditions for accessible water is not always possible or easy. Evidently, when towns grow, new residents need to set up a bit farther away from the river or community storage than already existing houses. This creates, for the newer inhabitants, more toil to fetch the water, the need to have a donkey or a cart, expending time and effort carrying, or investing in pipes to convey the water to their place, and possibly to pay continuously for energy (*pumps*) to raise water to higher spots.

Moreover, the best sites for cities and water were occupied since ancient times, so new settlements, forced by the overwhelming human growth of the last two centuries, are occurring in places without the appeal and qualities of those first towns and cities. Unfit locations are often aggravated by deteriorated water quality due to wastewater and debris discharged by upstream housing, industries, and agriculture.

HEALTH, FAIRNESS, AND ECONOMIES OF SCALE

In cities of high housing densities, ***public water supply*** started as a measure to improve hygiene and health, as well as a need for fairness among citizens, to give them an equal chance to have water and to pay similar amounts via taxes or equivalent. It is also much cheaper and less chaotic to have collective solutions than individual ones.

A public water service can concentrate and pay specialized personnel, devoted full time to these highly technical matters of searching, treating, transporting, raising, distributing, maintaining, and charging for water service.

Water service in most cities of the world is provided by governmental institutions (*either national. regional. municipal*), but in many other locations is operated by private utilities. There also exist mixtures of private and governmental (*public*) responsibilities. Nowadays, there is a tendency, often promoted by lending institutions, to give up (*"privatize"*) governmental services that have too many conflicts and poor quality.

In this article, the term "***public water supply***" refers to the water service provided by some official concessionaire (*independently if is private or government*) that attends to the needs of various clients in a city. For its character and to benefit from economies of scale, it is regularly a "monopoly" within the same city or region. This means that usually no competitors, doing similar tasks, are allowed within a location.

SUPPLY DIFFERENCES AND STYLES IN THE WORLD

Developed countries generally have better natural water resources than poor "developing" (*alias "third world"*) nations. Certainly the ease and abundance of water resources explains many of the differences in material progress among nations. Besides, public water supply quality in "first-world" countries is better, reflected in the continuity, quantity, quality, pressure of water, and the readiness to attend to consumer complaints or requests.

Such reliable and quality service in rich countries doesn't mean that their service is superior or more "efficient" than that offered in poorer and drier countries. Often it is just the opposite because cities that lack water use more ingenuity, toil, and productivity to do much more with fewer resources (*smaller in water availability, energy usage, investments*), covering larger populations, and have radically different, or even nil, water fees.

Service in rich cities typically leaves little care and worry to the individual household, except to pay its taxes or water fees. But as governments are poorer, institutions are weaker, or water scarcity is severer, situations change. There can be various combinations and styles among tasks and investments left to the individual homeowner and among duties performed by the public water utility or through other intermediate providers. There usually are more responsibilities and "choices" posed on the tenant as situations are more stringent. Table 1 presents some examples of a water supply system's components (*infrastructure, equipment*) often left as obligations (*duties*) of each homeowner or group of them.

Sometimes the government or the public privatized service can be in charge, or help, in some individual solutions such as cistern cleaning, rainwater harvesting, toilet retrofitting, and leak repair inside houses, to save water and be able to meet the water demand.

COMPONENTS AND EVOLUTION OF A WATER SYSTEM

All humans need or desire water to cover the following purposes in decreasing priority level or intensity: drinking,

Figure 1. Communal rainwater sotrage.

Table 1. Components of a Water Supply System

Source
Rain catchment and storage at community level (Fig. 1)
Rain catchment at domestic level (*rain harvesting*) (Figs. 2 and 3)
Hand pump well
Wells (*sakia, noria, shallow wells*)
Distribution and pressure
Individual transport (Fig. 4)
Open channel or aqueduct (Fig. 5)
Public standpost
Home connections (*built by the homeowner, built by the public facility, built by a concessionaire*), with valves or meter or without them (Fig. 6)
Electric or manual pumps to raise water to places where needed (*2nd floor, etc.*)
tankers (*buy complementary water from private distributors*). (Fig. 7)
Storage
Public regulation and storage tank
On the roof container (*tinaco*)
In-ground individual cisterns
In-floor collective container (*for a group of houses*)
Water quality
Chlorination
Filters
Boiling (*gas or wood consumption*)
Buying bottled water for drinking
Water saving
Meters and fees
Low consumption toilets, water saving showerheads, etc.
Rota cuts, intermittent service (*regular rationing*)
Very low water pressure (*just enough to reach the water intake, the house connection to the main at street level*)
Laws and regulations to install water saving devices
Reuse of gray water (*sullage*)

bathing, clothes washing, cooking, gardening, pet care, housekeeping, recreation, manufacturing a product, etc. Priorities and quantities vary with cultural, natural resources, and technological differences among regions.

Around the world, cultural preferences and technology are varying rapidly in these decades, and sometimes their fast evolution is confusing many people in thinking that natural resources also evolve at our will (*a mistake which is creating serious risks and damages to other species*). Additionally, there is a strong tendency toward similar (*globalization*) aspirations for comfort and life standards in most communities, although these are not always possible to meet due to economic constraints. The world would be much better if the environmental aspects of each region are considered carefully before embarking on seeking such water system standardization.

Not very far off in time, even nowadays in rich countries, nobody thought about (*"needed"*) water faucets or showers inside their dwellings. The components of a water supply system could then consist of

Figure 2. Rural domestic rain collection.

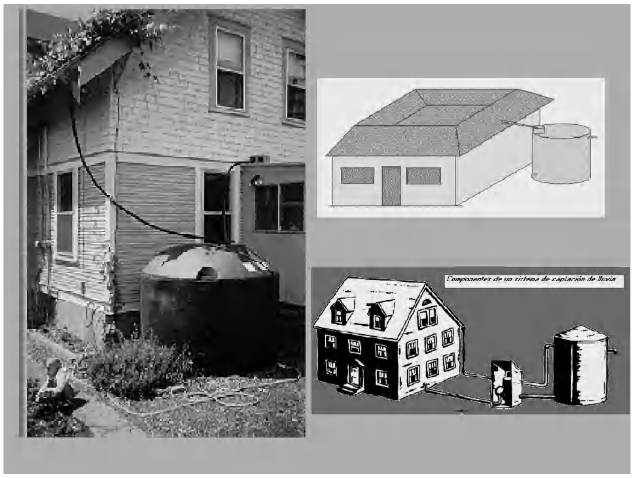


Figure 3. Urban domestic rain catchment.

Figure 4. Water transport.

Figure 5. Ancient acueduct.

Figure 6. House connections in dry tank.

Figure 7. Tanker supplying water.

- source (*storage for rain water, river intake, or shallow well*)
- gravity conduction or simple transport (*channel, simple aqueduct, buckets, animal cart, or pipes*)
- delivery at limited sites (*public fountains, stand posts*)

When water quality is not totally satisfactory or the quantity available from the source is insufficient during some seasons of the year or during some period of the day, a more “advanced” (*complex*) system is required (see Fig. 8) that has additional components:

- dam or long-term storage
- filter or chlorination
- short-term storage or regulatory tanks

Many public water supply systems in the world nowadays operate on a simple scheme, similar to those just mentioned. But as “progress” has advanced, pollution has increased, and people’s expectations and habits have been transformed; the complexity of the systems has also enlarged. In such a case, some additional components can be (Fig. 9):

- regional or international agreements to use and share water
- deep wells
- long conduits
- pumping stations,
- metering and gauging stations
- leak detection equipment
- valves of different kinds
- dual distribution systems (*different water qualities on each*)
- house connections, consumption meters
- reading and billing mechanisms.

Much damage was done earlier by considering the water supply network isolated from the drainage or sewerage solution. Both must be understood as a unique, integrated, system. In this case, additional elements are

- sewerage network
- wastewater treatment plants
- reuse networks
- efficient water use and conservation programs
- legislation to prevent certain water uses and pollution of sources

It should also be realized that present ***technological progress*** has made different kinds of resources more intermingled and **interdependent**. Then, “public water supply” doesn’t depend exclusively on water availability, but also on energy supply (*for pumping, treatment plants*), human resources (*requirements of trained personnel*), manufacturers and materials available in the region (*pipes, machinery*), and the political and legal framework (*standards, laws, institutions*).

PRESENT CONFLICTS AND NEEDS

Water supply and the possibility of having water and sanitation in our own houses, or at least very close to them, more than any law, invention, or medical advance is what

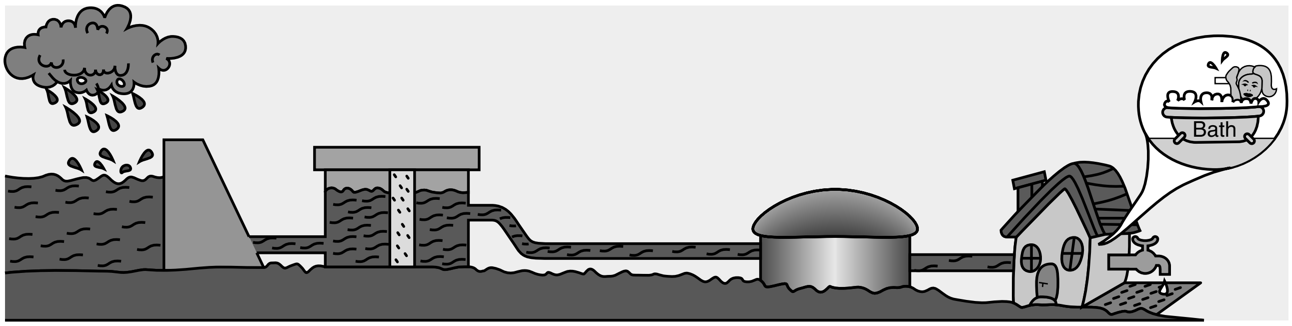


Figure 8. Elementary water supply and disposal system.

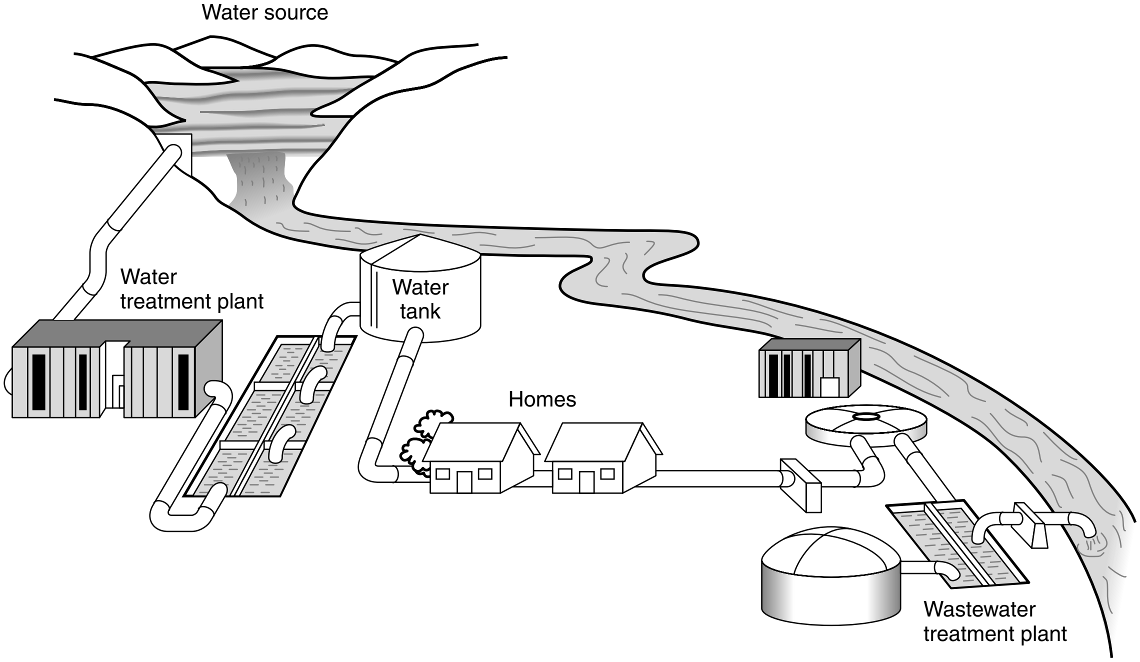


Figure 9. Increasing complexity for supply and disposal system.

has allowed extensive increments in comfort, health, and production and has accelerated the growth of cities. On the other hand, it is shocking that this main force, which made cities swell and consolidate in the past, is now causing the decline of security and comfort in many cities and regions. Past growth, mainly in Europe and well-gifted countries, was slower than that now occurring in poor regions. A slower pace gave the chance for trial and error, without so much risk as today, and also allowed time to mature and integrate useful capital (*material goods, infrastructure, knowledge, and educated people*).

The enormous global human population increase during the last decades, which will still continue during the next 40 years, has occurred almost entirely in the third world (*developing*) countries, ironically, where water scarcity is more evident, as shown by various studies of prestigious international organizations. These poorer countries, where 80% of humanity lives now, and where almost 90% will be in five decades (1–5), are facing "modernity" and high demands for welfare from their people, combined with mighty stresses on natural resources and without much time to think and try the best ways.

Risk or deterioration of those benefits provided by a water supply (*see value of a water supply*), comes from continuous and unrestricted demographic internal urban growth, aggravated by high immigration toward cities due to lack of employment, land, or water for irrigation in rural communities. Expectancies and water demands from these growing populations are difficult to meet without causing damage to other societies (*further in space or time*) or to the natural environment, particularly when the technologies and style of solutions proposed are still those used in the past (*no treatment of wastewater, intensive energy use for pumping, etc*).

The appeal of economies of scale, mentioned earlier, work in the opposite direction when cities are too big and complex (*smaller is better*). One example is Mexico City, where the *benefit/cost ratio* of augmenting the water supply is lower than in other cities of that country.

Some frequent and worrying signs of unsustainable water supply systems are

1. Water scarcity, caused when demands are greater than accessible volumes. Availability must consider the seasonal and regional variations of usable water.
2. Unrecoverable yearly drawdowns in aquifers.
3. Polluted rivers and lakes.
4. Lakes with decreasing water level, going dry or nearly extinguished.
5. Rivers not discharging any more into the ocean, due to deviations and use of their flows.
6. Deforestation threatening water recharge areas, creating erosion and flooding (*flow mode difficult to control*), and causing microclimate changes (*hotter spots*) that increase people's water demands.
7. Rubbish and contamination that menace aquifers and recharge areas.
8. Urban settlements and paving on zones of aquifer recharge or of high risk.
9. Untreated supplied water and free discharge of wastewater.
10. Supply services on rotation (*irregular*) and uncertainty of amounts provided.
11. Huge amounts of water lost through leaks, due to bad quality or status of water networks (*piping quality or poor operation and maintenance*).
12. Incorrect valuation of water. Fictitious or highly subsidized tariffs give the wrong message to the public (*hidden expenditure rob other services, regions, and/or the future*).
13. Institutional weaknesses as procrastination against nonpayment and clandestine connections.

WATER SERVICE BASIC DATA AND INDICATORS

To decide the size of the pipes and other items (*pumping stations, storage tanks, valves, etc*) of a public water network, it is essential to know first some characteristics of consumers' demands and of the supply sources. Studying the demand and ways to manage it, in case it surpasses the supply capabilities, is the prime step for any design. It is also important to know where and how is the existing infrastructure.

There are some typical key indicators used by most water utilities and recommended by international aid organizations (1,2,6). Indicators, parameters, or data describing the characteristics and status of a given water supply system can be grouped in various ways; one example is Table 2.

Tables 3, 4, and 5 list some indicators for three of the previous groups mentioned in Table 2.

This article cannot extend to a detailed discussion of these water service indicators or mention their representative values or ranks in some countries (*they can vary substantially. See reading list for more details*). Only two of them, coverage and demand, will be commented on briefly:

Table 2. Groups of Indicators of a Water Supply System

Water resources indicators
Personnel indicators
Physical indicators
Operational indicators
Quality of service indicators
Community organization and contributions (*e.g., tariff rates and structures*)
Financial indicators

Coverage

Coverage is the ratio of people served to the whole population in a location. It varies widely among countries. Developed nations have values of 100% or near it; in very poor countries, it may be as low as 10 or 20% (*Cambodia, Haiti, Mozambique, etc.*). Moreover, broad differences exist between urban and rural areas in many countries. Certain cities that have apparently satisfactory infrastructure coverage present serious deficiencies due to droughts or useless networks that imply continuous rationing of the supply.

Table 3. Operational Indicators

- A. Water consumption
  - A.1 Average water demand, requirement, or allotment
  - A.2 Unit Consumption
  - A.3 Water Consumption & Metering
  - A.4 Distribution of Water Consumption
  - A.5 Consumption by Main Users Category
  - A.6 Ratio of Peak Day to Average Day
  - A.7 Water Price & Income Elasticities
- B. Water distribution system
  - B.1 Coverage or population served
  - B.2 Length of Water Piped Systems
  - B.3 Storage Volume
  - B.4 Pipe Breaks
  - B.5 Pipe Breaks as a Function of Pipe Material
- C. Unaccounted for water
  - C.1 Water Losses
  - C.2 Composition of UFW
  - C.3 UFW Effective Reduction Programs
  - C.4 Sustainability of UFW Reduction Programs
- D. Wastewater
  - D.1 Length of Sewer Systems
  - D.2 Infiltration Flows in Sewer Systems
- E. Wastewater treatment
  - E.1 Typical Composition of Untreated Municipal Wastewater
  - E.2 Typical Constituent Removal Efficiencies
  - E.3 Removal of Microorganisms
- F. Personnel
  - F.1 Number of Staff
  - F.2 Staff Composition
  - F.3 Training Effort
- G. Miscellaneous indicators
  - G.1 Vehicles/1000 Water Connections
  - G.2 Meter Reading
  - G.3 Meter Maintenance and Replacement Practices

Table 4. Financial Indicators

- A. Efficiency indicators
  - A.1 Working Ratio
  - A.2 Operating Ratio
  - A.3 Accounts Receivable/Collection Period
  - A.4 Percentage Contribution to Investment
- B. Leverage indicators
  - B.1 Debt Service Coverage Ratio
  - B.2 Debt Equity Ratio
- C. Liquidity indicator
  - C.1 Current Ratio
- D. Profitability indicators
  - D.1 Return of Net Fixed Assets
  - D.2 Return of Equity
- E. Operating ratios
  - E.1 Personnel
  - E.1.1 Personnel Costs
  - E.1.2 Staff Productivity Index
  - E.2 Composition of Operational Costs
  - E.3 Unit Operational Costs

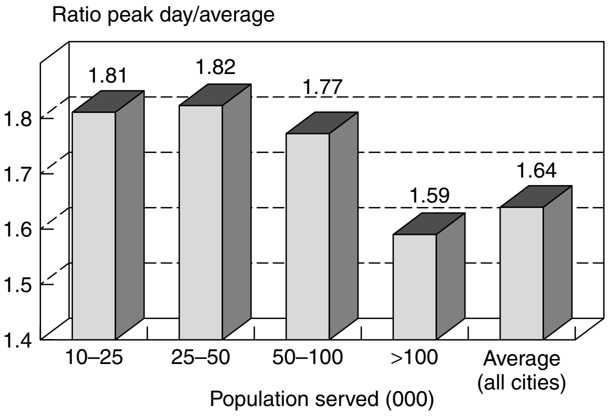
Table 5. Community Organization Contributions

- A. Tariff rates and structures
  - A.1 Tariff Structure
  - A.2 Domestic Tariff
  - A.3 Average Charge & Incremental Cost
  - A.4 Rate Discrimination by Consumer Group
  - A.5 Water Billings, Consumption, & Users

Demand (average water requirement)

Demand represents the volume that needs to be withdrawn from the water sources to satisfy all uses and inhabitants in a city. Usually, it is expressed as a per capita daily volume (*liters/person-day*). It has some similarity to "unit consumption" but is not necessarily the same, especially when the sources are insufficient to meet people's desire for water. The "demand" is a broader concept which includes other water uses, besides domestic. Some "uses" that never should be forgotten when reviewing or designing a supply network are the leaks and other UFW (*unaccounted for water*) that inevitably have to be fed to the system, to be lost so a certain water quantity really reaches individual houses. Figure 10 compares some values in developed countries for unit consumption at household level. Figure 11 shows some typical values in demand variation among seasons, and (Fig. 12) represents distribution of water volumes in a typical Canadian dwelling.

The design, improvement, or revision of a water supply network is relatively easy using modern hydraulic simulation programs. The real labor and complication is in defining, finding, measuring, and gathering the appropriate and correct data to make those calculations and in defining reasonable specifications and standards for



Source: AWWA. Water industry database; utility profiles, 1992.

Figure 11. Demand variations with town size.

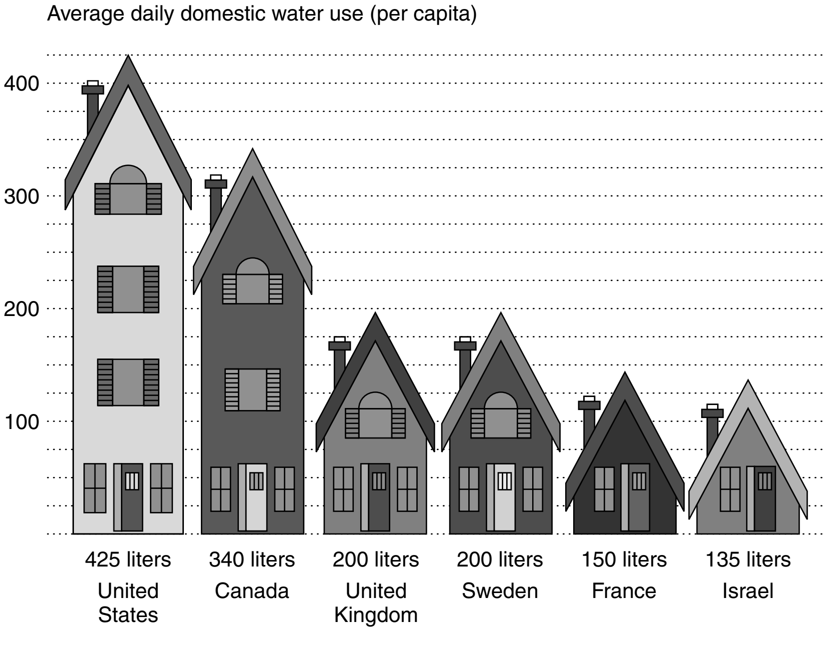


Figure 10. Comparison of household consumption in developed countries.

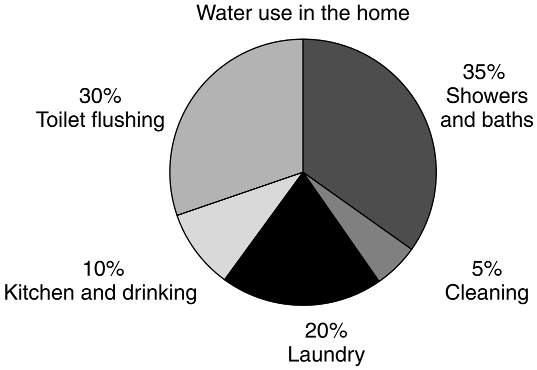


Figure 12. Water uses in a canadian house.

the system. Many textbooks and computer software forget to mention these difficulties. Basic data and indicators are not merely technical aspects, but are rather social, environmental, political and economic, and should be carefully tracked and understood by any person involved in a water supply project.

BIBLIOGRAPHY

1. WRI World Resources Institute. (1999). *Freshwater Data Tables*. WRI. http://www.wri.org/wri/facts/data-tables-freshwater.html.
2. WRI World Resources Institute, (Carmen, Revenga et al.). (1998). *Watersheds of the World. Ecological Value and Vulnerability*. Joint publication of World Resources Institute (WRI) and World Watch Institute. http://www.wri.org.
3. World Bank (Yepes, G. and Dianderas, A.). (1996). *Water and Waste Water Utilities Indicators*. 2nd Edn. Water and Sanitation Division, TWUWS, The World Bank, http://www.worldbank.org/html/fpd/water/pdf/indicators.pdf http://www.worldbank.org/html/fpd/water/topics/utility_o&m.html http://www.open.gov.uk/ofwat/leakage.htm.
4. World Bank. (2000). *World Development Report 2000/2001. Attacking Poverty*. The World Bank Group. http://www.worldbank.org/poverty/wdrpoverty/report/index.htm (*particularly see Table 9. Water use, deforestation, and protected areas*) http://www.worldbank.org/poverty/wdrpoverty/report/tab9.pdf.
5. National Geographic. (October, 1998). *Population. Millennium Supplement*. National Geographic Society. http://www.nationalgeographic.com/ngm/9810/index.html.
6. Alegre, H., Baptista, J.M., Hirner, W., and Cabrera, E. (2000). *The IWA System of Performance Indicators for Water Supply Services*. International Water Association IWA, manual of best practices (performance indicators). http://www.iwapublishing.com/template.cfm?name=isbn 1900222272.

READING LIST

CIWEM. (1984). *Water Distribution Systems. Water practice manual 4*. The Chartered Institution of Water and Environmental Management, CIWEM (*formerly Institution of Water Engineers and Scientists, IWES*). http://www.ciwem.org.uk/publications/manuals/index.asp.

CIWEM. (1983). *Water Supply and Sanitation in Developing Countries*. The Chartered Institution of Water and Environmental Management, CIWEM (*formerly Institution of Water Engineers and Scientists, IWES*). http://www.ciwem.org.uk/publications/manuals/index.asp.

CIWEM. (1986). *Water Services Planning. Water Practice Manual 6*. CIWEM (IWES). http://www.ciwem.org.uk/publications/manuals/index.asp.

Cullivan, D. and Edwards, D.B. (1988). *Guidelines for Institutional Assessment Water and Wastewater Institutions*. Water and sanitation for health project. WASH technical report No. 37, (reprint by EHP Environmental Health Project). http://www.dec.org/pdf_docs/pnaaz336.pdf.

Environment Canada. (1998). *The Management of Water*. National Water Issues Branch, Environment Canada. http://www.ec.gc.ca/water/en/manage/e_manag.htm.

US Environmental Protection Agency. (1977). *World of Fresh Water A Resource for Studying Issues of Freshwater Research*. EPA Table 1– 2. Water use by country. http://www.epa.gov/ORD/WebPubs/fresh/.

Gleick, P.H. (2000). *The Changing Water Paradigm. A Look at Twenty-first Century Water Resources Development*. International Water Resources Association IWRA. http://www.iwra.siu.edu/win/win2000/win03-00/gleick.pdf.

Hinrichsen, D. et al. (1999). *Solutions for a Water-Short World*. John Hopkins University. http://www.jhuccp.org/pr/m14edsum.stm http://www.jhuccp.org/prs/sm14/sm14chap1.stm.

James, W. (1999). *Urban Water Systems*. Guelph University, Canada. http://www.eos.uoguelph.ca/webfiles/james/homepage/Teaching/661/wj661Modules.html.

Lauria, D.T. (1994). *Planning Sustainable Water Systems in Developing Countries*. JAWWA Aqualink.

OIEAU, Office International de l' Eau (International Office for Water). (1998). *Paris Declaration*. International Conference on Water and Sustainable Development. http://www.oieau.fr/ciedd/ang/frames/final/declarfin.htm
http://www.oieau.fr/ciedd/esp/frames/final/declarfin.htm
http://www.waterlink.net/esp/decfinsp.htm.

Postel, S. (1984). *Water: Rethinking Management in an Age of Scarcity*. Worldwatch Institute paper 62, Worldwatch Institute, Washington, DC. http://isbn.nu/0916468623.

Saade, H.L. (1997). *Toward More Efficient Urban Water Management in Mexico*. Water International, IWRA. http://www.iwra.siu.edu/win/toc_22_3.html/mexsaade.htm.

Sumila, G. (2001). The Demand-Side Approach to Planning Water Supply. 1999, In: *The Challenge of Urban Government: Policies and Practices*. Freire, Mila, and Richard Stren. Herndon, VA, The World Bank Group. http://www.aemnet.hu/urbancourse2000/Reading/sumila%20 toronto.doc http://www.worldbank.org/wbi/publicfinance/urban/publications.html#1 http://publications.worldbank.org/ecommerce/catalog/product?item_id=213497.

Van der Hoek, W., Konradsen, F., Ensink, J., Mudasser, M., and Jensen, P. (2001). *Irrigation Water as a Source of Drinking Water: Is Safe Use Possible? A Case Study from Pakistan*. Tropical Medicine and International Health, CIAGAR, International Water Management Institute, IWMI. http://www.cgiar.org/iwmi/home/drinking.htm.

Van Wijk-Sijbesma, C. (2001). *The Best of Two Worlds? Methodology for Participatory Assessment of Community Water Services*. Water and Sanitation Program (WSP), International Water and Sanitation Centre (IRC). http://www.irc.nl/products/publications/descr/tp38e.html.

TEN KEY TRENDS THAT WILL SHAPE THE FUTURE OF THE WORLD WATER INDUSTRY

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As we move into the new millennium, economic observers, social critics, and stock watchers are turning their attention toward the challenges and issues that, surround the country's continuing supply of clean drinking water. Water issues are now routinely addressed on the front pages of the national press—*USA Today* recently featured a full pull-out section dealing with the issues of clean drinking water; water scarcity issues were featured in a recent cover article in the *Harper's Magazine*. Water is increasingly described in such terms as "the key commodity of the twenty-first century." Like oil in the twentieth century, the substance will determine the course of human development and economic progress, over which conflicts or even wars may arise.

Some observers have perhaps waxed a bit melodramatic; however, it *is* clear that these sorts of challenges and problems are not imaginary; nor are they somewhere in the far distant future. Water *quantity* issues have long impacted politics and economic development in the western United States, and now water *quality* issues are increasingly critical in the East. Debates over water rights are the source of intensifying conflict between countries or between regions within countries. The human health challenges and vast economic issue of poor drinking water in many less developed countries represent one of the world's most pressing problems; a recent United Nations report estimated that as many as 10 million people a year die from unsanitary drinking water and associated waterborne diseases.

RISING WATER PRICES

Water is still very cheap; the price of water is not yet even really a significant driver of change in the industry. Prices will continue to rise, particularly in countries like the United States where past government policies—and the failure to account fully for the true *economic* cost of water usage—have kept prices artificially low. As prices increase, decisions relating to water usage will begin to take on greater significance in the overall economy. Focus will begin to intensify on more efficient water usage and demand management techniques, and new treatment technologies and supply sources such as desalination and water recycling will begin to gain market share.

STRONGER ENFORCEMENT OF REGULATIONS

Regulatory attention and water quality enforcement levels will remain strong in the United States, both in terms of drinking water quality and wastewater discharges. Although public concern and congressional attention to broader environmental issues have waned in recent years, the topic of drinking water quality continues to move to the forefront of the public agenda. Regulation of drinking water standards will also be strengthened in most other regions of the world. The water industry will clearly continue to be driven and buffeted by regulatory forces; however, products and services that offer cost savings, revenue enhancements, improved productivity, or reduction of capital expenditures, will enjoy stronger market growth than those that offer just regulatory compliance services.

BROADER REGULATORY FOCUS

Regulation and enforcement has been shifting slightly toward nonpoint sources of runoff and water pollution. Early enforcement attention was focused on the more obvious and more concentrated "point" sources of pollution; admirable progress has been made in correcting these—typically industrial—problems, and recent focus has shifted more to nonpoint source pollution. This (mostly agriculture-related) problem has seen substantial improvement in recent years as well. Biological wetlands treatment systems for animal waste management and pesticide and herbicide runoff are one example of new technologies being perfected to treat agricultural waste problems. Both point and nonpoint sources, as well as storm-water and general "wet weather" management, are likely to receive continuing regulatory attention and scrutiny in the coming decades.

INCREASING PRIVATIZATION

Industrial outsourcing and municipal privatization will remain key trends in the business. The contract operation business has been growing as much as 25% per year, and many private firms continue to diversify into this business despite the fact that, to date, profitability has been elusive. The potential for large-scale water privatization is typically cited as the main driver behind the recent onslaught of foreign acquirers—a belief that the United States is the last large market where water supply is still largely under public ownership and operation.

To date, privatization has been driven by broad political predilections to minimize the scope of government or by the widely held assumption that focused and private for-profit companies can operate more efficiently than public organizations. Many of the institutional and tax barriers to more complete privatization have melted away. To operators and employees of publicly held water and wastewater plants, privatization pressures over the last few years have sent a clear message—"shape up or ship out." However, public agencies and municipalities *have* responded to both the threat and to the root causes of this incipient pressure to privatize. These forces to economize are leading to municipal "optimization" as an alternative to privatization. Optimization may involve cost-cutting and improvements in efficiency from initiatives such as benchmarking, automation of operations, staff reductions, and improved information and analysis to facilitate better decision-making. From a broader social point of view, if the simple threat of privatization ultimately improves the efficiency of municipal facilities, then the same economic and productivity goals will have been achieved. Privatization will undoubtedly continue to grow, but it seems unlikely that it will reach the levels of 80% or 90% of total municipal systems, as has been predicted in the past.

GREATER WATER REUSE

There is an inexorable trend toward broader water reuse and recycling systems as a key means of addressing water shortages. Reuse is not a new idea, and using technologies readily available today, wastewater can easily be cleaned to levels where it can be recycled back into primary usage. This general idea, however, has not yet gained widespread social acceptance; put simply, most people don't want to think about using—and particularly drinking—their own wastewater. We have all been conditioned to think of water as something that we take out of the environment, use, and then discharge back into a vaguely understood natural system. Most observers believe that the *direct* reuse of wastewater for human *drinking* is not likely to be a widespread reality in the foreseeable future. There is still the (clearly disproven but emotionally more appealing) assumption that wastewater is somehow cleaner if it momentarily flows down the Potomac River (or any other less than pristine natural waterway) a few miles, or if it is briefly discharged into and then pumped out of a "natural" underground aquifer. This type of *indirect* use of wastewater for drinking is clearly acceptable and widespread, but *direct* reuse of our own wastewater is still a bit of a stretch for most Americans.

However, the boundaries between "water" and "wastewater" are already beginning to fade. For example, on some major rivers in the United states, water is used and reused up to 20 times as it travels to the sea—the discharge water from one wastewater treatment plant comprises the raw water intake for a primary drinking water plant a few miles downstream. As a result of 30 years under the requirements of the Clean Water Act, discharged streams from wastewater treatment plants are often cleaner than the rivers and streams they flow into; in other words, treated wastewater is actually helping to clean up our rivers.

What many observers have failed to clearly recognize—and what suggests that there may be real business opportunities here in the near future—is the obvious fact that very little of our water is used for drinking. Compared to the roughly 1200 gallons of water per person per day that it currently takes to power the U.S. economy, each person drinks only about a gallon a day. This leaves 1199 gallons per person per day, a substantial portion of which could be recovered through reuse, without anyone ever having to drink "recycled" wastewater. The bottom line is that even if only small incremental gains could be made in terms of nonpotable water reuse, water availability concerns could be substantially impacted. Over the longer term, society will move beyond the "linear" thinking of today and develop a more "circular" philosophy of water usage.

MORE AND BETTER INFORMATION

As the Internet revolution races on, the effects of better and more rapid information are being felt in the water industry. For example, the introduction of the Consumer Confidence Report will undoubtedly spur broader awareness of water quality issues across the American public, in turn driving demand for better monitoring and treatment technologies to improve the quality of our drinking water. Real-time watershed monitoring technologies and telemetry systems are becoming more commonplace and will help improve the quality and lower treatment costs in public water systems. Automatic meter reading, and more accurate remote systems for monitoring water usage will in turn make us more aware and attentive to the issues of our often sloppy usage.

CONTINUING INDUSTRY CONSOLIDATION

The era of consolidation is not over in this industry. Despite all of the attention paid to Veolia, Suez, RWE and other consolidators during the past few years, the water business is still rather fragmented compared to many industries, and business leaders continue to promote loudly the opportunities for "another U.S. Filter." The large transactions have hit the front pages, but dozens and dozens of smaller and less visible deals are also constantly ongoing. This massive rearrangement—and a distinct shift toward foreign ownership of the water industry—will determine the water industry's future competitive landscape. The very occent announcements of major divestitures by both veolia and suez demonstrate that changing ownership will continue to be a major factor.

NEW TECHNOLOGY

The advance of modern technology is often held out by optimists as the answer to all of our environmental and natural resource challenges. Whether or not this will be true is open to debate, but there is no doubt that new technology will play a key role in the improved management and extension of our water resources. Key examples include the broader usage of reverse osmosis/membrane systems to desalinize seawater for human usage, the trend toward replacing chlorine and other water treatment chemicals by advanced oxidation and other emerging physical and mechanical technologies, water-saving drip irrigation systems for more efficient agriculture, a wide spectrum of recycling systems and technologies, and new packaging and transportation systems for moving freshwater from regions of abundance to regions of scarcity.

CONSERVATION AND MORE EFFICIENT USAGE

Almost all of the trends mentioned before underscore the questionable efficiency and economics of today's water system and infrastructure. Some simple steps in more efficient usage can go a long way toward solving water shortages. For example, even the most modern water transmission infrastructure systems often incur leakage of as much as 10 to 20%—losses which can be fixed relatively easily. Water conservation ideas are only just beginning to take advantage of the "low-hanging fruit"; a recent rebate plan in New York City to promote the use of low-flow toilets purportedly resulted in saving 90 million gallons a day (although many users find "low-flow" toilets to be a bit of a misnomer, as they simply have to be flushed more times)! As water prices rise, there will be increasing financial incentives for industrial companies to retool their manufacturing systems to use less water, or to reuse water more efficiently—and dollars get everyone's attention. And different types of applications can use different kinds of water—urban planners have pointed to the fallacy of spending billions of dollars annually to clean *all* of our water supply to drinking standards when, as mentioned, only a tiny fraction is actually used for drinking. More sophisticated systems and infrastructure in the future (such as dual potable and nonpotable piping in the home) may allow us to be more efficient in our management and use of limited water resources.

MORE INNOVATIVE POLICIES AND REVOLUTIONARY APPROACHES TO WATER USE

From a broader social and economic perspective, we will see many changes in infrastructural approaches and broader water management policies. For example, water "carriage"—analogous to the wheeling of electricity in the power utility business, where one utility may use another's infrastructure for delivering water—is being experimented with in England. One historical trend that is likely to begin to reverse in the future is the construction of large-scale dams for power and irrigation purposes; the broader social and economic impact of large-scale dams is being gradually reevaluated, and it is conceivable that in the future we could see some of the big dams coming down. Water and hydropower utilities are beginning to come together in certain regions, realizing that water management issues are the driving forces behind each. In short, the entire way we think about and use water will be markedly different just a couple of generations from now.

CONCLUSION

As the saying goes, "it is very difficult to make predictions, especially about the future." The water industry has confounded many observers in the past and continues to perplex many today; for example, if the demands are so great and the opportunities so huge, why aren't more water companies currently performing better in the stock market? No doubt, the business will continue to be a tough one to define, segment, and understand, and it will probably take some more unexpected turns in the future. One thing, however, is clear, and distinguishes this industry from almost all others—water is an essential prerequisite of life. A continuing and dependable source of clean water is a critical necessity for our standard of living and our modern industrial economy. *And we are not going to find a substitute for water*. For well-managed organizations—both private and public—and for the thoughtful and prudent investor, the fundamentals of the water industry suggest the potential for strong growth and consistent profitability far into the new millennium.

ZEBRA MUSSEL CONTROL WITHOUT CHEMICALS

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Since the introduction and spread of the zebra mussels *(Dreissena polymorpha)* in the mid-1980s, industry and municipal water users of North America have been plagued by the mussel shells, which have clogged water intakes, costing vast amounts of downtime and loss of production (1).

The U.S. Coast Guard has since named the zebra mussel the number one threat to American waterways as well as a threat to fish and other aquatic species. The possible effects on numerous communities is also of great concern (2). In 1994, the Great Lakes Environmental Research Laboratory stated that the barnacle-like zebra mussel poses a multibillion dollar threat to industrial and public drinking water supplies and may become a costly nuisance to shippers, boaters, commercial fishermen, anglers, and beach-goers as well—far more costly in human terms than all previous Great Lakes invaders combined (3).

The life cycle of the *Dreissena polymorpha* begins at the egg stage, advances to the veliger, postveliger, juvenile-settling stage, and then to a full sized adult. In the settling stage, mussels colonize very rapidly in areas where calcium and algae are plentiful. A water velocity of 6 feet per second, with high concentration of algae and calcium, is an ideal location for the zebra mussel to settle and develop its shell consisting of 93% calcium (4). The mussel ideally settles in an intake pipe where the food source is constantly supplied by the moving water.

The adult life span is 3–5 years, and it reproduces year round, averaging 35,000 eggs per year (5). Zebra mussels look like small clams, and they have yellowish and/or brownish "D"–shaped shells, usually of alternating dark and light bands of color (thus the name "zebra") (Fig. 1).

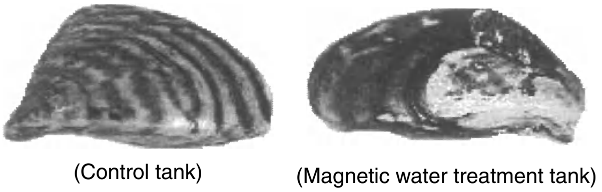

(Control tank) (Magnetic water treatment tank)

Figure 1. Shell consisting of mostly calcium will dissolve when subjected to magnetic treatment.

Zebra mussels can grow as large as 2 inches, but most are under one inch long, usually grow in clusters containing numerous individuals, and are generally found in shallow (6 to 30 feet deep) water. The zebra mussel is the ONLY freshwater mollusk that firmly attaches itself to solid objects, including rocks, boat hulls, and internal walls of pipes.

Methods to control the zebra mussel became top priority in many municipalities and industries that use water from the Great Lakes. In desperation, chemicals (mostly chlorine) became the quick fix; however, the toxic discharge back into the fresh water lakes increased the fish kill and killed other wildlife species. The U.S. Army Corps of Engineers sought other (nonchemical) means to control the spread of the mussel threat and set up workshops in which academic and industry professionals were invited participate.

The National Research Council listed several technologies more friendly to the environment than chlorine and other chemical biocides. Among those identified were *filtration systems, thermal techniques, electric pulse and pulse plasma techniques, ultraviolet treatment, acoustic systems, magnetic fields, deoxygenation*, and *antifouling coatings*.

Under the heading of magnetic fields, the Council stated, “Water to be treated is passed through a magnetic field of specified flux that is generated by ferromagnetic or electromagnetic devices. The biological and chemical effects of magnetic systems are not well understood, but it is thought that the organic and inorganic constituents of living organisms in the water are altered by the magnetic field” (6).

Magnetic conditioners up to capacities of 12,000 G.P.M. and pipe 60” in diameter (Fig. 2) treatment has been used successfully to control hard water scale ($CaCO_3$) in boilers, cooling towers, and other heat transfer systems for many years. The need for chemicals to control hardness and scale can be eliminated or greatly reduced and can provide energy savings (7). The mussel shell has a high calcium content (formed from the hard water intake), so a 2-year study began in 1993 to determine what effects, if any, magnetic fields would have on the zebra mussel. The results were very encouraging, as shown in (Fig. 3).

Dr. Graham O. Davies, president of the Water Board of Long Beach, Indiana, graciously offered the use of his facilities for the study and obtained the approval of the EPA for the installation of the magnetic unit and test equipment (Fig. 4). The Bardygula-Nonn study (8) used a flow-through magnetic water treatment device. Based on the results, it was suggested that magnetic water treatment might be a means of controlling zebra mussel populations to prevent macrofouling (Fig. 3). Besides the shell deterioration, the magnetic water treatment appeared to have other negative impacts on zebra mussels, including ciliary damage, byssal thread destruction, valve growth reduction, and increased mortality of juveniles.

A 4 year study started in 1995 at Purdue University (9) had three objectives: (1) to determine if the results of

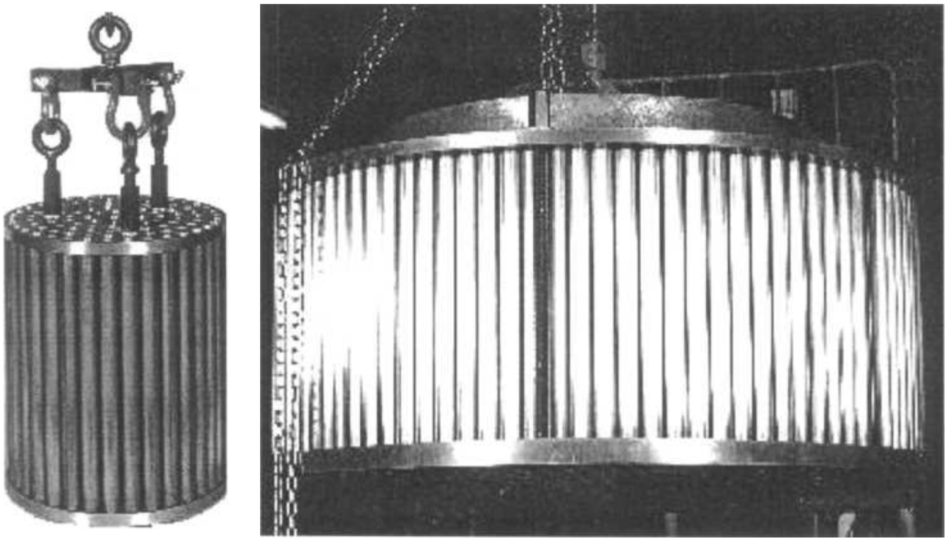

(20" dia. – 2,000 g.p.m.) *Magnetic Perma-core*^{TM} (60" dia. – 12,000 g.p.m.)

Figure 2. Magnetic assembly for inline treatment.

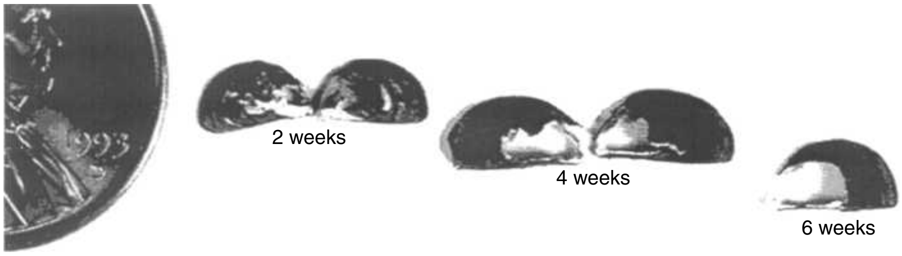
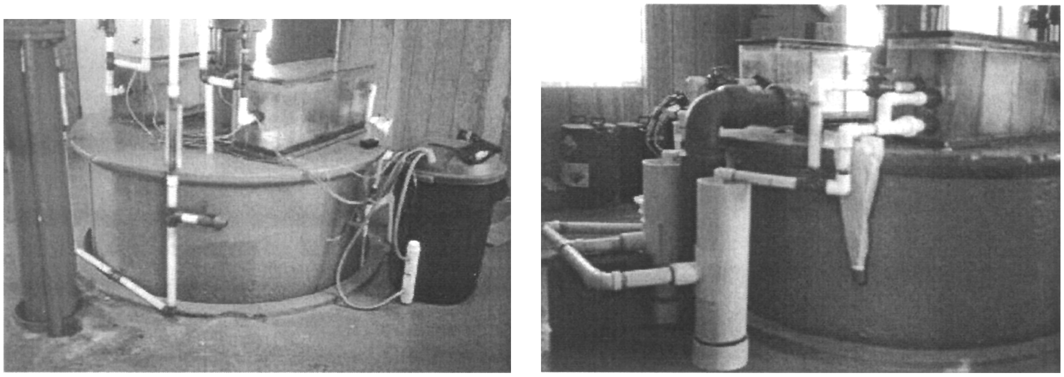


Figure 3. Zebra mussels exposed to magnetic water treatment- no chemicals were used.



(Long beach facilities showing control tank (left) and magnetically treated water tank (right) with nutrient feeding tank)

(back view of the tanks with plankton nets filtering discharge water)

Figure 4. Research arrangement for side by side evaluation for mussels placed in the control tank vs. magnetic treated water.

the previous study could be reproduced in a controlled laboratory set-up, (2) to examine the effects of magnetic water treatment on adult zebra mussels in an industrial application, and (3) to examine the influence of magnetic water treatment on settling of veligers in an industrial application.

In the laboratory at Purdue, 65 of the 123 mussels from the control tank (those not used for dissection or elemental analyses) were alive at the end of the experiment, leaving 58 dead (Fig. 5). In the experimental tank, 33 of the 123 mussels were alive at the end of the experiment and 90 died during the course of the study (Table 1). The differential mortality levels observed from each tank were significantly different ($X_2 = 17.4$ m df $=$ in, $p < .005$). Therefore, significantly more zebra mussels died in the tank of magnetically treated water than in the tank of untreated water. This suggests that the magnetic treatment of water does have adverse effects on zebra mussels, under laboratory conditions, and increases the mortality rate. This coincides with the previous Bardygula-Nonn study.

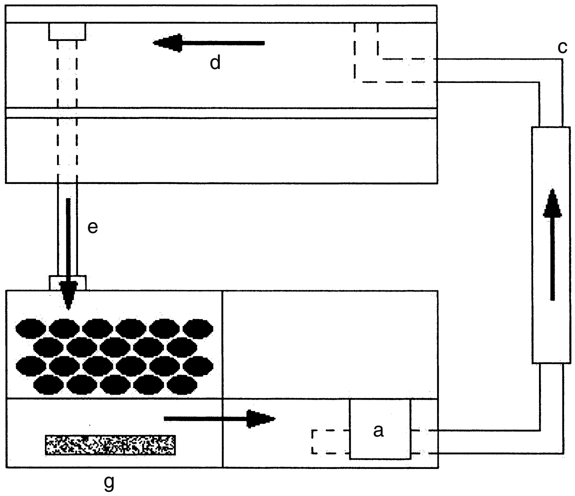


Figure 5. Diagram depicting setup of aquaria (control & treatment): (**a**) submersible pump, (**b**) magnetic treatment (treatment) or “dummy” unit without magnet (control), (**c**) water return line, (**d**) mussel bed, (**e**) overflow feed line, (**f**) biological filter media, and (**g**) aerator unit (air stone).

INDUSTRIAL FIELD STUDIES ON ADULT MUSSELS

Mussels treated for 30 days had significantly lower wet-tissue weights than control mussels (F = 8.10, $p < .005$). Glycogen levels of the treated mussels were 17.6% lower compared with control mussels, a difference that was significant ($t = 2.23$, df $= 118$, $p = .028$). Treated mussels had a greater increase in shell length during the 30-day trial than control mussels. The difference was significant at ($t = 3.16$, df $= 118$, $p = .002$). No differences were observed between the control and treatment circuits for water quality or environmental parameters during the 30-day trial.

Table 1. Survival of Zebra Mussels Over the Course of the Laboratory Study

	Control Tank	Experimental Tank
Alive at end	65	33[a]
Died during	58	90
TOTALS	123	123

[a] $X_2 = 17.4$, $p < .005$; therefore, there is a significant difference between tanks in the survival of the mussels.

There was no significant increase in shell length of treated mussels during the 60-day trial compared with control mussels (as seen in the 30-day trial). Glycogen analyses were not done for these samples. The results of the Purdue study suggest that magnetic water treatment can reduce settlement of zebra mussels in an industrial setting and that the mortality of zebra mussels is increased when they are exposed to magnetically treated water. A combination of reduced chemicals such as chlorine and a magnetic unit may sometimes be required. Interestingly, the head chemist at an industrial field site reduced their first year’s chemical use by 50%, then by 75%, and presently no chemicals at all are being used in the magnetically treated supply line (Fig. 6). The parallel control line remains at the 100% chemical-feed rate (9).

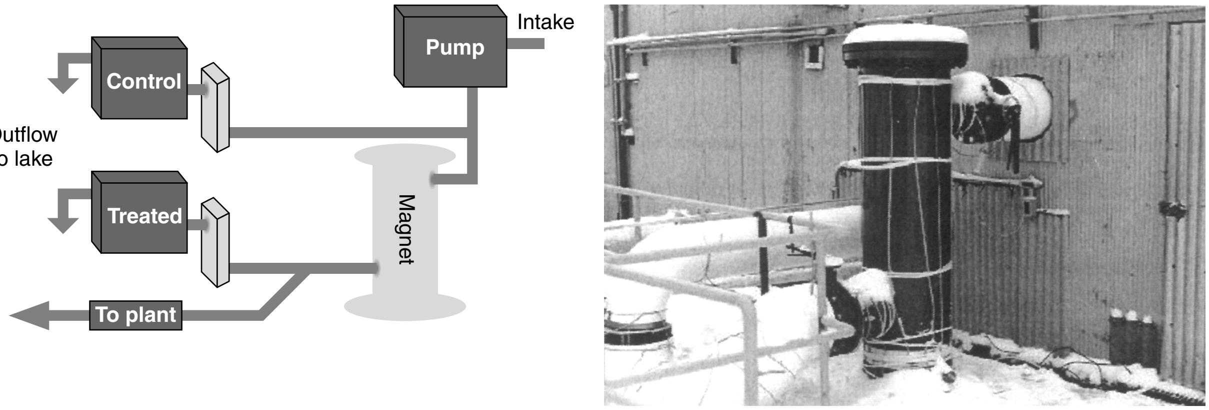


Figure 6. Diagram of industrial setup. Industrial magnetic water treatment system installed at a manufacturing plant on a parallel feed line with a flow rate of 1600 gallons per minute.

INDUSTRIAL FIELD STUDIES ON VELIGER SETTLING

A 53% reduction in settlement was observed in the treatment sampler compared with the control sampler. Chi-square analysis of settlement data revealed that the reduction was significant ($p > .001$). No significant differences were observed in recorded water quality parameters between the two sampling boxes. The results of this study suggest that magnetic water treatment can reduce settlement of veligers in an industrial water intake.

RESEARCH CONCLUSIONS

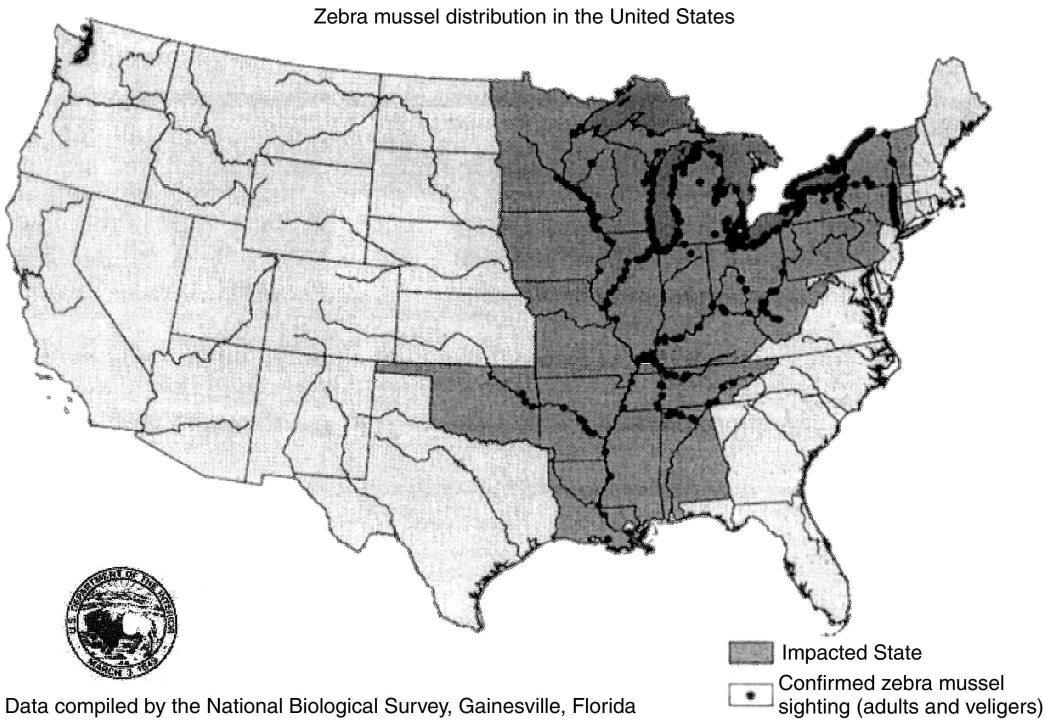
At this time, it is not clear how magnetically treated water could cause the greater mortality observed in the experimental tank compared with the control tank. Perhaps the changes, which occur when water is magnetically treated, serve as a stressor or influence cell membrane functions. It is known that magnetic water treatment causes the electrons of calcium ions to move, temporarily, into different orbitals (10). Perhaps this change in the ions can influence the zebra mussel's calcium uptake or metabolism. Calcium is especially important in shell formation, cell membrane function, muscular contraction, and ciliary contraction in zebra mussels. Therefore, if magnetism were affecting free calcium ions in the water, it would have potentially wide ranging effects on the zebra mussel's metabolic functions, which could generally explain an increase in mortality.

Ongoing research has shown that, by inserting probes at each of the alternating reversing magnetic pole sites and using active filters to eliminate any common noise (0.40 Hz) at the outputs, not only is a voltage induced in the conductor (water) but also a frequency. The frequency is a complex waveform whose fundamental frequency is <30 Hz. This falls into the extremely low frequency (ELF) spectrum of electromagnetic energy. More research is being done today on this aspect of the technology (9).

The biological effects of ELF radiation are well documented (11). ELF radiation lowers the energy barrier of cellular ion transport between the high-dielectric aqueous phase and low-dielectric lipid-containing barriers. This will influence the ion influx and efflux for the biological systems. The bonding interactions of ions with cellular membranes and tissue, which will consequently influence normal cellular functions, are also affected by ELF radiation. ELF, it has been shown, affects ion binding to cellular-membrane macromolecules, influences transmembrane ion transport, and alters membrane-signaling events. Ryan has suggested that ELF might affect the mussel's ability to assimilate calcium from water and also remove calcium from the shells and bodies of the zebra mussels. Proper containment of zebra mussel is necessary to prevent further spread of this nuisance non-indigenous species throughout the United States fresh water rivers and lakes (Fig. 7). Besides the distribution through connecting water ways, the mussel can survive a 3,000 mile trip by boat and trailer if the boat is not adequately cleaned after being pulled from a contaminated lake.

BIBLIOGRAPHY

1. Herbert, P.D.N., Muncaster, B.W., and Mackie, G.L. (1989). Ecological and genetic studies on dreissena polymorpha (pallas): A new mollusk in the great lakes. *Can. J. Fish. Aquat.* SC:**46**: 1587–1591.
2. Litherland, (1994). LCDR Phil, *Executive Officer, Naval Engineering Support Unit, U.S. Coast Guard*, Denver, CO. Zebra Mussel Workshop.
3. Beeton, A.M. (1994). *Director, Great Lakes Environmental Research Laboratory—Great Lakes Sea Grant Institute*. U.S. Army Corps of Engineering, Zebra Mussel Research program.
4. Burky, A.J. and Way, C.M. (1994). *Dayton University, U.S. Army Engineer Waterways Experimental Station, U.S. Army Corps of Engineers*, Zebra Mussel Workshop.
5. Liston, C.R. and McNabb, C.D. (1994). *Bureau of Reclamation. Research activities at the Bureau of Reclamation related to potential invasions of the zebra mussel*.
6. National Research Council—Stemming Tide. (1996). *Controlling Introduction of Non-indigenous Species By Ships' Ballast Water*. National Academy Press, Washington, DC.
7. Department of Energy Federal Technology Alert. (1998). "*Non-Chemical Technologies for Scale and Hardness Control.*" DOE/EE-0162.
8. Bardygula-Nonn, L.G. (1994) *Acute and Sub-acute effects of magnetically treated water on adult zebra mussels (Dreissena polymorpha) ZMT Industries, Inc. Fort Wayne, IN.*



Data compiled by the National Biological Survey, Gainesville, Florida

Figure 7. The zebra mussel was first discovered in Lake St. Clair in June of 1988 and has traveled throughout the Midwest region and other parts of the country.

9. Barnes, D.K., Camp, J.W. and Blaney, L.M. (1991) *Effects of Magnetically Treated Water on Zebra Mussels*. Purdue University, Westville, IN.
10. Molden, T.C. *Molden Associates—Research Report on frequency generated when flowing water passes through an alternating reversing polarity magnetic field. Water Services Technology Inc., Laporte, IN.*
11. Lin, I.J. (1981). *Conditions of Industrial Waters by Magnetic and Mechanical Means*. Department of Chemical Engineering, Technion—Israel Institute of Technology, Haifa, Israel.
12. Ryan, M.F. *Extremely Low Frequency Electromagnetism: An effective non-chemical method to control zebra mussel infestation*. Department of Chemistry and Physics, Purdue University Calumet, Hammond, IN.

PACKAGE PLANTS

National Drinking Water
Clearinghouse

Small water treatment systems often find it difficult to comply with the U.S. Environmental Protection Agency (EPA) regulations. Small communities often face financial problems in purchasing and maintaining conventional treatment systems. Their problem is further complicated if they do not have the services of a full-time, trained operator. The Surface Water Treatment Rule (SWTR) requirements have greatly increased interest in the possible use of package plants in many areas of the country. Package plants can also be applied to treat contaminants such as iron and manganese in groundwater via oxidation and filtration.

PACKAGE PLANTS: ALTERNATIVE TO CONVENTIONAL TREATMENT

What is a Package Plant?

Package technology offers an alternative to in-ground conventional treatment technology. They are not altogether different from other treatment processes although several package plant models contain innovative treatment elements, such as adsorptive clarifiers. The primary distinction, however, between package plants and custom-designed plants is that package plants are treatment units assembled in a factory, skid mounted, and transported to the site.

These units are most widely used to treat surface water supplies for removal of turbidity, color, and coliform organisms with filtration processes. However, many other treatment technologies are available to small systems as package plants. These technologies or a combination of them can be incorporated into a package plant to provide comprehensive water treatment, including:

- disinfection (chlorination, ozonation, ultraviolet radiation),
- filtration (bag and cartridge filters, membrane filtration including reverse osmosis or ultra filtration, slow sand filtration, pressure filtration, diatomaceous earth filtration),
- aeration,

- ion exchange,
- adsorption (using powdered activated carbon or granular activated carbon), and
- softening.

How to Select a Package Plant

Package plant systems are most appropriate for plant sizes that treat from 25,000 to 6,000,000 gallons per day (GPD) (94.6 to 22,710 cubic meters per day). Influent water quality is the most important consideration in determining the suitability of a package plant application. Complete influent water quality records need to be examined to establish turbidity levels, seasonal temperature fluctuations, and color level expectations. Both high turbidity and color may require coagulant dosages beyond many package plants design specifications. Pilot tests (tests that evaluate treatment processes and operations on a small scale to obtain performance criteria) may be necessary to select a package plant for more innovative designs using high flow rates and shorter detention time unit processes. Package treatment equipment manufacturers often perform these tests.

System Description and Design Considerations

Package plants can differ widely with regard to design criteria, and operating and maintenance considerations.

Package Plant Advantages

Package plants arrive on site virtually ready to operate and built to minimize the day-to-day attention required to operate the equipment.

Other major advantages of package plants are compact size, cost effectiveness, relative ease of operation, and design for unattended operation.

The main advantages of a packaged factory-finished system are savings in engineering, design and installation costs, and operation and maintenance. These features make package plants attractive to communities that must operate on a tight budget.

Package plants can effectively remove turbidity and bacteria from surface water of fairly consistent quality, provided that they are run by competent operators and are properly maintained. Package plants also can be designed to remove dissolved substances from the raw water, including color-causing substances and trihalomethane precursors (which are organic materials in source water that can react with chlorine to form disinfection by-products).

Package Plant Limitations

Highly variable influent water quality requires a high level of operational skill and attention, and that tends to negate the package plant advantages of low cost and automation.

Despite the relatively large number of package plants in use, many states are reluctant to endorse them completely.

The requirements of the Safe Drinking Water Act and its amendments might challenge package capability. Challenges include the possible inability of package plants to treat multiple types of contaminants.

Many communities are currently using package plants to treat water supplies, but little data has been collected to demonstrate long-term performance and operations of these systems. State agencies responsible for reviewing plans for the installation of package systems must review each potential plan on a case-by-case basis, with only their own experience to judge the potential for success or failure. Presently, there is no national verification process for package plants.

Types of Package Plant Filtration Systems

Conventional Package Plant. Conventional package plants are manufactured by several firms to a variety of specifications. As their name indicates, they contain the conventional processes of coagulation, flocculation, sedimentation, and filtration. Typical design standards for these units are:

- 20 to 30 minute flocculation detention time,
- 2 hour sedimentation detention time, and
- rapid sand filters rated at 2 gallons per minute (gpm) per square foot (1.34 liter/second/square meter).

Tube-Type Clarifier Package Plant. Tube-type clarifier package plants use tube settlers to reduce settling detention time (the average length of time water remains in the tank or chamber).

A flow diagram of a tube-type clarifier package plant is illustrated in (Fig. 1). This type of plant has two versions with different capacity ranges; one version can treat from 10 to 100 gpm (0.63 to 6.3 liters/second), and the other, equipped with dual units, can treat from 200 to 1,400 gpm (12.6 to 88.3 liters/second).

In these package systems, the disinfectant, primary coagulant, and polymer coagulant aid are added before the influent enters the flash mixer; then the water enters the flocculation chamber where mechanical mixers gently agitate the water for 10 to 20 minutes depending on the flow.

The flocculated water then enters the tube settlers, which consist of many 1 inch (2.5 centimeters [cm]) deep, 39 inches (99 cm) long split hexagonal shaped passageways. The large surface area of the many 1 inch (2.5 cm) deep tube settlers achieves an effective clarification overflow rate of less than 150 GPD/square foot (6.1 cubic meters/day/square meters). Adequate clarification is attained with less than 15 minute detention times.

The clarifier water then enters a gravity flow mixed-media filter (a filter with a coarse-to-fine gradation of filter media or several types of filter media). A constant filtration rate is maintained by a low-head filter effluent pump discharging through a float-operated, level control valve. After a preset headloss is reached, backwashing of the filter is initiated automatically. (Headloss is pressure or energy loss as a result of turbulence caused by the velocity of water flowing and the roughness of the channel walls.) A manual backwash cycle can be initiated any time (if desired). Settled sludge from the tube settlers is flushed during the backwashing cycle. Combining backwashing and tube settler flushing simplifies operations and reduces operator skill requirements.

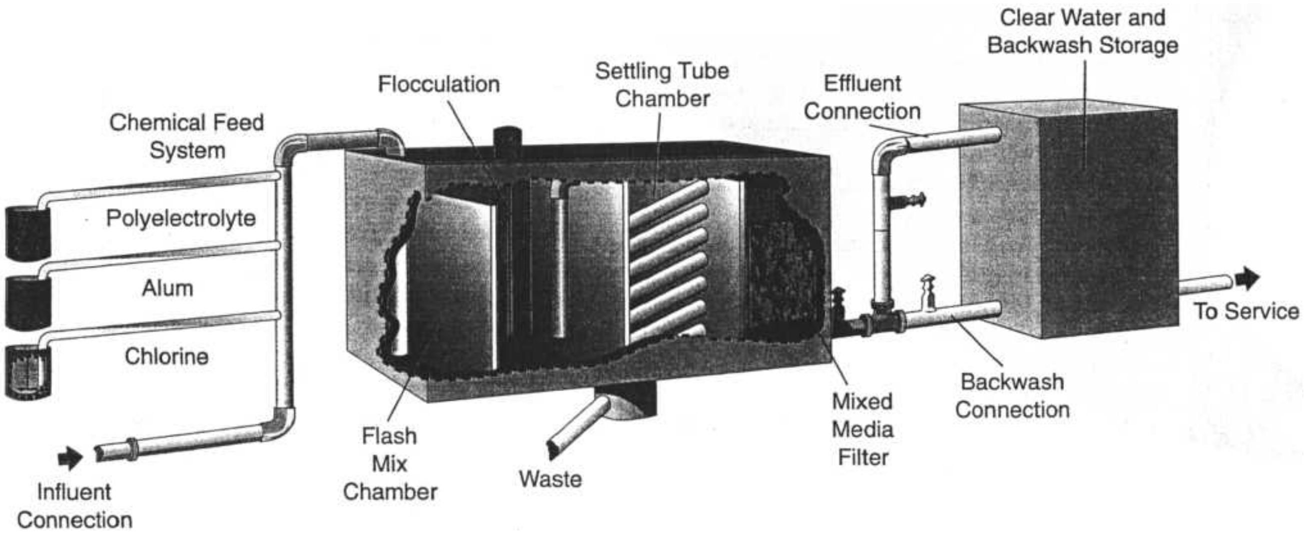


Figure 1. Tube-type clarifier package plant. *Source*: U.S. Environmental Protection Agency, 1989.

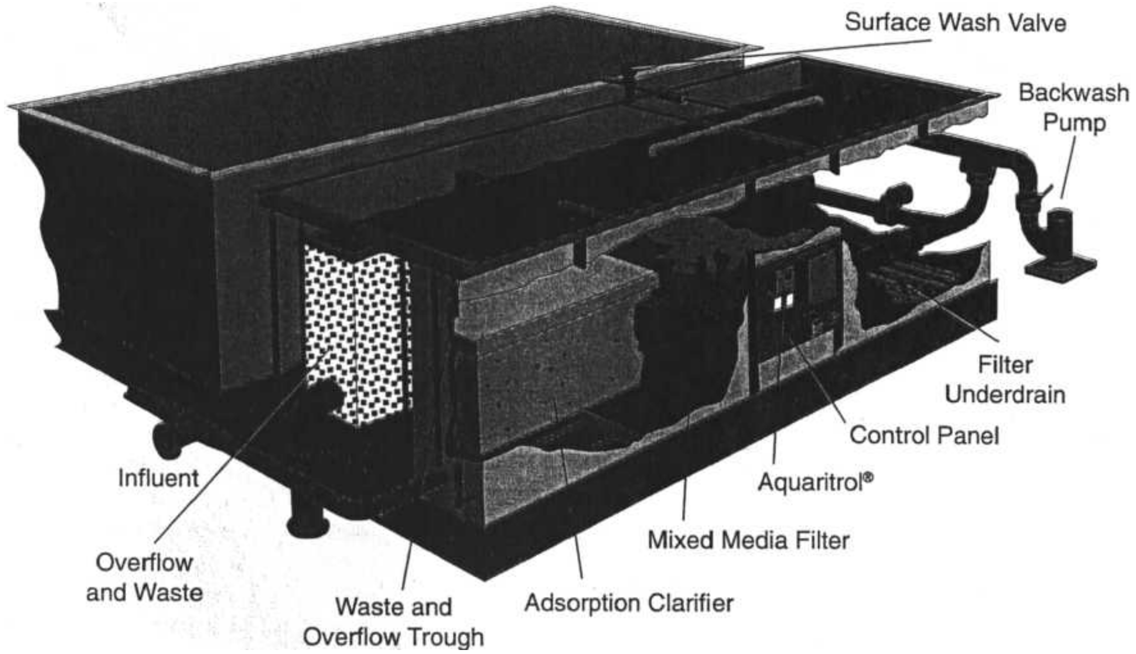


Figure 2. Adsorption clarifier package plant. *Source*: U.S. Environmental Protection Agency, 1989.

Adsorption Clarifier Package Plant. Adsorption clarifier package plants use an upflow filter with low density plastic bead media (called the adsorption clarifier) to replace the flocculation and sedimentation basin, thereby combining these two steps into one. A mixed media filter completes the treatment. Figure 2 shows a typical example.

While passing through the adsorption media, the coagulant and water are mixed, contact flocculated, and clarified. The mixing intensity, as measured by the mean velocity or gradient, ranges from 150 to 300 feet per second. Flocculation is accomplished through turbulence as water passes through the adsorption media. In addition, flocculation is enhanced by contact between the flocculated materials and the floccoated media. Turbidity is reduced through adsorption of the coagulated and flocculated solids onto the adsorption media and the previously adsorbed materials. The adsorption clarifier can achieve 95 percent or greater removal at 10 gpm/square foot (6.8 liters/second/square meter). This highly efficient clarification method results in extremely compact designs.

Adsorption clarifiers are cleaned by a combination of air scouring followed by water flushing. The air scouring starts the cleaning process for the plastic media used in the clarifier. Adsorption clarifier cleaning is initiated more frequently than filter backwashing because more solids are removed by the clarifier. The clarifier cleaning process is automatically initiated either by a timer or a pressure switch that continuously monitors headloss across the adsorption media.

The air introduced under the adsorption media causes a vigorous scrubbing action. The scrubbing action dislodges solids, which are washed away by the flow of the incoming water. Flushing is generally timed to occur between every fourth and eighth hour. Complete cleaning of the adsorption media is not desired because performance is enhanced by some residual solids.

Operation and Maintenance

Package plant operation is simplified by automated features such as effluent turbidimeters connected to chemical feed controls and other operating parameters, such as backwashing. Chemical feed controls are especially important for plants without full-time operators or with variable influent characteristics. Maintenance requirements are well documented in manuals. However, the operator needs to be well acquainted with water treatment principles and the plant manual, and should have attended a comprehensive training session.

The effluent turbidimeters and fail-safe controls are built into many plants to ensure that the finished water does not exceed set turbidity levels. Automated chemical feed systems are especially appropriate for plants without full-time operators or with highly variable influent characteristics.

Typical plant operator and maintenance manuals contain operating principles, methods of establishing proper chemical dosages, operating instructions, and trouble shooting guides.

Periodic visits by the manufacturer to make adjustments to the plant and inspect the equipment operation and performance are recommended. The first visit should be no more than six months after initial operation; the next should follow in another six months. Subsequently, annual visits should be sufficient.

Operators are the critical factor in overall success of any package plant, particularly in situations where raw water quality varies. When the automation fails, the operator needs to turn off the automatic controls/instrumentation and operate the plant manually.

Where Can I Find More Information?

Information in this fact sheet was obtained primarily from two sources:

(1) *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*, EPA/625/4-89/023; and
(2) “Package Plants for Small Systems: A Field Study” by Susan Campbell, Benjamin W. Lykins Jr., James Goodrich, Dallas Post, and Trudie Lay. *AWWA Journal*, Nov. 1995 pages 39–47.

Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities can be ordered free from the U.S. Environmental Protection Agency Office of Research and Development at (513) 569-7562.

The National Drinking Water Clearinghouse (NDWC) offers this document also, but at a cost to help recover photocopying expenses. *Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities*, a 209-page book, costs $30.05. To order, call the NDWC at (800) 624-8301 or (304) 293-4191 and request item #DWBKDM04. NDWC products also may be ordered via e-mail at ndwc_orders@ndwc.wvu.edu. Postal charges are added to orders.

Also, the NDWC’s Registry of Equipment Suppliers of Treatment Technologies for Small Systems (RESULTS) is a public reference database that contains information about technologies in use at small water systems around the country. For further information, call the NDWC at one of the above numbers.

Additional free copies of Tech Brief fact sheets are available at the above numbers or you may download Tech Briefs from our Web site at http://www.ndwc.wvu.edu.

ANAEROBIC SEWAGE TREATMENT

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WHAT IS SEWAGE?

Sewage is the wastewater generated by a community, namely: a) domestic wastewater, from bathrooms, toilets, kitchens, etc., b) raw or treated industrial wastewater discharged in the sewerage system, and sometimes c) rainwater and urban runoff (1). Domestic wastewater is the main component of sewage, and it is often taken as a synonym. Sand and coarse material (paper, bottles, etc.) are not considered part of sewage. They are transported by sewage but handled as solid waste when they arrive at a treatment facility. The sewage flow rate and composition vary considerably from place to place, depending on economic aspects, social behavior, type and number of industries in the area, climatic conditions, water consumption, type of sewers, etc. The main pollutants in sewage are suspended solids, soluble organic compounds, and fecal pathogenic micro-organisms. In addition, a variety of chemicals, like heavy metals, trace elements, detergents, solvents, pesticides, and other unusual compounds like pharmaceuticals, antibiotics, and hormones can also be detected in sewage. With urban runoff come potentially toxic compounds like oil from cars and pesticides that may reach the treatment plant and, eventually, a water body.

WHY SHOULD WE TREAT SEWAGE?

Direct discharge of raw or poorly treated sewage into the environment is one of the main sources of pollution on a global scale (2). Improved sanitation would have a significant impact on people's lives in terms of safety, privacy, convenience, and dignity (3). Sanitation is also a good starting point for addressing long-term poverty issues and reducing child mortality, because children are more susceptible to suffer from inadequate water supply and sanitation services. The lack of water, sanitation, and hygiene for all was dubbed as "... one of the biggest scandals of the last 50 years" (4). Simple, affordable, and efficient sewage treatment systems are urgently needed, especially in developing countries, where most of the conventional technologies currently in use in industrialized nations are too expensive and complex (5). Sustainable sewage treatment technologies will help to preserve water ecosystems and their biodiversity, indispensable for the provision of clean water, flood control, and other vital services.

Today, several technological options are available for sewage treatment, ranging from traditional waste stabilization ponds (WSP) to conventional aerobic systems (like trickling filters or activated sludge), from anaerobic reactors to integrated systems in which a variety of biological processes can be applied. Anaerobic processes are attracting the attention of sanitary engineers and decision-makers more and more, especially the upflow anaerobic sludge bed (or blanket) (UASB) reactor developed in the early 1970s by Lettinga and co-workers (6). Anaerobic sewage treatment in UASB reactors is an absolute success in tropical countries like India and Brazil, but it is also finding its way in other regions, even in subtropical and more temperate countries. Recent studies showed that it can be successfully applied at temperatures as low as 15 °C for a variety of different types of sewage (7–9). The lack of sewage treatment is not at all a technological or economic problem but a political one. In fact, governments, even from developing countries, have been spending billions of dollars per year on water and sanitation, usually to build expensive, centralized sewers and sewage treatment facilities for a few privileged citizens instead of low-cost appropriate sanitation systems for the needy majority.

THE PROCESS OF ANAEROBIC DIGESTION

Anaerobic bacteria, belonging to the domain Archaea, are the most ancient forms of life on earth. They evolved about 3.7 billion years ago in an oxygen-free atmosphere and fed from the nutrients in the aqueous environment around them. When, because of the action of cyanobacteria and algae, the atmosphere became dangerously full of oxygen, anaerobic bacteria were relegated to niches where anaerobic conditions could still be found. Anaerobic bacteria thrive today in the bottom of marshes, swamps, and wetlands, and in the stomach of ruminants, insects, and humans, where they degrade organic matter and produce biogas, a mixture of methane and carbon dioxide with a small percentage of hydrogen sulfide and traces of other gases.

The anaerobic (bio)degradation of complex, particulate organic material has been described as a multistep process of series and parallel reactions catalyzed by several groups of bacteria (10,11). Seven subprocesses are now recognized during anaerobic digestion: (1) hydrolysis of complex, particulate organic materials (proteins, carbohydrates, and lipids); (2) fermentation of amino acids and sugars; (3) anaerobic oxidation of long-chain fatty acids and alcohols; (4) anaerobic oxidation of intermediary products such as short-chain fatty acids (except acetate); (5) acetate production from carbon dioxide and hydrogen (homoacetogenesis); (6) conversion of acetate to methane (aceticlastic methanogenesis); and (7) methane production by reduction of carbon dioxide by hydrogen.

Hydrolysis was found to be the rate-limiting step in the degradation of wastewaters like sewage, high in volatile suspended solids (12). Hydrolysis rate in anaerobic systems is normally described as a first-order process with respect to the concentration of degradable particulate organic matter (13). Preliminary conversion mechanisms such as cell death and lysis are the first steps in the process of transforming viable micro-organisms to available substrate and can also be included in a kinetic model of the anaerobic digestion of aerobic sludges. However, these processes have been found not to be rate-limiting (14). Even if cell death and lysis were an important factor in the overall kinetics of anaerobic degradation, these processes are not applicable in the case of treatment of raw domestic sewage, and therefore hydrolysis may be considered as the only possible rate-limiting step in this case (15).

Some factors affecting the rate and extent of the anaerobic degradation of organic matter are temperature, pH, particle deposition, internal mixing in the reactor, and presence of toxic compounds. Further details on the effect of these factors is beyond the scope of this work and can be found in Heertjes and van der Meer (16), Rittmann and Baskin (17), Bouwer (18), Bohle (19), and van Haandel and Lettinga (1), among others.

ANAEROBIC SEWAGE TREATMENT

Anaerobic processes have been used to treat domestic and industrial wastewater for more than a century (20,21). The septic tank is the oldest and most widely used example. The striking success of the UASB reactor (Fig. 1) made anaerobic systems come back to the forefront, and they are now used for the treatment of several types of wastewater.

The UASB concept is based on the establishment of a dense sludge bed in the bottom of the reactor, in which all biological processes take place. This sludge bed is formed by accumulation of incoming suspended solids and by bacterial growth. In upflow anaerobic systems, and under certain conditions, it was also observed that bacteria could naturally aggregate in flocs and granules (22). These dense aggregates have good settling properties and are not susceptible to washout from the system under normal reactor conditions. Retention of granular or flocculent active sludge within the UASB reactor enables good treatment performance at high organic loading rates. Natural turbulence caused by the influent flow and the biogas production provides good wastewater biomass contact in UASB systems. Several configurations can be imagined for a wastewater treatment plant including a UASB reactor. In any case, a sand trap, screens for coarse material, and drying beds for the sludge must

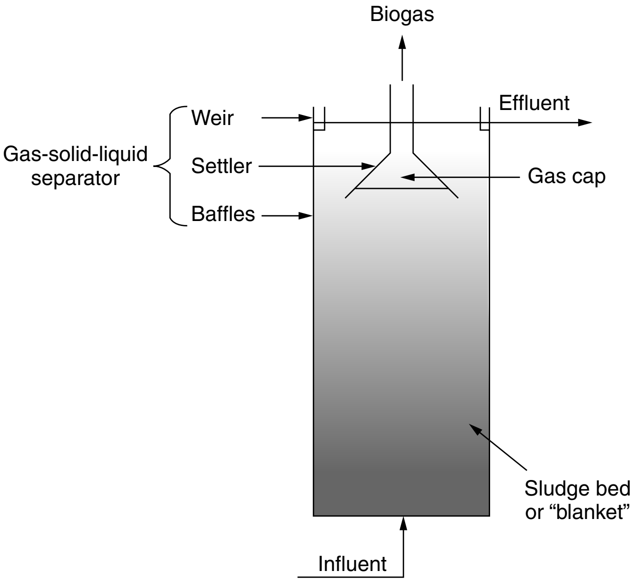

Figure 1. Basic scheme of a UASB reactor for sewage treatment.

exist. The UASB reactor may replace the primary settler, the anaerobic sludge digester, the aerobic step, and the secondary settler of conventional aerobic treatment plants like activated sludge or trickling filters.

UASB-based anaerobic treatment systems are recognized to be highly efficient, simple to construct and operate, and flexible to be applied on either a very large or a very small scale. UASB reactors have low space requirements and consume negligible amounts of energy, if any. Moreover, energy is produced during the process in the form of methane. The production of sludge is very low in comparison with aerobic methods, because of the slow growth rates of anaerobic bacteria. Besides, the sludge is well stabilized for final disposal, and it can be preserved for considerable periods of time without a significant reduction of its activity, allowing its use for the startup of new reactors. The process requires no additional nutrients, and an adequate and stable pH can be maintained without the addition of any chemicals. Anaerobic systems are well suitable for campaign industries because the adapted anaerobic sludge can be stored unfed within the reactor for entire seasons. The use of anaerobic systems can lead to a high degree of self-sufficiency.

Some disadvantages of anaerobic sewage treatment have been put forward, like low pathogen and nutrient removal. In fact, pathogens are only partially removed, except helminth eggs, which are effectively captured in the sludge bed. The removal of nutrients is also not complete and a post-treatment is generally required if the nutrients cannot be reused for agriculture or aquaculture within a reasonable distance from the treatment plant. The startup of anaerobic reactors usually takes longer compared with aerobic processes, unless good inoculum is available to speed up this stage. Hydrogen sulfide is produced during the anaerobic process, especially when high concentrations of sulfate exist in the influent. A proper handling of the biogas is then required to avoid bad smell. A significant proportion of the total amount of methane produced by the reactor is actually dissolved in the effluent. Its recovery may be required to minimize smell nuisances and methane emissions to the atmosphere. Substantial improvements have been made in tackling most of these alleged disadvantages (23).

Anaerobic treatment was considered economically more attractive and conceptually more holistic than aerobic treatment (24). The costs of aeration and sludge handling, the two largest costs associated with aerobic sewage treatment, would be reduced dramatically because no oxygen is needed in the process and the production of sludge is much smaller than in aerobic treatment (17). Moreover, the sludge (biomass) produced in aerobic processes has to be stabilized before it can be safely disposed of, which adds to the complexity of aerobic treatment plants. Anaerobic treatment can make a substantial contribution to the protection of the environment and the preservation of natural resources as part of a sustainable and appropriate wastewater treatment system for developing countries.

EXAMPLES OF SEWAGE TREATMENT IN ANAEROBIC REACTORS

UASB Reactors

The full-scale application of UASB reactors to domestic wastewater has been a success in tropical areas with sewage temperature above 25 °C (25). Studies in this field started many years ago in Cali, Colombia, where UASB reactors were found to be cheaper than facultative ponds and oxidation ditches, especially when capital costs were included (26). The efficiency of UASB reactors for sewage treatment was found to be similar in tropical and subtropical regions (sewage temperatures around 18–23 °C) using the same design parameters (9). The application of UASB reactors to sewage treatment under even lower temperature conditions has been studied in the Netherlands since 1976 (27,28). Promising results were obtained in Jordan, with UASB reactors treating strong raw sewage at a temperature of 18 °C in winter and 25 °C in summer (8). Encouraging results have also been obtained in the Mediterranean area (29). Although substantial experience on the design and operation of UASB reactors for sewage treatment has been gathered lately, most of the results have not been published (30). Under specific conditions, the use of two-stage anaerobic reactors (8,31–33), additional heated sludge digesters (7), or chemically enhanced primary sedimentation (34) have been proposed to further improve the performance of anaerobic systems.

Other Technologies

Technologies other than the UASB, like the anaerobic filter (35), traditional anaerobic digesters currently in use in China, the anaerobic attached film expanded bed (AAFEB) system (36), plug-flow reactors, and modified anaerobic baffled reactors (37), among others, have also been used for the anaerobic treatment of sewage.

Post-Treatment

Anaerobic sewage treatment systems generally fail to comply with COD discharge standards, as established by Council Directive 91/271/EEC on Urban Waste Water Treatment, dictated by the European Union Council of Ministers (38) (125 mgCOD/L), or the guideline proposed by the World Health Organization (39) for unrestricted irrigation (less than 1000 fecal coliform per 100 mL and less than 1 helminth egg per L). Therefore, a post-treatment step is mandatory in most cases to remove remnant COD, fecal coliform (as an indicator of pathogenic micro-organisms), helminth eggs, and even nitrogen and phosphorus when direct reuse is not feasible. WSP are among the most efficient and cost-effective post-treatment methods available (40). Other post-treatment methods are the biorotor system, or rotating biological contactor (41), integrated duckweed and stabilization pond system (42), trickling filters (43), and activated sludge (44), among others. See the review presented by Tawfik (41).

On-Site Systems

Application of modified UASB reactors for single households in isolated locations, like farms and recreational facilities not connected to the centralized sewerage system, was studied under different temperature conditions in the Netherlands (45) and Indonesia (46). These systems were called UASB septic tanks, because they shared features of both methods. Sludge gradually accumulates in the reactor, as in septic tanks, but they are operated in upflow mode, as UASB reactors. The design is almost as simple as that of conventional septic tanks, but the treatment efficiency is much higher (47). Suggestions for improving the treatment efficiency in these systems include the use of two- or three-stage UASB reactors and the adoption of post-treatment methods, like small aerobic lagoons (46). The UASB process was also applied to treat sewage from small-size communities in Brazil (48). The potential of anaerobic technology in so-called DESAR (Decentralized Sanitation And Reuse) schemes is huge, and more efforts should be directed to test these systems in the field (23).

WHAT IS THE FUTURE OF ANAEROBIC SEWAGE TREATMENT?

Anaerobic reactors should be more widely applied in tropical countries as the main pretreatment step for sewage. Conditions for anaerobic digestion are so good under these conditions that the application of any other system to treat the organic pollution in sewage is highly questionable on technical, environmental, economic, and social grounds. The application of UASB reactors for sewage treatment could be safely expanded to subtropical regions, and clear indications exist that even in temperate regions its use should not be discarded altogether. Anaerobic systems should also be used in DESAR schemes where the preservation of water, nutrients, and energy is indispensable. Anaerobic systems can significantly contribute to the achievement of more sustainable sanitation in most developing countries, and their potential should be recognized and explored by universities, private companies, and governments.

BIBLIOGRAPHY

1. van Haandel, A.C. and Lettinga, G. (1994). *Anaerobic Sewage Treatment. A Practical Guide for Regions with a Hot Climate*. John Wiley, Chichester, UK.
2. Gijzen, H.J. (2002). Anaerobic digestion for sustainable development: a natural approach. *Water Sci. Technol.* **45**(10): 321–328.
3. United Nations. (2003). *Water for People-Water for Life*. The United Nations World Water Development Report, UNESCO Publishing, Berghahn Books, Paris, France.
4. WSSCC (Water Supply and Sanitation Collaborative Council). (2003). *A guide to investigating one of the biggest scandals of the last 50 years*, Third World Water Forum, Kyoto, Japan.
5. Grau, P. (1996). Integrated water and waste management. *Water Sci. Technol.* **33**(8): 39–46.
6. Lettinga, G., van Nelsen, A.F.M., Hobma, S.W., de Zeeuw, W., and Klapwijk, A. (1980). Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. *Biotechnol. Bioengineer.* **22**: 699–734.
7. Mahmoud, N.J.A. (2002). *Anaerobic pre-treatment of sewage under low temperature (15°C) conditions in an integrated UASB-digester system*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
8. Halalsheh, M.M. (2002). *Anaerobic pre-treatment of strong sewage*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
9. Seghezzo, L. (2004). *Anaerobic treatment of domestic wastewater in subtropical regions*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
10. Gujer, W. and Zehnder, A.J.B. (1983). Conversion processes in anaerobic digestion. *Water Sci. Technol.* **15**: 127–167.
11. Pavlostathis, S.G. and Giraldo-Gomez, E. (1991). Kinetics of anaerobic treatment: a critical review. *Crit. Rev. Environ. Control*. **21**(5,6): 411–490.
12. de Baere, L.A., Rozzi, A., and Verstraete, W. (1984). Solubilization of particulate organic matter as the rate-limiting step in anaerobic digestion loading. *Trib. Cebedeau.* **37**(484): 75–81.
13. Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhyni, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., and Vavilin, V.A. (2002). Anaerobic digestion model No.1 (ADM1), Scientific and Technical Report No.13, IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes, IWA Publishing, London, UK.
14. Pavlostathis, S.G. and Gossett, J.M. (1985). A kinetic model for anaerobic digestion of biological sludge. *Biotechnol. Bioengineer.* **28**: 1519–1530.
15. Sanders, W.T.M. (2001). *Anaerobic hydrolysis during digestion of complex substrates*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
16. Heertjes, P.M. and van der Meer, R.R. (1978). Dynamics of liquid flow in an up-flow reactor used for anaerobic treatment of wastewater. *Biotechnol. Bioengineer.* **20**: 1577–1594.
17. Rittmann, B.E. and Baskin, D.E. (1985). Theoretical and modelling aspects of anaerobic treatment of sewage, In: *Proceedings of the Seminar / Workshop on Anaerobic Treatment of Sewage*. M.S. Switzenbaum (Ed.). Amherst, MA, pp. 55–94.
18. Bouwer, E.J. (1987). Theoretical investigation of particle deposition in biofilm systems. *Water Research*. **21**(12): 1489–1498.
19. Bohle, A.G. (1993). Performance of static flocculators. *Water Sci. Technol.* **27**(10): 181–194.

20. McCarty, P.L. (1981). One hundred years of anaerobic treatment. In: *Anaerobic Digestion*. D.E. Hughes et al. (Eds.). Elsevier, Amsterdam, p. 3.
21. McCarty, P.L. (2001). The development of anaerobic treatment and its future. *Water Sci. Technol.* **44**(8): 149–156.
22. Hulshoff Pol, L.W., de Zeeuw, W.J., Velzeboer, C.T.M., and Lettinga, G. (1983). Granulation in UASB-reactors. *Water Sci. Technol.* **15**: 291–304.
23. Lettinga, G. (2001). Digestion and degradation, air for life. *Water Sci. Technol.* **44**(8): 157–176.
24. Mergaert, K., Vanderhaegen, B., and Verstraete, W. (1992). Applicability and trends of anaerobic pre-treatment of municipal wastewater. *Water Research*. **26**(8): 1025–1033.
25. Alaerts, G.J., Veenstra, S., Bentvelsen, M., and van Duijl, L.A. (1993). Feasibility of anaerobic sewage treatment in sanitation strategies in developing countries. *Water Sci. Technol.* **27**(1): 179–186.
26. Schellinkhout, A., Lettinga, G., van Velsen, L., and Louwe Kooijmans, J. (1985). The application of the UASB-reactor for the direct treatment of domestic wastewater under tropical conditions, In: *Proceedings of the Seminar/Workshop on Anaerobic Treatment of Sewage*. M.S. Switzenbaum (Ed.). Amherst, MA, pp. 259–276.
27. Lettinga, G., Roersma, R., Grin, P., de Zeeuw, W., Hulshof Pol, L., van Velsen, L., Hobma, S., and Zeeman, G. (1981). Anaerobic treatment of sewage and low strength waste wasters, In: *Proceedings of the 2nd International Symposium on Anaerobic Digestion*. D.E. Hughes et al. (Eds.). Travemünde, Germany, pp. 271–291.
28. Grin, P., Roersma, R., and Lettinga, G. (1985). Anaerobic treatment of raw domestic sewage in UASB reactors at temperatures from 9–20 °C, In: *Proceedings of the Seminar/Workshop on Anaerobic Treatment of Sewage*. M.S. Switzenbaum (Ed.). Amherst, MA, pp. 109–124.
29. Collivignarelli, C., Urbini, G., Farneti, A., Bassetti, A., and Barbaresi, U. (1991). Economic removal of organic and nutrient substances from municipal wastewaters with full-scale UASB fluidized- and fixed-bed reactors. *Water Sci. Technol.* **24**(7): 90–95.
30. Wiegant, W.M. (2001). Experiences and potential of anaerobic wastewater treatment in tropical regions. *Water Sci. Technol.* **44**(8): 107–113.
31. Wang, K. (1994). *Integrated anaerobic and aerobic treatment of sewage*, Ph.D. thesis, Wageningen Agricultural University, Wageningen, the Netherlands.
32. Elmitwalli, T.A. (2000). *Anaerobic treatment of domestic sewage at low temperature*, Ph.D. thesis, Wageningen University, the Netherlands.
33. Mgana, S.M. (2003). *Towards sustainable and robust on-site domestic wastewater treatment for all citizens*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
34. Kalogo, Y. and Verstraete, W. (2000). Technical feasibility of the treatment of domestic wastewater by a CEPS-UASB system. *Environ. Technol.* **21**: 55–65.
35. Young, J.C. and McCarty, P.L. (1969). The anaerobic filter for waste treatment. *J. Water Pollut. Control Fed.* **41**: R160.
36. Jewell, W.J., Switzenbaum, M.S., and Morris, J.W. (1981). Municipal wastewater treatment with the anaerobic attached microbial film expanded bed process. *J. Water Pollut. Control Fed.* **53**(4): 482–490.
37. Yu, H. and Anderson, G.K. (1996). Performance of a combined anaerobic reactor for municipal wastewater treatment at ambient temperature. *Resources Conservation Recycling*. **17**: 259–271.
38. European Union Council of Ministers. (1991). *Official J. Eur. Commission*. **L135**: 40–52.
39. WHO. (1989). *Health Guidelines for the Use of Wastewater in Agriculture and Aquaculture*. Technical Report Series No 778, WHO, Geneva, Switzerland.
40. Cavalcanti, P.F.F. (2003). *Integrated application of the UASB reactor and ponds for domestic sewage treatment in tropical regions*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
41. Tawfik, A. (2002). *The biorotor system for post-treatment of anaerobically treated domestic sewage*, Ph.D. thesis, Wageningen University, Wageningen, the Netherlands.
42. van der Steen, P., Brenner, A., van Buuren, J., and Oron, G. (1999). Post-treatment of UASB reactor effluent in an integrated duckweed and stabilization pond system. *Water Research*. **33**(3): 615–620.
43. Chernicharo, C.A.de L. and Nascimento, M.C.P. (2001). Feasibility of a pilot-scale UASB/trickling filter system for domestic sewage treatment. *Water Sci. Technol.* **44**(4): 221–228.
44. von Sperling, M. (1996). Comparison among the most frequently used systems for wastewater treatment in developing countries. *Water Sci. Technol.* **33**(3): 59–72.
45. Bogte, J.J., Breure, A.M., van Andel, J.G., and Lettinga, G. (1993). Anaerobic treatment of domestic wastewater in small scale UASB reactors. *Water Sci. Technol.* **27**(9): 75–82.
46. Lettinga, G., de Man, A., van der Last, A.R.M., Wiegant, W., van Knippenberg, K., Frijns, J., and van Buuren, J.C.L. (1993). Anaerobic treatment of domestic sewage and wastewater. *Water Sci. Technol.* **27**(9): 67–73.
47. Zeeman, G. (1997). *Decentralized Sanitation Systems*. The role of anaerobic treatment in UASB-septic-tank systems, Paper presented to the Third Japan-Netherlands Workshop on Integrated Water Quality Management, the Netherlands, May 26–30, p. 6.
48. Vieira, S.M.M., Carvalho, J.L., Barijan, F.P.O., and Rech, C.M. (1994). Application of the UASB technology for sewage treatment in a small community at Sumare, São Paulo State. *Water Sci. Technol.* **30**(12): 203–210.

PERSISTENCE OF PATHOGENS IN WATER

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WATERBORNE PATHOGENS SIGNIFICANT TO HEALTH

Natural water sources become contaminated with pathogenic micro-organisms by the discharge of inadequately treated wastewater. Four major pathogen groups can be found in wastewater: over 100 types of enteric viruses, 7 types of pathogenic bacteria, 10 types of protozoan parasites, and 6 types of helminthes of health significance to humans and animals. The concentration of pathogenic micro-organisms in wastewater is affected mainly by the amount of precipitation, the season of the year, and the socioeconomic status of the community. For most pathogenic micro-organisms, the methods of detection are expensive, time-consuming, and difficult to perform. Therefore, data on the prevalence of pathogenic micro-organisms in wastewater effluents and natural water sources is limited to types for which a detection technique was developed. The recently developed molecular biology-based techniques enhanced our capability in detecting human pathogenic micro-organisms in water sources.

The viruses that are detected most often in polluted water are enteroviruses, because of the availability of tissue culture for virus cultivation and enumeration. In wastewater, researchers reported on the presence of 1000 pfu/L enteroviruses (1). Discharge of inadequately treated wastewater may result in the viral contamination of natural water sources. Enteric viruses have been detected in rivers, lakes, and even in groundwater. Using reverse transcription-PCR (RT-PCR), it was reported that 24 out of 48 well water samples (50%) were found positive for enteric viruses, including enteroviruses, rotaviruses, hepatitis A virus, adenoviruses, and noroviruses, and 10 out of 12 river water samples (83%) were found positive for viruses by RT-PCR (2).

Giardia cysts and *Cryptosporidium* Oocysts were detected in 100% raw wastewater samples at a concentration of 10^3 cysts/L and 5×10^2 oocysts/L, respectively (3). Most conventional wastewater treatment processes result in the reduction of parasites in the treated effluent; however, the remaining low numbers may pose a health risk. *Cryptosporidium* was detected in 50% of effluent samples of oxidation ponds. Mayer and Plamer (4) reported 99.9% removal for *Giardia* and 99% for *Cryptosporidium* by biological treatment of wastewater. *Cryptosporidium* and *Giardia* were removed by 90% and 99%, respectively, by activated sludge treatment. Despite difficulties in detecting procedures, the number of Cryptosporidium oocysts detected ranges from 0.005 to 252.7 oocysts/L of surface waters in different countries of the world. In a study conducted in Japan, it was found that oocysts of *Cryptosporidium* increased in numbers from late summer to early autumn, and the maximum number of oocysts detected in three rivers was 3.3 to 5 oocysts/L (5). The reported frequencies of occurrence of contamination of surface water with *Giardia* and *Cryptosporidium* are from 60–96% in the United States and from 20–64% in Canada. Their levels in surface waters were found to be very low, ranging from 0.5 to 5,000 oocysts in 100 liters of water. Analysis of 139 surface water samples in Finland revealed the presence of *Giardia spp.* in 19 (13.7%), *Cryptosporidium* oocysts in 14 (10.1%), and Noroviruses in 13 (9.4%) of the samples (6). The pathogens were isolated less frequently during the winter than during the summer months. Based on risk analysis, it has been proposed that the action levels to prevent outbreaks with these protozoa should occur when concentration in 100 liters water sampled are >5 *Giardia* cysts and 10 to 30 oocysts of *Cryptosporidium* (7).

PERSISTENCE OF PATHOGENS IN WATER

Most of the persistence data for micro-organisms was generated in laboratory experiments. Micro-organisms are seeded into water of certain quality and incubated at test temperature. The concentration of micro-organisms in the suspension is measured as a function of time. To investigate the effect of environmental factors under field conditions on the survival of micro-organisms, investigators have used environmental chambers. The chambers are of small volume that contain the micro-organisms in the matrix, but allow limited exchange with the surrounding environment by means of permeable membrane. Using sentinel chambers, Keswick and Gerba (8) reported the survival of micro-organisms ranked in increasing order were *E.coli*, fecal streptococcus, f2 bacteriophages, SA-11 rotavirus, echovirus 1, coxsackievirus B3, and poliovirus 1. Enteric viruses and bacteria were reported to survive longer in groundwater than in surface water, which was attributed to a number of factors, including lower temperatures, protection from sunlight, and limited microbial antagonisms.

Temperature is the most important factor that influences pathogenic micro-organisms persistence in the natural water and in the environmental setting in general (9). Inactivation rates increase with temperature, and temperature can therefore be a useful predictor of pathogen die-off in the environment (10). Moisture content and loss of moisture are also related to pathogen survival (10). In general, the survival of many micro-organisms is prolonged at lower temperatures, whereas at elevated temperatures, inactivation or die-off is fairly rapid. It is important to examine more than one stressor because, under natural environmental settings, multiple factors may influence the persistence of pathogens. A study was conducted in our laboratory to examine the impact of temperature, salinity, and organic material load on the persistence of *E.coli*, Coxsackievirus A9, and *Cryptosporidium* parvum. At 30 °C, the fastest die-off was observed for Cox A9 virus, where die-off of 5 orders of magnitude was recorded regardless of the water quality. At 15 °C, Cox A9 persistence was similar to that of *Cryptosporidium*, and no change was observed in the concentration of both organisms after 30 days incubation. Whereas a die-off of 5 orders of magnitude was recorded for *E.coli*. The die-off of *E.coli* was faster than that of the other tested micro-organisms regardless of the water quality In a previous study, we compared the persistence of *E.coli*, F+coliphages, poliovirus 1, and hepatitis A virus in phosphate buffered saline (PBS), groundwater, and raw wastewater. In this study, it was determined that micro-organism type and temperature are the most important factors influencing the persistence of micro-organisms in natural waters. Indigenous F+ bacteriophages persisted longest followed by Poliovirus 1, HAV, and the bacterial indicator *E.coli*. The enhanced inactivation of viruses at higher temperatures may be attributed to greater microbial activity in the natural waters. The microbial activity of *P.aeroginosa* has been shown to accelerate the die-off of enteric viruses and other pathogenic micro-organisms. At lower temperatures, where the microbial activity is low, *Cryptosporidium* oocysts' concentration was reduced by only one order of magnitude after 160 days of incubation. Microbial activity has been shown to enhance the die-off of HAV in wastewater, and the time needed for the inactivation of 90% of the virus at 25 °C was 8.3 days as compared with 15.1 days in autoclaved waste (11).

Short-wave ultraviolet (UV) components of sunlight are lethal to enteric pathogens. UV is used for disinfection in water and wastewater treatment processes. The site of the UV damage is the nucleic acid, where the damage inhibits the multiplication capability of the micro-organisms. UV damage may be reduced by the DNA repair mechanisms present in some cells. In marine water, the inactivation rate of *Cryptosporidium* oocysts, poliovirus 1, *Giardia* cysts, and salmonella increased when exposed to natural sunlight, with oocysts exhibiting the highest persistence Sattar et al. (12) demonstrated a detrimental effect on oocyst survival of exposure to sunlight and UV light.

Most of the data generated for the prevalence of the protozoan parasites *Cryptosporidium* and *Giardia* in natural water sources is based on microscopic determination of their presence and viability. As the concentration of the parasites in natural water is low, there were no attempts reported to correlate the viability and the infectious state of naturally occurring parasites in natural waters. Although laboratory experiments have shown that the protozoan parasites may persist for longer periods of time in natural waters, their infectivity potential should be determined in order to more accurately assess the health risk posed by these parasites in natural waters.

PREDICTING THE PERSISTENCE OF PATHOGENS IN WATER

Data on the persistence of pathogens in water generated in laboratory and field experiments can be used to establish models to predict the time needed to inactivate pathogens under various natural sittings. The die-off of sensitive micro-organisms can be described by linear regression equation

$$Y = b + aX$$

where Y represents the response, b represents the y-axis intercept, X represents the independent variable (time), and a is the slope. The value of the slope a is influenced by factors affecting the persistence of pathogens in water. For example, at 15 °C, the slopes recorded for *E.coli*, Coxsackievirus A9, and *Cryptosporidium* in stream water were -0.14, -0.06, and -0.01, respectively. At 30 °C, the die-off slopes for *E.coli* and *Cryptosporidium* did not change; however, that of coxsackie A9 increased to -0.14. The effect of part of the environmental variables on the survival of micro-organisms was found to be significant. The effect of temperature on the persistence of pathogenic micro-organisms was found significant in numerous studies (9). Therefore, the effect of temperature can be predicted by the linear regression equation. On the other hand, water quality effect was not found to be significant. Furthermore, the interaction of water quality with temperature was not found to be significant. The effect of micro-organism type on the persistence in water is significant, and also the interaction of micro-organism type and temperature was found to be significant (9). It is possible to classify micro-organisms into three groups according to their capacity to persist in waters and, consequently, use a multiple linear regression equation in which a slope value for each independent variable will be assigned (10).

CONCLUSIONS

1. Pathogenic micro-organisms may be introduced to natural water sources and may be present at concentrations that may pose health risks.
2. At low temperatures, viruses and protozoa parasites may persist for prolonged periods of time in natural water sources, which will enable their transmission to people consuming the contaminated waters.
3. Most studies in which the persistence of fecal coliforms was compared with those of pathogenic viruses and protozoan parasites revealed that the bacterial indicator is more sensitive than the pathogens and, therefore, it dose not accurately represent the health risks posed by these pathogens in natural waters.

BIBLIOGRAPHY

1. Ferguson, C., Husman, A.M., Altvilla, N., Deere, D., and Ashbolt, N. (2003). *Crit. Rev. Environ. Sci. Technol.* **33**: 299–361.
2. Borchardt, M.A., Haas, N.L., and Hunt, R.J. (2004). *Appl. Environ. Microbiol.* **70**: 5937–5946.
3. Nasser, A.M., Molgen, S., and Rubin, K. (1998). *Prevalence of Cryptosporidium and Giardia in Waste and Suface Water in Israel*. OECD Workshop Interlaken 98 on Molecular Technologies for safe drinking water, Interlaken, Switzerland.
4. Mayer and Plamer. (1996).
5. Tsushima, X. et al. (2002). *J. Vet. Med.* **65**: 121–123.
6. Horman, A. et al. (2004). *Appl. Environ. Microbiol.* **70**: 87–95.
7. Hass, C.N. and Rose, J.B. (1995). *J. Am. Water Works Assoc.* **87**: 81–84.
8. Keswick, B.H. and Gerba, C.P. (1980). *Environ. Sci. Technol.* **14**: 1290.
9. Nasser, A.M. and Oman, S. (1999). *Water Res.* **33**: 1748–1752.
10. Hurst, J.C. (1991). *Modeling the Environmental Fate of Microorganisms*. C. Hurst (Ed.). ASM, Washington, DC, pp. 137–159.
11. Deng, Y.M. and Cliver, D.O. (1995). *Appl. Environ. Microbiol.* **61**: 87–91.
12. Sattar, S.A., Chauret, C., Springthorpe, V.S., Battigelli, D.A., Abbaszadegan, M., and LeChevallier, M. (1999). *AwwARF and Ontario Ministry of Environment and Energy*. Denver, CO and Toronto, ON.

READING LIST

Rose, J.B. (1988). *J. Am. Water Works Assoc.* **80**: 53–58.

Stezenbach, L.D., Arrowood, J.M., Mershell, M.M., and Sterling, C.R. (1988). *Wat. Sci. Technol.* **20**: 193–198.

LeChevallier, M.W., Norton, W.D., and Lee, R.G. (1991). *Appl. Environ. Mocrobiol.* **57**: 2610–2616.

Ongerth, J.E., Hunter, G.D., and DeWalle, F.B. (1995). *Water Res.* **29**: 1295–1299.

Nasser, A.M. (1994). *CRC Crit. Rev. Environ. Sci. Technol.* **24**(4): 281–323.

WELL HEAD PROTECTION

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Groundwater, especially karst aquifers (1) or groundwater under the direct influence (2) of surface water, is vulnerable to contamination from possible contaminating activities (PCAs) (3) related to land use. A wellhead protection (WHP) plan (WHPP) essentially includes the integrated proactive management practice(s) that protect the quality of groundwater that is a source of drinking water. WHP is part of an integrated (from source to consumer's tap) multibarrier system to reduce risks to public health from drinking water. WHP fits into the World Health Organization's (WHO's) Water Safety Plan that recommends the use of hazard analysis and critical control points (HACCPs) as a risk management tool in drinking water operations (4). In the United States, many public water systems (PWSs) are required to conduct source water assessment (SWA) (3,5–7). For PWSs that source from groundwater, a WHPP can be part of their SWA program (SWAP). A PWS must develop its WHPP in accordance with guidelines established by regulatory agencies (1–3).

An important step in WHP is the delineation of one or more WHP zones (WHPZs) to form a WHP area (WHPA) that includes surface and subsurface zone(s) that reasonably contribute water to the well(s) that are being protected from potential source(s) of contamination. Methods and criteria for delineating protection zones range from simple geometric shapes to complex numerical groundwater models based on the specified time of travel (TOT) of contaminant (1,8–11). The most appropriate criterion and method for delineating the WHP zones are selected after careful assessment of many factors, including regulatory acceptance, susceptibility of the aquifer(s) to contamination, available hydrogeological data, computational and technical resources, and the hydrogeologic setting of the aquifer. "Derived/estimated" protection zones must be adjusted to meet the required minimal distances mandated by regulations. Delineation of a WHPA by itself does not protect groundwater quality. Delineation must be followed with the implementation of appropriate management strategies to prevent groundwater contamination and periodic evaluation of their effectiveness. Using a computer-based geographical information system (GIS) to map the protection zones is recommended (12). Cooperation among appropriate jurisdictional agencies and stakeholders is beneficial and may increase the effectiveness of the WHPP.

INTRODUCTION

Groundwater is vulnerable to contamination from many PCAs such as leaching effluents from septic and underground storage tanks (USTs) or leaching pesticides and/or fertilizers. Emerging major concerns are xenobiotics (13) and organic wastewater compounds (14) in effluents from wastewater treatment plants and/or confined animal feeding operations (CAFOs) that may impair the beneficial use and/or environmental value of the groundwater. Xenobiotics include pharmaceuticals, hormones, and other compounds found in medicines and other personal care products. The U.S. Environmental Protection Agency (EPA) reported that over 200 different chemicals have been detected in groundwater in 38 states (15).

The goal of WHP is to manage PCAs to reduce, or preferably prevent, potential impairment of groundwater to assure public health. The U.S. EPA (16) estimated that, between 1971 and 1996, contaminated source waters (surface and groundwater) were the cause of 86% of waterborne disease outbreaks within the United States. The protection of surface water may often be linked to the protection of groundwater and vice versa. The failure of a pumping station from a lightning strike led to an outbreak of cryptosporidiosis in Brushy Creek, Texas, following the accidental discharge of raw sewage into a creek 2 mi upstream of the 120- and 200-ft deep municipal wells (17).

The U.S. EPA (16) observed that deep wells are not immune from biological contamination. Lawson et al. (18) reported an outbreak of gastroenteritis caused by Norwalk virus in water produced from a 600-ft deep well. In the aftermath of the Walkerton incident, Health Canada (19) identified WHP as one of the protective measures that should be implemented and maintained "if source water is subject to human fecal contamination or if human enteric viruses have been responsible for past waterborne outbreaks." The U.S. EPA (16) proposed the Groundwater Rule (GWR) to address risks of consuming waterborne pathogens in groundwater.

Many states require source water assessment before permitting new drinking water sources (such as wells) for PWSs (3). For proposed PWS wells, WHP begins with the proper siting and construction of well(s) in accordance with good sanitary practices and recommended well design standards (20). A successful WHPP protects public health and avoids the expense of treating polluted water or drilling replacement wells (7). There are additional benefits from implementing WHP (21–23). The U.S. EPA identified over 90 measures as possibilities for measuring success of source water contamination prevention at the national level (24).

The United Kingdom Margate Act (11) of 1902 and Brighton Act of 1924 are examples of earlier efforts directed toward the protection of groundwater produced from wells used for drinking. The Margate Act empowered a water authority to control drains, cesspools, and so on over an area of 1500 yards from any well (11). In 1986, the U.S. Congress introduced a Wellhead Protection Program (WHPP) as part of the Amendments to the Safe Drinking Water Act (SDWA) (25). A wellhead protection area (WHPA) as defined by that Act as "the surface and subsurface area surrounding a water well or well field, supplying a public water system through which contaminants are reasonably likely to move toward and reach such well or well field." The U.S. EPA (16) sometimes refers to a WHPA as "groundwater protection area." The California Department of Pesticide Regulation (DPR) defines a groundwater protection area (GWPA) as "an area of land that is vulnerable to the movement of pesticides to ground water according to either leaching or runoff processes" (26).

Amendments to the SDWA in 1996 required states to establish source water assessment programs (SWAPs) (6). Sourcewater protection is the generic term for describing management activities to protect the quality of water used for drinking water irrespective of the nature of the source: surface water, groundwater, or groundwater under the influence of surface water. Source water protection is the leading first barrier of the multibarrier approach to protecting the quality of drinking water delivered to consumers. Other elements of the multibarrier protection framework against pollution are source water treatment (including disinfection), distribution system integrity (including cross-connection control programs), and public information. The Minnesota Department of Health (7) differentiates between "source water assessment" plan and a "wellhead protection plan" as two different documents, with separate and distinct purposes. A PWS that sources from groundwater can use the completed SWA plan in developing a WHPP (7).

DEVELOPING A WHPP FOR A PWS

Many countries have developed regulations governing the practice of WHP (2,9–11). In the United States, the SDWA mandated states to develop WHP programs that must include some specified elements (9,22). The U.S. EPA must approve state WHP programs before implementation. As of 2004, the U.S. EPA has approved WHP programs for all states except Virginia (27). WHP programs developed by states provide regulatory guidance to PWSs on how to develop appropriate WHP plans (3,7).

Typical steps for developing a WHP plan include the following: (1) defining the statement and purpose of the WHP; (2) defining the members, roles, and duties of the team; (3) delineating the WHP zones; (4) inventorying the PCAs; (5) assessing the vulnerability; (6) developing management programs; (7) developing contingency plans for alternative water supplies; and (8) developing an optional source water protection program (9,22,28). Those steps are mainly sequential, but some steps can also be iterative.

Many PWSs have developed WHP plans, some of which included stakeholder participation. Some examples are available on the Internet (29,30). The U.S. EPA (31,32) maintains a directory of useful tools for developing a WHPP. Witten et al. (28) identified some financing strategies for wellhead protection.

DELINEATION CRITERIA AND METHODS

An important step is the delineation of one or more protection zones to which WHP management measures would be tailored. Five major criteria that may be used singly or in combination to delineate a protection zone are distance, drawdown, time of travel (TOT), assimilative capacity, and flow boundaries (8,9). Factors that determine the preferred delineation criterion/criteria include local regulatory requirements, number of wells involved, complexity of aquifer(s), spatial extent, and available resources and professional skills. The delineation methods can be deterministic or stochastic. Kunstmann and Kinzelbach (33) describe stochastic methods for delineating a WHPA.

The distance criterion is the simplest and least expensive. It is based on a fixed perimeter radius around the well professionally "judged" adequate to provide reasonable protection. The drawdown criterion is based on the zone of influence (ZOI) where groundwater level declines due to pumping from the well. The TOT criterion requires the delineation of isochrones (i.e., contours of equal time) representing the duration it takes for water to reach a well or a contaminant to reach a well in concentration exceeding a target level. The assimilative capacity criterion permits reduction in the spatial extent of the zone of contribution (ZOC) of the WHPA when contaminants can be attenuated to concentrations lower than the target level before reaching the well through biogeochemical processes such as dilution, dispersion, sorption, or biodegradation. The flow boundary criterion uses physical and hydrogeologic features that control groundwater flow to define the spatial extent, that is, the ZOC of the WHPA.

The U.S. EPA (9) categorized the methods for delineating into four major groups of increasing complexity: geometric, simple analytic (SA), hydrogeologic mapping (HM), and computer modeling (CM). Geometric methods involve the use of a predetermined fixed radius or simplified shapes that have been precalculated for a range of pumping and aquifer conditions. Examples are the arbitrary fixed radius (AFR), calculated fixed radius (CFR), and modified CFR.

AFR involves drawing a circle of defined distance around the well on a base map. The defined distance (radius) is based on professional judgment and regulatory acceptance. CFR is similar to the AFR but the radius is calculated based on the volume of cylinder with pore volume equal to the volume of water pumped during the specified period.

SA methods use appropriate analytical solutions to groundwater flow, such as the uniform flow equation, and known aquifer characteristics to derive protection zones. HM involves the use of a combination of hydrological, geological, and geochemical data and geologic mapping techniques to delineate the area contributing water to the well(s). HM methods are appropriate in settings where geologic features greatly influence groundwater flow such as in karst aquifers (15,34). CM methods numerically simulate groundwater flow and contaminant transport to calculate rate and direction of flow, travel times, and so on. The model developed may be used to compare the system's response to proposed management options (15).

The U.S. EPA (9) lists the advantages and disadvantages of each delineation method. The number of person-hours required to delineate a WHPA per well range from 1–5 for AFR to 10–200+ for numerical modeling (8). Figures illustrating the delineation methods are in given in Reference 9. Some states prefer specific methods for delineating WHPAs for special wells. California (13) prefers detailed hydrogeologic analyses when delineating WHPAs for nonvertical wells (e.g., horizontal wells). California (13) prefers using the delineation method that utilizes the most available detailed information. A combination of methods can be used to delineate one or more zones. For example, the innermost zone to the well may be based on a fairly simple geometry while the outermost protection zone may be delineated using complex numerical models.

WHP ZONES

A WHPA consists of one or more WHPZs, to which appropriate management measures can be tailored. The innermost WHPZ is usually delineated to protect against biological contaminants and to protect the integrity of the well. Some outermost zones regarded as buffer zones may be optional. In California (3), the suggested approach is to define four zones and an optional buffer zone. The required zones in California are (Fig. 1):

Well Site Control Zone (WSCZ). The closest zone to the wellhead is the area immediately surrounding the well. The WSCZ is managed to prevent seepage of contaminants, vandalism, or tampering. The recommended minimum radius is 50 ft.

Zone A2 or the Microbial/Direct Chemical Contamination Zone. This is the surface area above the aquifer that contributes water to well(s) within a 2-yr TOT. This zone was established to comply with the requirement of the proposed Groundwater Rule (8) based on research that bacteria and viruses are not likely to survive beyond 2 yr in soil and groundwater. Recommended minimum radii

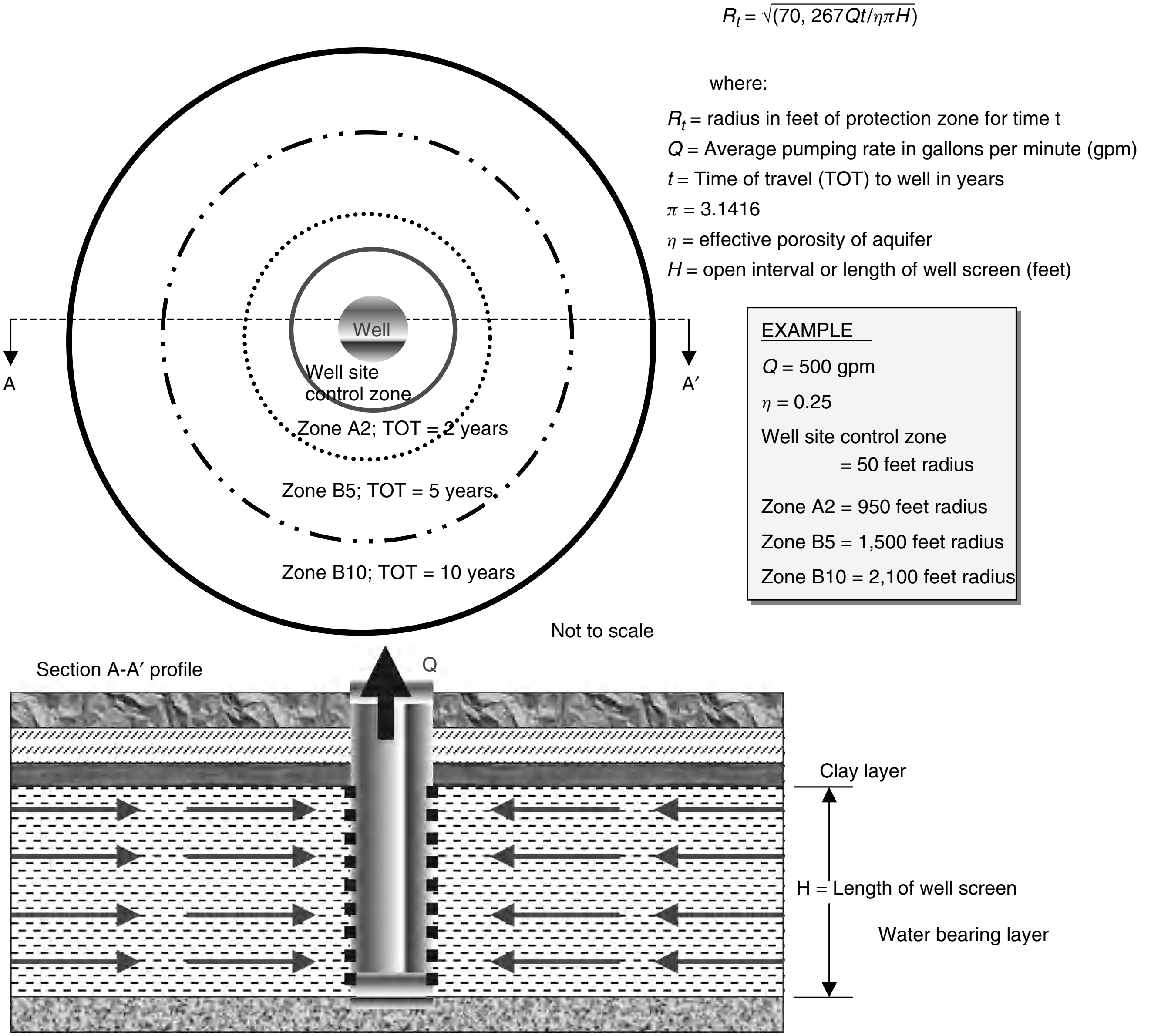

Figure 1. Wellhead protection zones delineated by calculated fixed radius (CFR) method.

are 600 ft and 900 ft for porous aquifer (PA) and fractured rock aquifer (FRA), respectively.

Zone B5. This chemical contamination zone is that surface area above the aquifer between the 2- and 5-yr TOT. This zone provides additional response time to manage a chemical spill. Recommended minimum radii are 1000 ft and 1500 ft for PA and FRA, respectively.

Zone B10. This chemical contamination zone is that surface area above the aquifer between the 5- and 10-yr TOT. This zone allows for some natural attenuation of contamination and development of mitigation measures. Recommended minimum radii are 1500 ft and 2250 ft for PA and FRA, respectively.

Buffer Zone (Optional). This zone is generally beyond Zone B10. The zone offers a higher level of protection and may be extended to include the entire recharge area, especially where there are potential sources of significant contamination such as landfills or other hazardous materials.

The delineated zones can be refined in shape and/or size based on professional judgment and/or local knowledge of some site-specific hydrogeology. In California, the final assessment map must be based on a USGS quadrangle 7.5-minute series topographic map (3).

INVENTORY OF PCAS

The purpose is to identify all possible contaminating activities (PCAs) by location within the WHPA. Typical resources used in developing the inventory of PCAs include land use maps, business license records, hazardous waste databases, and the Internet (35,36). A field reconnaissance can identify other potential sources of contamination.

The comprehensive inventorying of PCAs can be in phases with initial focus on sources that could pose the greatest risk. The inventory should include past and present sources of contamination and might require geophysical investigations for inactive sources such as abandoned wells and waste disposal sites. The information gathered should include the type of source, potential contaminants from each source, and location of source. The information gathered must be updated periodically. Many PWSs use global positioning systems (GPSs) to locate PCAs and GIS system to map the locations. The Groundwater Foundation (37) has developed a primer on using such technologies to develop an inventory of PCAs.

VULNERABILITY ASSESSMENT (VA) OR SUSCEPTIBILITY ASSESSMENT

The U.S. EPA (38) defines groundwater “vulnerability” as “the relative ease with which a contaminant introduced into the environment can migrate to an aquifer under a given set of management practices, contaminant properties, and aquifer hydrogeologic characteristics.” Groundwater vulnerability can be specific (specified contaminant) or intrinsic (any contamination in general) and must consider long-term effects (39). The purpose of VA in WHP planning is to evaluate and rank the risks of the identified PCAs that pose the most significant threats to groundwater quality within the WHPA. VA under WHP should not be confused with the VA required under the U.S. Public Health Security and Bioterrorism Preparedness and Response Act of 2002 (PL 107–188). The Bioterrorism Act addresses the vulnerability of the entire water system (not just source waters) to intentional acts (e.g., terrorism) intended to substantially disrupt the ability of the system to provide a safe and reliable supply of drinking water. The U.S. EPA (16) proposed a groundwater rule that requires hydrogeologic assessments to identify wells sensitive to fecal contamination.

There are many methods for evaluating and mapping groundwater vulnerability to contamination ranging from a simple process to detailed numerical modeling of fate and transport of chemicals of concern (9,26,39–42). VA must factor the type and proximity of the PCA and site-specific hydrogeological information such as the presence of karst formations and any physical barrier that may affect the fate and transport of the PCA (3). DRASTIC [Depth to water table, net Recharge, Aquifer media, Soil media, Topography (slope), Impact to vadose zone, and hydraulic Conductivity of the aquifer] is a widely used method for evaluating relative vulnerability to groundwater contamination (9,41). Many VA models have technical limitations. Focazio et al. (40) illustrated the use of scientifically reliable tools for groundwater VA.

MANAGEMENT MEASURES (MMS)

Among the factors that influence the choice of MMs are availability of alternate sources of water, types of contaminants, hydrogeologic setting, and community and regulatory acceptance. MMs must be tailored to be most appropriate for each WHPZ. Land uses in the zone closest to the well are usually managed to avoid all possible risks, including those from bacteria, viruses, and chemical spills (2).

WHP MMs may be regulatory or nonregulatory. Nonregulatory MMs include public education to increase community awareness of the WHPP, economic incentives, land acquisition (43), and conservation easements. Regulatory MMs include local ordinances and zoning/land use planning. Additional examples of MMs are provided by the U.S. EPA (8,9,15). It is preferable that a WHP plan, that includes land use controls, use scientifically and legally defensible criteria to delineate the protection zones (40). Where feasible, installation of groundwater quality monitoring well(s) between the significant potential sources of contamination and the wellhead and periodic sampling could provide an early warning detection system.

CONTINGENCY PLANNING

A contingency plan (CP) should be developed to deal with emergency threats to groundwater quality and natural disasters such as floods. It is advisable to coordinate with the local emergency planning committee. The following elements are typically included in the CP: basic water system information, WHPA boundaries, a list of potential contaminant sources and locations, short-term and long-term water supply options, water rationing plans, and emergency response plans (ERPs). The development of a CP can be coordinated with other efforts such as that of the ERP required under the Bioterrorism Act. The U.S. EPA (44) maintains a list of ERP guidance documents and planning tools.

CONCLUSION

Wellhead protection planning is now one of the major programs within the SDWA related to protecting the quality of groundwater. The other programs are groundwater rule, sole source aquifer, source water assessment, underground injection control (UIC), source water petition, and comprehensive groundwater protection grants. The U.S. EPA is strengthening the linkages between the Clean Water Act (CWA) and the SDWA. The U.S. EPA is coordinating the source water protection program in each state with federal and state underground storage tank programs using GIS to map underground storage tank sites within source protection zones of drinking water sources.

Wellhead protection zones and plans should be periodically reviewed and updated. Regular sanitary surveys and vulnerability assessments could reveal operational deficiencies especially after special events such as floods. Curriero et al. (45) found that over half of the waterborne disease outbreaks in the United States in the past 50 years were preceded by heavy rainfall. Outbreaks due to groundwater contamination, which accounted for approximately 36% of all outbreaks, were more associated with extreme precipitation occurring within a 3-month lag preceding the outbreaks (45).

BIBLIOGRAPHY

1. U.S. EPA. (2002). *Delineation of Source-Water Protection Areas in Karst Aquifers of the Ridge and Valley and Appalachian Plateaus Physiographic Provinces: Rules of Thumb for Estimating the Capture Zones of Springs and Wells*. EPA 816-R-02-015. U.S. EPA Office of Water, Washington, DC.
2. Ontario Ministry of the Environment. (2001). Protocol for delineation of wellhead protection areas for municipal groundwater supply wells under direct influence of surface water, Ontario, Canada. Available at http://www.ene.gov.on.ca/envision/techdocs/index.htm. Accessed November 2004.
3. California Department of Health Services (DHS), Division of Drinking Water and Environmental Management. (2000). *Drinking Water Source Assessment and Protection (DWSAP) Program*. California Department of Health Services, Division of Drinking Water and Environmental Management, Sacramento, CA. Available at http://www.dhs.ca.gov/ps/ddwem/dwsap/DWSAP_document.pdf. Accessed November 2004.
4. http://www.who.int/water_sanitation_health/dwq/gdwq3/en/. Accessed November 2004.
5. U.S. EPA. (1997). *State Source Water Assessment and Protection Programs Guidance*. Final Guidance EPA-816-R-97-009. U.S. EPA Office of Water, Washington, DC.
6. http://www.epa.gov/safewater/protect/swap.html. Accessed November 2004.
7. http://www.health.state.mn.us/divs/eh/water/swp/swa/index.htm. Accessed November 2004.
8. U.S. EPA. (1987). *Guidelines for Delineation of Wellhead Protection Areas*. EPA/440/6-87-010. Office of Ground-Water Protection, Washington, DC.
9. U.S. EPA. (1994). *Handbook Ground Water and Wellhead Protection*. EPA/625/R-94-001. Office of Research and Development, Washington, DC.
10. Australian and New Zealand Environment and Conservation Council. (1995). *Guidelines for Groundwater Protection in Australia*. Canberra, ACT 2600.
11. National Groundwater and Contaminated Land Centre. *Groundwater Source Protection Zones*. Environment Agency, Olton, Solihull, UK. Available at http://www.environment-agency.gov.uk/commondata/105385/gspz_on_web.pdf. Accessed November 2004.
12. Bice, L.A., Van Remortel, R.D., Mata, N.J., and Ahmed, R.H. (2000). *Source Water Assessment Using Geographic Information Systems*. National Risk Management Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, OH. Available at http://www.epa.gov/ORD/NRMRL/wswrd/SWAPJ18.PDF. Accessed November 2004.
13. Ongerth, J.E. and Khan, S. (2004). Drug residuals: how xenobiotics can affect water supply sources. *J. AWWA* **94**(5): 94–101.
14. Lee, K.E. et al. (2004). *Presence and Distribution of Organic Wastewater Compounds in Wastewater, Surface, Ground, and Drinking Waters, Minnesota, 2000–02*. U.S. Geological Survey Scientific Investigation Report 2004–5138.
15. U.S. EPA. (1993). *Wellhead Protection: A Guide for Small Communities*. EPA/625/R-93/002. Office of Research and Development, Washington, DC.
16. U.S. EPA. (2000). National primary drinking water regulations: groundwater rule; Proposed Rule 40 CFR Parts 141 and 142. *Fed. Reg.* **65**(91): 30194–30274.
17. http://www.epa.gov/safewater/ndwac/ndwac051701day1.html. Accessed November 2004.
18. Lawson, H.W. et al. (1991). Waterborne outbreak of Norwalk virus gastroenteritis at a southwest U.S. resort: role of geological formations in contamination of well water. *Lancet* **337**: 1200–1204.
19. Health Canada. (2003). *Virological Quality of Drinking Water*. Document for Public Comment—prepared by the Federal-Provincial-Territorial Committee on Drinking Water. Available at http://www.hc-sc.gc.ca/hecs-sesc/water/publications/virological_quality_dw/toc.htm.
20. California Department of Water Resources. (1990). *California Well Standards*. Bulletin 74–90. Department of Water Resources, Sacramento, CA.
21. Fenske, B.A. and Williams, M.B. (2004). *Demonstrating Benefits of Wellhead Protection Programs*. AWWA Research Foundation, Denver, CO.
22. Makinde-Odusola, B. (2003). Wellhead protection. In: *Encyclopedia of Water Science*. X. Stewart and X. Howell (Eds.). Marcel Dekker, New York, pp. 1024–1028. Available at http://www.dekker.com. Accessed November 2004.
23. http://www.health.state.mn.us/divs/eh/water/swp/whp/benefits.html. Accessed November 2004.
24. http://www.epa.gov/safewater/protect/strategyupdate.html. Accessed November 2004.

25. American Water Works Association (AWWA). (2001). *Safe Drinking Water Advisor: A Compliance Assistance Resource*. AWWA, CD-ROM Edition.
26. http://www.cdpr.ca.gov/docs/gwp/gwpamaps.htm. Accessed November 2004.
27. http://www.epa.gov/safewater/whpnp.html. Accessed November 2004.
28. Witten, X. et al. (1995). *A Guide to Wellhead Protection*. Planning Advisory Service Report No. 457/458. American Planning Association, Chicago, IL.
29. http://www.ci.redmond.wa.us/insidecityhall/publicworks/environment/grhistory.asp.
30. http://www.gem.msu.edu/casestd/casestd.html. Accessed November 2004.
31. http://www.epa.gov/safewater/protect/sources.html. Accessed November 2004.
32. http://www.epa.gov/safewater/protect/feddata/delineation.html. Accessed November 2004.
33. Kunstmann, H. and Kinzelbach, W. (2000). Computation of stochastic wellhead protection zones by combining the first-order second-moment method and Kolmogorov backward equation analysis. *J. Hydrol.* **237**: 127–146.
34. Bachman, S. et al. (1997). *California Groundwater Management*. Groundwater Resources Association of California, Sacramento, CA.
35. http://www.epa.gov/safewater/protect/feddata/inventory.html.
36. Stevens, K.B. et al. (2003). *Chemical Occurrence Data Sets for Source Water Assessment*. AWWA Research Foundation, Denver, CO.
37. The Groundwater Foundation. (2003). *Using Technology to Conduct a Contaminant Source Inventory—A Primer for Small Communities*. Lincoln, NE. Available at http://www.groundwater.org/ProgEvent/ACTT_Primer1202.pdf. Accessed November 2004.
38. U.S. EPA. (2004). *Handbook of Groundwater Protection and Cleanup Policies for RCRA Corrective Action*. EPA530-R-04-030. Office of Solid Waste and Emergency Response, Washington, DC.
39. National Research Council. (1993). *Groundwater Vulnerability Assessment, Contamination Potential Under Conditions of Uncertainty*. National Academy Press, Washington, DC. Available at http://books.nap.edu/books/0309047994/html. Accessed November 2004.
40. Focazio, M.J. et al. (2002). *Assessing Ground-Water Vulnerability to Contamination: Providing Scientifically Defensible Information for Decision Makers*. USGS Circular 1224.
41. Rupert, M.G. (2001). Calibration of the DRASTIC groundwater vulnerability mapping method. *Groundwater* **39**(4): 625–630.
42. U.S. EPA. (1993). *A Review of Methods for Assessing Aquifer Sensitivity and Groundwater Vulnerability to Pesticide Contamination*. EPA-813-R-93002.
43. Stone, D. and Schindel, G.M. (2002). The application of GIS in support of land acquisition for the protection of sensitive groundwater recharge properties in the Edwards aquifer of south-central Texas. *J. Cave Karst Studies* **64**(1): 38–44.
44. http://cfpub.epa.gov/safewater/watersecurity/home.cfm?program_id=8. Accessed November 2004.
45. Curriero, F.C. et al. (2001). The association between extreme precipitation and waterborne disease outbreaks in the United States, 1948–1994. *Am. J. Public Health* **91**(8): 1194–1199.

CHEMICAL DRINKING WATER STANDARDS, PAST, PRESENT, AND FUTURE

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Water resources in the United States have already been shown to contain the chemical byproducts of water treatment and disinfection, industrial chemicals (both organic an inorganic), human drugs (prescription and nonprescription), veterinary and human antibiotics, pharmaceuticals (e.g., from the clinical treatment of cancer using chemotherapy drugs), sex and steroidal hormones, antioxidants, detergents and detergent metabolites, fire retardants, plasticizers, polycyclic aromatic hydrocarbons, petroleum products, and a wide range of pesticides that are either regulated, anticipated to be regulated, or unregulated. As any given water resource will contain a mixture of individual chemical compounds, scientists, engineers, and environmental policy professionals need to ask the question, can existing drinking water standards, that are based on individual chemical-specific water quality criteria, be shown to protect the public health? In attempting to answer this question, we hope to put into context the validity of chemical drinking water standards in a world where the boundaries between water and wastewater are becoming increasingly blurred.

CHEMICAL POLLUTANTS OF THE PAST

Prior to the 1940s and the mass production of synthetic organic chemicals, the vast majority of industries produced chemicals that were dominated by inorganic compounds or biodegradable organic compounds, for example, canneries, dairies and feedlots, distilleries, fertilizers, foundries (iron and steel), metal plating, mining and smelting, pulp and paper, paint products, meat packing, tanneries, textiles, and timber products. In addition, a growing number of petroleum-based compounds were also being produced and used in coal-derived chemicals manufacturing, manufactured gas production, petroleum refining, and wood treating. As a result, common water pollutants included inorganic acids (chloride and sulfate), arsenic, copper, cadmium, chromium, cyanide, lead, nickel, nitrate, and zinc as well as phenols and a wide spectrum of petroleum hydrocarbons.

Some of these common pollutants were contained in the 1925 standards for drinking water (1). The 1925 standards state that, with respect to chemical and physical characteristics, for water to be suitable for drinking and culinary purposes, it should be free from toxic salts and should not contain an excessive amount of soluble mineral substances or any chemicals employed in treatment. In addition, when any of the following compounds exceed their standards, the water should be rejected for use:

Constituent	Concentration (mg/L)
Copper	0.2
Iron	0.3
Lead	0.1
Magnesium	100
Zinc	5.0
Chloride	250
Sulphate	250
Total Solids	1,000

By 1946 (2), grounds for rejection of the water supply was expanded and based on the following standards:

Constituent	Concentration (mg/L)
Arsenic	0.05
Chromium (6+)	0.05
Lead	0.1
Fluoride	1.5
Selenium	0.5

whereas the following chemical substances should preferably not occur in excess of the following standards:

Constituent	Concentration (mg/L)
Copper	3.0
Iron	0.3
Magnesium	125
Zinc	15
Chloride	250
Sulphate	250
Phenolic	0.001

Phenolic compounds (commonly associated with wastes produced by manufactured gas production, wood treating, and synthetic chemical manufacturing) were the first organic chemicals added to the drinking water standards. However, by the 1950s, the high-volume use of the synthetic organic surfactant, alkyl benzene sulfonate, in detergents and the widespread distribution of highly toxic halogenated pesticides, shown to be responsible for fish kills around the United States, resulted in the addition of more organic compounds to the 1962 water quality standards.

Based on the 1962 (3) standards, grounds for rejection of the water supply should occur when the following standards are exceeded:

Constituent	Concentration (mg/L)
Arsenic	0.01
Barium	1.0
Cadmium	0.01
Chromium (6+)	0.05
Cyanide	0.2
Lead	0.05
Selenium	0.01
Silver	0.05
Fluoride	0.6–1.7 (based on air temperature)
Copper	1.0

whereas the following chemical substances should not occur in excess of the following standards:

Constituent	Concentration (mg/L)
Alkyl Benzene Sulfonate	0.5
Carbon Chloroform Extract	0.2[1]
Phenols	0.001
Iron	0.3
Manganese	0.05
Zinc	5.0
Cyanide	0.01
Nitrate	45
Chloride	250
Sulphate	250
Total Dissolved Solids	500

As a result of the continued and extensive use of halogenated and nonhalogenated hydrocarbons since the 1940s and the recognition of halogenated disinfection byproducts in treated drinking water, the current drinking water standards now include 27 inorganic criteria and 63 organic criteria. The current National Primary Drinking Water Standards for chemicals are:

Contaminant	Maximum Contaminant Level(MCL) (Micrograms per liter)[2]
Inorganic Compounds	
Antimony	6.0
Arsenic	50.0
Barium	2000.0
Beryllium	4.0
Bromate	10.0
Cadmium	5.0
Chlorine gas (as Cl_2)	4000.0
Chlorine dioxide (as ClO_2)	800.0
Chlorite	1000.0
Chromium (total)	100.0
Copper	1300.0
Cyanide	200.0
Fluoride	4000.0
Lead	15.0
Mercury	2.0
Nitrate	10000.0
Nitrite	1000.0
Selenium	50.0
Thallium	2.0
Organic Compounds	
Acrylamide	1000.0
Alachlor	2.0
Atrazine	3.0
Benzene	5.0
Benzo(a)pyrene	0.2
Carbofuran	40.0
Carbon tetrachloride	5.0
Chloramines (as Cl_2)	4000.0
Chlordane	2.0
Chlorobenzene	100.0

2,4-D	70.0
Dalapon	200.0
DBCP	0.2
O-Dichlorobenzene	600.0
p-Dichlorobenzene	75.0
1,2-Dichloroethane	5.0
1,1-Dichloroethylene	7.0
cis-1,2-Dichloroethylene	70.0
trans-1,2-Dichloroethylene	100.0
Dichloromethane	5.0
1,2-Dichloropropane	5.0
Di(2-ethylhexyl)adipate	400.0
Di(2-ethylhexyl)phthalate	6.0
Dinoseb	7.0
Dioxin	0.00003
Diaquat	20.0
Endothall	100.0
Endrin	2.0
Epichlorohydrin	20000.0
Ethylbenzene	700.0
Ethylene dibromide	0.05
Glyphosate	700.0
Haloacetic acids (HAA5)[3]	60.0
Heptachlor	0.4
Heptachlor epoxide	0.2
Hexachlorobenzene	1.0
Hexachlorocyclopentadiene	50.0
Lindane	0.2
Methoxychlor	40.0
Oxamyl(Vydate)	200.0
Polychlorinated biphenyls	0.5
Pentachlorophenol	1.0
Picloram	500.0
Simazine	4.0
Styrene	100.0
Tetrachloroethylene	5.0
Toluene	1000.0
Total Trihalomethanes (TTHM)[4]	100.0
Toxaphene	0.003
2,4,5-TP (Silvex)	50.0
1,2,4-Trichlorobenzene	70.0
1,1,1-Trichloroethane	200.0
1,1,2-Trichloroethane	5.0
Trichloroethylene	5.0
Vinyl chloride	2.0
Xylenes (total)	10000.0

[1] Measures extractable organic residues (i.e., pesticides).

[2] The maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health effect of persons would occur, and which allows for an adequate margin of safety.

[3] The HAA5 compounds are dibromoacetic acid, dichloroacetic acid, monobromacetic acid, monochloroacetic acid, and trichloroacetic acid.

[4] The TTHM compounds are bromodichloromethane, bromoform, chloroform, and dibromochloromethane.

The National Secondary Drinking Water standards are nonenforceable guidelines regulating contaminants that may cause cosmetic effects or aesthetic effects in drinking water. The United States Environmental Protection Agency (USEPA) recommends secondary standards for water systems but does not require systems to comply. However, individual states may choose to adopt them as enforceable standards.

Contaminant	Secondary Standard (Micrograms per liter)
Aluminum	0.05
Chloride	250
Iron	0.3
Manganese	0.05
Silver	0.1
Sulfate	250
Total Dissolved Solids	500
Zinc	5.0

All of these pollutants are associated with industrial and chemical use practices evolving over the last 100 years.

CHEMICAL POLLUTANTS OF THE PRESENT AND FUTURE

The National Research Council estimates that there are approximately 72,000 organic chemicals in commerce within the United States, with nearly 2000 new chemicals being added each year (4). Given this number of chemicals, it would seem impossible that the USEPA can identify every chemical that poses a hazard to the public health. In fact, it is impossible. For example, under the Toxic Substances Control Act that was established in 1979, the USEPA has conducted an assessment program to determine which new chemicals present an unreasonable risk to human health or the environment. Since 1979, the USEPA has only reviewed some 32,000 new chemical substances. With so many chemicals left to evaluate, the USEPA chose to exclude all chemicals that are produced in amounts less than 10,000 pounds per year as well as all polymers from further consideration. The remaining 15,000 chemical subset has been identified as being the broad focus of the USEPAs existing chemical testing and assessment program with the primary focus being on the 3000 high-production-volume chemicals that are produced/imported at levels above 1 million pounds per year (4).

Once toxicity data are collected from animal studies, the USEPA must still identify those chemicals that should be regulated in drinking water. As of 1998, USEPA had completed their evaluation of approximately 400 compounds for potential regulation in drinking water. Of these top 400, a list of 50 chemicals were selected for consideration as future drinking water standards. The 50 chemicals that make up the 1998 Drinking Water Contaminant Candidate List are:

Acetochlor
Alachlor ESA (and acetanilide degradation products)
Aldrin
Aluminum
Boron

Bromobenzene
DCPA nonacid degradate
DCPA diacid degradate
DDE
Diazinon
1,1-dichloroethane
1,1-dichloropropene
1,2-diphenylhydrazine
1,3-dichloropropane
1,3-dichloropropene
2,2-dichloropropane
2,4-dichlorophenol
Dieldrin
2,4-dinitrophenol
2,4-dinitrotoluene
2,6-dinitrotoluene
Disulfoton
Diuron
DPTC (s-ethyl-dipropylthiocarbanate)
Fonofos
Hexachlorobtadiene
p-isopropyltoluene (p-cymene)
Linuron
Manganese
Methyl bromide
Methyl-t-butyl ether (MTBE)
2-Methyl-phenol (o-cresol)
Metolachlor
Metrobuzin
Molinate
Naphthalene
Nitrobenzene
Organotins
Perchlorate
Prometon
RDX
Sodium
Sulfate
1,1,2,2-tetrachloroethane
Terbacil
Terbufos
Triazines (and degradation products)
2,4,6-trichlorophenol
1,2,4-trimethylbenzene
Vanadium

A minimum of 5 compounds must be selected for regulation under the primary drinking water standards. The 2003 revised Drinking Water Contaminant Candidate List is now composed of the following 42 chemicals:

1,1,2,2-tetrachloroethane
1,2,4-trimethylbenzene
1,1-dichloroethane
1,1-dichloropropene
1,2-diphenylhydrazine
1,3-dichloropropane
1,3-dichloropropene
2,4,6-trichlorophenol
2,2-dichloropropane
2,4-dichlorophenol
2,4-dinitrophenol
2,4-dinitrotoluene
2,6-dinitrotoluene
2-methyl-Phenol (o-cresol)
Acetochlor
Alachlor ESA and other acetanilide pesticide degradation products
Aluminum
Boron
Bromobenzene
DCPA monoacid degradate
DCPA diacid degradate
DDE
Diazinon
Disulfoton
Diuron
EPTC (s-ethyl-dipropylthiocarbamate)
Fonofos
p-Isopropyltoluene (p-cymene)
Linuron
Methyl bromide
Methyl-t-butyl ether (MTBE)
Metolachlor
Molinate
Nitrobenzene
Organotins
Perchlorate
Prometon
RDX
Terbacil
Terbufos
Triazines and degradation products
Vanadium

As this list becomes more focused, a major problem still remains. Approximately seven years after the first Drinking Water Contaminant Candidate List was proposed, no new chemicals have been added, which is a disturbing result as well as a disturbing trend. From a scientific and practical point of view, the USEPA never has had the time or resources to comprehensively evaluate and regulate the entire list of 72,000 chemicals. However, to limit selection to a minimum of five chemicals is just absurd. It is extremely difficult to accept the premise that of all the chemicals used in this country there are only five additional chemicals need be added to the Candidate

List every few years that are a hazard to human health. Consequently, many hazardous chemicals that should be regulated on the basis of their potential toxicity to humans will go unregulated, and when these unregulated chemicals occur in drinking water, there will be no requirement to warn the consumer[5]. Furthermore, based on the USEPAs performance to-date and their pace of evaluating and regulating chemicals in drinking water, we might all be dead by the time the USEPA ponders the fate of its initial list of 50 chemicals. Such delays are inherent in current federal policy. For example, the Toxic Substances Control Act requires the USEPA demonstrate that a chemical is dangerous before it can take any action against that chemical (i.e., regulate that chemical). It is because of this type of policy that the presence of unregulated chemicals in our drinking water poses one of the greatest threats to America's public health. The current Drinking Water Contaminant Candidate List does not even consider a wide range of chemicals that are present in home care products (e.g., phthalates and nonylphenols) or drugs and pharmaceuticals (e.g., Ibuprofen, Clofibrate [cholesterol treatment], Estrogen, Bleomycin [cancer treatment]) that have already been identified in our water resources.

The fact that there are 1) whole new classes of chemicals that are not even evaluated by the USEPA as a potential threat to drinking water, 2) chemical mixtures in drinking water that are not regulated, and 3) approximately 2000 new chemicals produced and/or used in the United States each year, drinking water standards cannot be demonstrated to actually protect the public health.

Given this condition, it is our recommendation that water provided by either public- or privately-operated water utilities not solely rely on federal or state drinking water standards to protect their consumers. Water utilities should treat their raw water resource with the appropriate water treatment technologies (e.g., granulated activated carbon, ion exchange, reverse osmosis, advanced oxidation) to remove all potentially harmful inorganic and organic pollutants from their final product.

Based on our interviews with both public- and privately-operated water utilities, the cost to apply advanced water treatment technologies to remove the maximum amount of either inorganic or organic compounds would only require a 20% increase in the water utility customer's water bill. Given this level of available treatment, the only technical issue that remains is how to monitor for pollutant removal. Treatment efficiency can be determined by producing a chemical fingerprint of the raw water and the treated product, which can be accomplished by using standard liquid and gas chromatography methods, Raman spectroscopy methods, or the use of new ion diffusion spectroscopy.

Protection of our drinking water resources will become increasing difficult because (5) the boundaries between water and wastewater are already beginning to fade. Therefore, the only real future defense against the consumption of polluted drinking water is to abandon our reliance on water quality standards and implement appropriate water treatment technologies to minimize pollutants in our drinking water.

BIBLIOGRAPHY

1. Anonymous. (1925). Report of Advisory Committee on Official Water Standards. *Public Health Reports*. **40**(15).
2. Anonymous. (1946). Public Health Service Drinking Water Standards. *Public Health Reports*. **61**(11).
3. USPHS. (1962). Public Health Service Drinking Water Standards. *Public Health Service Publication*. **956**.
4. National Research Council. (1999). *Identifying Future Drinking Water Contaminants*. National Academy Press, Washington, DC.
5. Maxwell, S. (2001). Ten key trends and developments in the water industry. *J. Amer. Water Works Assoc.* **93**(4).

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[5] Community water systems are only required to notify consumers if regulated pollutants exceed their established criteria.

INDUSTRIAL WATER

MAGNETIC WATER CONDITIONING

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INTRODUCTION

Hard water contains minerals such as calcium, magnesium, and other hard ions that can form scale on a variety of surfaces that come into contact with the water, especially when it is heated. Magnetic water conditioning is a nonchemical technology that can prevent the formation of scale in hard water.

There are two basic categories of magnetic water conditioning devices: nonpermanent magnetic units (electromagnetic and electrostatic units) (Fig. 1) and permanent magnet units (Fig. 2). Electromagnetic units generate a magnetic field through the use of electromagnets, in which an electric current passes through a wire. Electrostatic units also use electricity to impose an electric field on the water flow, which attracts or repels ions in the water and generates a magnetic field.

Permanent magnetic units, the focus here, utilize permanent magnets rather than electricity to generate the magnetic field. Most permanent magnetic units utilize standard two-pole magnets, but one manufacturer utilizes a unique multiple, reversing pole magnet (Fig. 2) (1). The magnetic field exerts a force on ions as they pass through the field, which changes the crystallization behavior of the ions and promotes bulk solution precipitation rather than the formation of an adherent scale. Unwanted particulates can be removed by filtration, water/solids separation, blowdown, bleed-off, or draining.

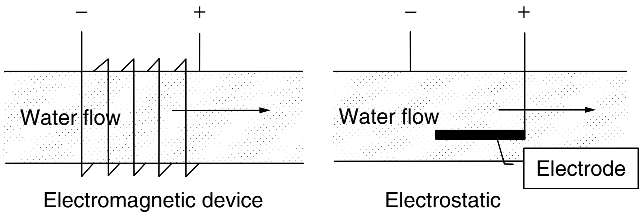

Figure 1. Diagram of classes of nonpermanent magnetic devices. (From Reference 1.)

Permanent magnetic units and electromagnetic units can be located so they are invasive (the magnet is located in line with the water flow) or noninvasive (the magnet is located so it is external to the water flow) as shown in Fig. 3. In-line systems are shielded magnets that are installed inside a section of pipe (see also Fig. 2). External units clamp onto the pipe through which the water flows.

THE PROBLEM OF HARD WATER AND SCALE

Hardness in water is due primarily to calcium and magnesium carbonates and bicarbonates (carbonate hardness that can be temporarily removed by heating) and calcium sulfate, calcium chloride, magnesium sulfate, and magnesium chloride (noncarbonated or permanent hardness that cannot be removed by heating). The sum of carbonate and noncarbonated hardness is total hardness, expressed as calcium carbonate. The World Health Organization (3) classifies hardness (in mg/L) as $CaCO_3$ as: 0–60, soft; 60–120, moderately hard; 121–180, hard; more than 180, very hard. Hard water, depending on the alkalinity, pH, temperature, and other factors, is responsible for the buildup of scale. Excessive hardness has a number of adverse effects in home, commercial, and industrial applications.

Hard water poses a significant problem in industrial boilers, cooling towers, and other heat transfer equipment. When hard water is heated, bicarbonates precipitate as carbonates and adhere to the pipe or vessel. In boiler and hot water tanks, the scale resulting from hardness reduces the thermal efficiency of heat transfer devices and eventually causes a restriction of the flow of water in piping systems. As a consequence, there is an increase in the system pressure that is required to move the water through a scale-restricted piping system. Both of these

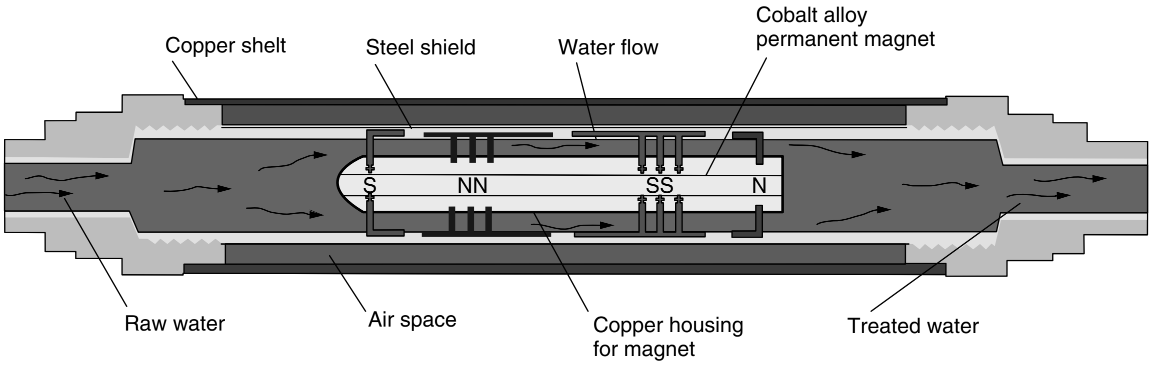

Figure 2. Diagram of a multipole permanent magnetic device. (From Reference 2. Available at: http://www.superiorwatercond.com/Products/our_superior_technology.html. Used with permission.)

problems increase the energy costs and maintenance costs of using and maintaining affected equipment. Table 1 provides example increases in energy consumption as a function of scale thickness.

The total cost of scaling in heat exchanger applications is estimated to be over $32 billion for the United States, Japan, German, the United Kingdom, Australia, and New Zealand combined, and over $14 billion in the United States alone (4).

In addition to increasing energy costs, hard water impairs the performance of detergents, which leads to dingy clothing and deterioration of fabrics and unsatisfactory cleaning of dishes and utensils in home, commercial, and industrial applications. Hard water results in spotting in car washes. Coffee makers, steamers, dishwashers, ice-makers, and other similar restaurant equipment are easily clogged by hard water and scale reduces the energy efficiency of these devices. In agricultural applications, hardness can reduce the efficiency of misting nozzles and irrigation systems.

APPLICATIONS OF PERMANENT MAGNETIC WATER CONDITIONING UNITS

According to the U.S. Department of Energy Technology Alert on nonchemical technologies for scale and hardness control, magnetic water conditioning "can be used as a replacement for most water-softening equipment," including lime or lime-soda softeners, ion exchange, and reverse osmosis (1). Magnetic water conditioning technology can also be used as a preconditioner to allow conventional devices to work more efficiently and last longer. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) identifies magnetic technology as a nonchemical treatment method that "has been used for scale control in boiler water, cooling water, and other process applications" (5).

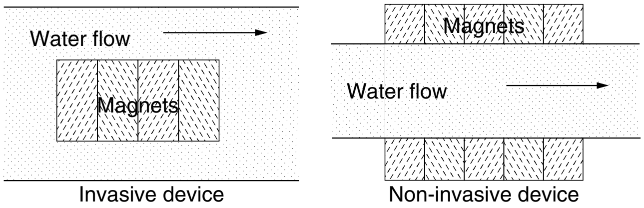

Figure 3. Diagram of invasive and noninvasive magnetic devices. (From Reference 1.)

Table 1. Example Increases in Energy Consumption as a Function of Scale Thickness

Scale Thickness, in.	Increased Energy Consumption, %
$\frac{1}{32}$	8.5
$\frac{1}{16}$	12.4
$\frac{1}{8}$	25.0
$\frac{1}{4}$	40.0

Source: Reference 1.

There are many benefits of this "green" technology over traditional technologies. The elimination or reduction of chemicals translates into dollar savings (which can reach thousands of dollars each year in some applications) when the costs of chemicals, labor, and equipment needed for chemical scale control are considered. Potential adverse health and environmental effects from the use of these chemicals are also eliminated or significantly reduced. Another advantage over chemical softening and ion exchange is that permanent magnetic water conditioning does not increase sodium concentrations in water and, thus, is a better option in those instances where sodium ions pose a health or other concern.

Periodic descaling of heat exchange equipment can be nearly eliminated, which, in turn, translates into savings because there is less downtime (as a consequence of scale formation), and the chemicals and labor needed for descaling are eliminated or significantly reduced. A related benefit is that heat exchanger tubes and related equipment failures caused by scale buildup are reduced, thus extending equipment life. In each of the applications in the section above on the problem of hard water and scale, permanent magnetic water conditioners can prevent the formation of scale and reduce existing scale. Because the technology keeps solids in solution, solids separation is needed in those applications where the process cannot tolerate particulate matter.

Even though applications are worldwide, magnetic water conditioning can be considered to be an emerging technology, whose future applications are likely to have significant impacts in colloidal chemistry and other fields. Any environmental, health, or industrial problem that is caused by hardness deposits could, in theory, be aided by magnetic treatment. A few examples to illustrate the diverse applications follow.

- In a dental study, patients who irrigated their teeth with an irrigator fitted with a magnetic device had 44% greater reduction ($p < 0.0005$) in calculus volume and a 42% greater reduction in calculus area ($p < 0.0001$) when compared to a control group that irrigated with conventional irrigation (without a magnetic device) (6).
- The Indianapolis 500 Brickyard Crossing Golf Course has realized a 71% reduction in the use of wetting agents and fertilizers and a related cost savings of 62% after the installation of the magnetic unit. The payback time for the magnetic unit at this facility, which does not pay for its water, is about 4.5 years based only on the wetting agent and fertilizer usage. The facility reports other benefits, including improved distribution and penetration of water, which substantially eliminates both wet and dry areas (7).
- In a case study, the DOE compared the costs and benefits of traditional lime softening and alternative permanent magnetic treatment for a recirculating boiler water system with a flow of 1000 gal/min at a hypothetical facility using extremely hard water (350 mg/L as CaCO3) (1). The magnetic technology had a simple payback of less than one year and

> produced an annual cost savings of over $200,000 per year over traditional lime softening. The DOE estimated a life-cycle savings of $2.77 million for the magnetic technology. Benefits assigned to the magnetic technology included energy savings and pollution reduction.

Permanent magnetic water conditioners are available in many sizes, ranging from small residential units (1 gal/min) to very large commercial and industrial units. The cost of magnetic water conditioning varies, depending on the amount of water to be treated. The costs are lower or in the same range as conventional water treatment systems; however, since the process is a physical rather than chemical process, there are no chemicals to buy and no on-going maintenance costs, which produces energy, labor, equipment, and chemical cost savings.

Magnetic technology, like other technologies, must be installed and used correctly. It is not appropriate in all applications. Additional guidelines developed by various manufacturers (1) include:

- *Installation*. Magnetic technology must be sized and installed correctly.
- *Water Quality*. Magnetic technology is not appropriate for soft water and some manufacturers report upper limits for hardness. Iron, which can cause fouling of the magnet, and silica, which can form scale with or without calcium, must be within specified limits.
- *Applications in Boilers and Heat Exchange Equipment*. Additional precautions must be taken with respect to alkalinity (to prevent corrosion), hydrogen sulfide (to prevent corrosion), and cycles of concentration.
- *Electrical Interference*. Magnetic units must be installed at an appropriate distance (at least 48 in.) from three-phase systems to avoid electrical interference, which causes magnetic lines of force to stray.

SCIENTIFIC SUPPORT FOR THE TECHNOLOGY

Historically, references to magnetic water conditioning date to the late 1800s, when lodestones (a naturally occurring permanent magnet) and naturally occurring magnetic mineral formations were used to decrease the formation of scale in cooking and laundry applications. From this modest beginning, magnetic water conditioning technologies have been and are being used throughout the world in a variety of applications to control scale. The acceptance of magnetic water conditioning, however, has not been universal, and there has been resistance to the technology in the United States, particularly by the water softening industry. Historically, the scientific literature has produced studies both positive and negative to magnetic water conditioning, and skeptics have centered their arguments against the technology largely on the lack of a consensus regarding the mechanism of action and lack of reproducibility in scientific studies. However, the more recent literature is increasingly supportive of the technology. Troup and Richardson (8) summarize earlier studies (pre-1978) for preventing scale formation and Baker and Judd (9) provide an informative review up to the mid-1990s. A few additional studies are noteworthy.

Barrett and Parsons (10) replicated the work of Higashitani and co-workers and found that magnetic treatment affects calcium carbonate formation under quiescent conditions, and the effect is reproducible. Both authors also determined that magnetic treatment produces a memory effect when the water is stored. Barrett and Parsons hypothesize that the formation of calcium carbonate is affected by the suppression of nucleation and acceleration in crystal growth.

Bogatin and others (11) propose that magnetic treatment of irrigation water increases the number of crystallization centers and the change of the free gas content, and that irrigation with magnetically treated water is the most effective for soils with high soda content. Other important parameters for effective treatment include flow rate through the apparatus, hardness, and pH.

Cho and co-workers (4) provide definitive evidence that physical water treatment (using a permanent magnet, solenoid coil, and high voltage electrode devices) is effective for the mitigation of fouling in cooling tower applications. (Fouling is contamination of a surface on which a liquid is boiling, that is, scale formation.) In this pivotal study, the authors demonstrated that multipole permanent magnets (with alternating fields) produced a significant reduction of 84% in fouling resistance compared to no treatment, and that a permanent magnet without alternating fields was not effective in reducing fouling. The authors also determined that previous studies showing no effect may have been limited because the treatment devices were not configured in an optimum way, giving support to manufacturers' instructions to install and operate the devices according to directions. The study proposed bulk precipitation as the mechanism of action. The magnetic field (or electric field, depending on the device) precipitates mineral ions in the water solution and forms clusters (i.e., colloidal particles of submicron size) in solution. As the temperature of the solution inside the heat transfer equipment increases, the solubility of the mineral ions decreases and the clusters grow in size and produce soft sludge coatings on the heat transfer surface rather than hard scale.

CONCLUSION

Permanent magnetic water conditioning technology is a physical process for reducing scale formation. It is a "green" technology that does not use chemicals or electricity to produce its effect. Because the magnetic unit does not have moving parts, it lasts for many years with very little, if any, maintenance.

These advantages enable permanent magnetic water conditioning to save energy, reduce the use of chemicals that treat and soften water, reduce the disposal of wastes from water treatment units such as water softeners, and conserve water. All of these benefits improve the environment and the health of our communities and reduce the costs of preventing and removing scale.

BIBLIOGRAPHY

1. U.S. Department of Energy. (1998). *Federal Technology Alert. Non-Chemical Technologies for Scale and Hardness Control*, DOE/EE-0162. U.S. Department of Energy, Pacific Northwest National Laboratory, Richland, WA.
2. Superior Manufacturing Division of Magnatech Corporation, Ft. Wayne, Indiana produces these units. The magnetic core is a single bar, multifield, multipole cobalt alloy permanent magnet.
3. *Guidelines for Drinking-Water Quality*. Vol. 2, p. 264. As cited in Salvato, J.A. (1992). *Environmental Engineering and Sanitation*, 4th Edn. Chap. 3, Water Supply. Wiley, Hoboken, NJ, p. 270.
4. Cho, Y.I., Lee, S., and Kim, W. (2003). Physical water treatment for the mitigation of mineral fouling in cooling-tower water applications, CH-03-3-3 (RP-1155). *ASHRAE Trans.* **109**: Pt. 1.
5. ASHRAE, Inc. (1999). Water Treatment, Chap. 47. In: *1999 ASHRAE Applications Handbook/SI Edition. HVAC Applications*, p. 47.5.
6. Watt, D.C., Rosenfelder, C.J., and Sutton, C.D. (1993). The effect of oral irrigation with a magnetic water treatment device on plaque and calculus. *J. Clin. Periodontal.* **20**: 314–317.
7. Ritchie, I.M. and Lehnen, R.G. (2001). Magnetic conditioning of fluids: an emerging green technology. In: *5th Annual Green Chemistry and Engineering Conference*, June 26–28. National Academy of Sciences, Washington, DC.
8. Troup, D.A. and Richardson, J.A. (1978). Scale nucleation on a heat transfer surface and its prevention. *Chem. Eng. Commun.* **2**: 167–180.
9. Baker, J.S. and Judd, S.J. (1996). Review paper, magnetic amelioration of scale formation. *Water Res.* **30**(2): 247–260.
10. Barrett, R.A. and Parsons, S.A. (1998). The influence of magnetic fields on calcium carbonate precipitation. *Water Res.* **32**(3): 609–612.
11. Bogatin, J. et al. (1999). Magnetic treatment of irrigation water: experimental results and application conditions. *Environ. Sci. Technol.* **33**: 1280–1285.

WATER IMPACTS FROM CONSTRUCTION SITES

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Surface water and, to a lesser degree, groundwater are impacted by runoff from construction sites, parking lots, roadways, and other nonpoint sources. Soil particles and dissolved constituents in runoff reduce the beneficial uses of water and have become a major regulatory challenge. Erosion rates at construction sites may be 10 to 20 times greater than for undisturbed lands (1). Construction sites, including environmental remediation activities and redevelopment, might contain a variety of natural and manmade contaminants that might exceed regulatory levels. Sediment runoff from nonpoint sources is primarily the result of wind and water erosion. Construction sites are locations where special erosion control measures may be needed to prevent storm water runoff and sediment buildup in nearby waterways and groundwater recharge areas (1,2).

To put this challenge into perspective, approximately 1.7 to 1.9 billion m^3 (1.4 to 1.5 million acre-feet) of the storage areas of reservoirs and lakes are permanently filled each year with sediment. The U.S. government annually spends over $500 million each year to remove the sediment from harbors, rivers, and other waterways, primarily through the oversight of the U.S. Army Corps of Engineers. It has been estimated that erosion-related pollutants cost the United States about $3.2 billion to $13 billion each year (3). Since 1990 when the report was written, the challenge from nonpoint source pollution is better understood and studied. Over the years, the methods have been designed for effective sediment and erosion control to significantly reduce pollution and sediment volume from construction sites and other nonpoint sources. A good summary of the erosion control at construction sites and various engineered solutions are found in Fifield (1,2).

The objective of sediment and erosion control is to reduce the water-quality impacts from nonpoint sources, and many of the regulations and statutory requirements that attempt to ensure that construction projects are performed in a way that minimizes potential impact to the environment. The U.S. Congress has passed several laws to protect the environment from nonpoint sources, including construction sites. These laws include the National Environmental Policy Act, the Clean Water Act, the Coastal Zone Management Act, the Safe Drinking Water Act, the National Wild and Scenic Rivers Act, the Endangered Species Act, the Resource Conservation and Recovery Act, and the Federal Insecticide, Fungicide and Rodenticide Act. In addition to these federal acts, various state and local laws or guidelines have also been enacted.

Erosion occurs when raindrops, moving water, or wind transports soil particles. Both wind and water are transport agents for soil particles. Wind erosion is normally a problem in semiarid and arid regions where ground vegetation may be limited. Controlling wind erosion at construction sites is common and is frequently managed by spraying water to keep the dust and soil particles from becoming airborne. Silt fences consist of vertical plastic sheeting or other materials that catch and retain soil particles from leaving construction sites.

Water erosion at construction sites is common in humid regions where rainfall events are frequent. According to Fifield (2), six types of water erosion exist: Splash erosion is the dislodging of soil particles by raindrop impacts; sheet-flow erosion is the uniform removal of the saturated soil particles conveyed in storm runoff; rill erosion is a long, narrow depression or soil incision caused by increased topographic relief and higher runoff velocities; gully erosion is the deep and wide depression or incision caused by concentrated storm runoff flows; stream bank erosion is the removal of soil by a natural drainage pattern such as toe cutting and bank sloughing; and shoreline erosion is the removal of soil by high-energy wave action, which results in sloughing and mass wasting of shoreline cliff faces. Water-related erosion on construction sites is usually the result of raindrop impacts and sheet flows, although specific conditions at construction sites can contribute to water erosion near rivers or beaches.

One way to minimize water impacts at construction sites is to use sediment containment systems. Sediment containment systems create conditions for deposition of soil particles that are in suspension. Two types of sediment containment units exist: retention and detention systems. Retention systems tend to be large and, for individual construction sites, may be difficult for lack of space. Properly designed sediment retention systems provide the necessary volume for containment of all the incoming storm water runoff, including both the water and sediment portions. Within the sediment storage area, a properly designed retention system will have the capacity to allow for the sedimentation of the suspended soil particles. Finally, the sediment retention system will be designed to discharge the storm water at a controlled rate. Evaporation and seepage must be calculated to allow for the retention system to drain before the next incoming storm water surge. Retaining all storm waters from a construction site is generally not feasible because of space and time constraints.

Instead of trying to retain all storm water, a well-designed sediment detention system captures only a specific size of particles while being able to drain the large volume of storm water passing through. To be effective at reducing the suspended soil particles, detention containment systems must hold the storm water only long enough for the deposition of the suspended soil particles to occur (2).

Surface water runoff from construction sites, parking lots, roadways, and other nonpoint sources can enter groundwater through recharge areas. Turbidity, naturally occurring heavy metals as well as pesticides, hydrocarbons, and other organic contaminants, can be major sources of nonpoint pollution into surface waters during construction, which entails disturbing existing ground cover, trees, rocks, and soil. The total suspended solids (TSS) are the total amount of sediment in the water. The dissolved portion of solids in water is called total dissolved solids (TDS). In addition to high TSS and TDS, a large volume of sediments in surface water includes changes in water chemistry, such as too much salt, iron, lead, copper, and zinc or other metals. Along with the sediment, an influx of chemicals poisonous to fish and other aquatic life can occur. Other effects include the destruction of fish breeding grounds, the flattening of streambed channels, and the increased potential of surface flooding as river and lake storage capacity is reduced because of sediment buildup. Other wastes from construction include wash water from concrete mixers, paints and wash water from painting equipment, and wastes from cleaning of vehicles and equipment.

The solution to erosion and sediment control issues is site-specific erosion plans and sediment and waste containment systems. Site-specific sediment control systems in the past have used commonly available materials (plantings, rocks, sand bags, and straw-bales). More recently, engineered systems with synthetic materials have been tested and proven in the field. Surface and groundwater impacts from nonpoint source pollution, especially at construction sites, can be minimized and managed effectively.

BIBLIOGRAPHY

1. Fifield, J.S. (2004). *Designing for Effective Sediment and Erosion Control on Construction Sites*. Forester Communications Inc., Santa Barbara, CA. Available: www.foresterpress.com.
2. Fifield, J.S. (2004). *Field Manual on Sediment and Erosion Control Best Management Practices for Contractors and Inspectors*. Forester Communications Inc., Santa Barbara, CA. Available: www.foresterpress.com.
3. Forest, C. (1990). *Erosion Control in the United States Today: An Overview*. *Proceedings of Conference XXI of the International Erosion Control Association*, February 14–17.

INDUSTRIAL COOLING WATER—BIOFOULING

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The accumulation of living matter in cooling water systems may be the result of the activity of microorganisms such as bacteria, algae, and fungi, or the growth of macroorganisms that include mussels, barnacles, hydroids, and serpulid worms and plant material such as water weeds. The extent of the deposition of both micro- and macroorganisms, depends very much on the origin of the water employed in the cooling water circuit. In general, the water is taken from a natural source, which contains the organisms and nutrients to sustain life and growth. Some sources, such as borehole water, are relatively free of organic material, but in "open" cooling water circuits, it rapidly becomes contaminated from contact with the atmosphere. Water from other sources, including freshwater rivers, canals or lakes, estuarine or seawater, is already heavily contaminated before it is taken into an industrial system.

The presence of living matter on surfaces, particularly heat transfer surfaces, may promote fouling by mechanisms, including particle deposition, scale formation, and corrosion. In general, this is due to the metabolic activity of the living matter that creates localized changes in the properties of the water, particularly pH.

To maintain efficient operation of a cooling water system, it is necessary to combat the detrimental effects of the accumulation of unwanted deposits. It is particularly important with respect to heat transfer surfaces because the deposit represents a resistance to heat flow across the surface, thereby seriously reducing the capability of the system to operate according to the design requirements. Generally, the principal difficulties in cooling water circuits arise from the presence of microorganisms, because it is possible to reduce the gross effects of macroorganisms generally, by filtration at the cooling water intake.

SURFACES AND BIOLOGICAL FOULING

For both micro- and macroorganisms, although there are some exceptions, settlement on a surface is an essential element in biological activity. The advantages of residing on a surface include a continuous supply of nutrients, removal of waste products by the movement of the water, and some measure of protection from predators. Furthermore, it has been suggested (1) that for bacteria, the surface provides an enhanced protection from changes in the surrounding environment, compared to those microorganisms that are "free swimming" (planktonic) in the water. The changes that organisms might experience include variations in water pH, changes in nutrient concentration, and in some systems, the inorganic salt concentration. Changes in water velocity, in turn, affect the shear forces acting on the biofilm and hence the tendency for removal. It has been suggested that the colonization of a surface by bacteria depends on an adsorbed conditioning layer made up of macromolecules that are in plentiful supply in water from natural sources due to the breakdown of living matter. It is considered that the bacteria form a chemical bond with this layer of macromolecules. The movement of water in relation to the atmosphere in cooling towers and spray ponds usually means that the water becomes saturated with oxygen, conducive to the growth of organisms that depend on oxygen for survival, for example, aerobic bacteria.

Bacteria

Mozes and Rouchet (2) suggested that three zones are present in a biofilm consisting of bacteria:

1. the layer of cells in direct contact with the surface
2. the bulk biofilm
3. the layer of cells residing at the interface between the bulk biofilm and the water phase

Conditions are likely to be different for each of these groups of cells. The activity of the microorganisms will vary, depending on the mass transfer of nutrients, including oxygen for aerobic species, to and through the biofilm, and similarly for the removal of waste products of metabolism. If the biofilm is relatively thick, it is more than likely that the nutrient concentration will become zero either at the solid surface or somewhere in the bulk biofilm. Under these conditions, it is possible for the cells to die with potential consequences for the integrity of the biofilm.

Mass transfer depends on a concentration driving force, the extent of the turbulence at the water/biofilm interface, and the openness of the biofilm structure that either restricts or facilitates nutrient transport. The turbulence at the biofilm surface is very dependent on the water velocity across the surface.

Heat exchanger surfaces are particularly suitable for bacterial growth, because of these desirable benefits and also because the surface temperature is usually conducive to growth. In natural conditions, bacteria colonize stones and rocks, but in cooling water circuits, they use the metal surfaces in contact with water. Metal surfaces give rise to metal ions that could interfere with adhesion of the biofilm to the surface (3). Some metallic ions, for example, copper ions, may act as a biocide. As the colonies of bacteria grow on a surface, extracellular products (usually polysaccharides) are formed and accumulate around the clusters of cells to give a complex matrix of cells and these extracellular polymers. Apart from keeping the structure together, it is understood that the function of extracellular material is first and foremost to protect the cells. Protection may be afforded against predators or noxious substances in the water that might adversely affect the cells or kill them. It is also believed that the extensive growth of polysaccharides, when nutrients are in ample supply, is a method of storing nutrient material against a time when the supply is reduced or eliminated, so that survival is ensured. The spaces within the matrix are filled with water that represents 90–95% of the mass of the biofilm. Work by Stoodley et al. (4) demonstrated that water flows in the duct-like voids in a biofilm and facilitates the availability of nutrients for the cells in the matrix and the removal of waste products. The structure of the biofilm, therefore, has implications for the mass transfer of nutrients from the bulk water to the individual organisms in the biofilm, particularly those remote from the bulk water flow. The structure of the biofilm is very much a function of the conditions under which it was formed, particularly the magnitude of the water velocity across the cells that colonized the surface. Higher velocities tend to produce more compact structures. The use of nutrients by the cells reduces the local nutrient concentration in the vicinity of the biofilm, thereby enhancing the concentration driving force for mass transfer between the bulk water and the biofilm. It is possible that the cells close to the solid surface may be starved of nutrients that may cause changes in metabolism or even cell death.

OPERATING CONDITIONS AND BACTERIAL BIOFILM FORMATION

Because of the versatility of bacteria and the favorable conditions for growth in heat exchangers, bacterial biofilms on heat transfer surfaces represent a serious problem in cooling water circuits. The principal difficulties are the reduction of heat transfer efficiency and the increased energy required to pump the water through the system for a given bulk water flow rate necessary to achieve the desired heat removal. Substantial increases in operating costs may be the result.

The development of a biofilm generally follows the accepted pattern for most fouling phenonema, as shown by the idealized curve in Fig. 1. For a short interval of the order of a few days, there is little evidence of any biofilm accumulation. This is when the adsorption of macro organic molecules takes place and the surface becomes "conditioned," allowing microorganisms to colonize the surface. Once the surface has been colonized and providing sufficient nutrients are available, there is relatively rapid growth of the biofilm. After a period of accelerated growth, the rate of growth reduces to a point where the biofilm thickness remains reasonably constant, although variations in thickness about a mean are likely due to sloughing of lumps of the biofilm from the surface. It is generally understood that sloughing is due to the effects of the shear forces at the water/biofilm interface induced by the water velocity. As the biofilm develops and becomes thicker, its structure becomes less robust and more susceptible to the effect of fluid shear. As a result, there is a balance between growth and removal of the biofilm.

Figure 1 provides an indication of the general shape of the biofilm growth curve, but the shape of individual curves varies depending on the prevailing conditions. For instance, higher velocities are likely to produce thinner but robust biofilms, compared with biofilms formed under low velocities that have a more open structure. Biofilms formed at a temperature near the optimum for maximum growth for the prevailing species are thicker than those formed at a lower or higher temperature. Higher availability of nutrients encourages growth. As for all living material, the presence of trace elements is vital for healthy growth. All these influences change with the seasons, including the cooling water velocity which is likely to be lower in the winter months when the lower temperature of the water reduces the demand for cooling water for a given cooling requirement.

The topography of the surface on which the biofilm develops is also a factor. In general terms, rough surfaces favor biofilm accumulation, whereas smooth surfaces are less hospitable to biofilm growth. Bacteria carry a surface charge, so that its value in relation to the electric charge on the surface also influences the rate of colonization.

Suspended particulate solids in the water flow can also affect the development of biofilms. Reduced biofilm accumulation can be anticipated due to the scouring action of particles, although the nature and size of the particles themselves also exert an influence. Sand particles can remove biofilms very effectively, but at the same time, erosion of the metal surface could become a serious problem. On the other hand, softer clay particles may become part of the deposit structure and, under those circumstances, may reduce the robustness of the biofilm matrix.

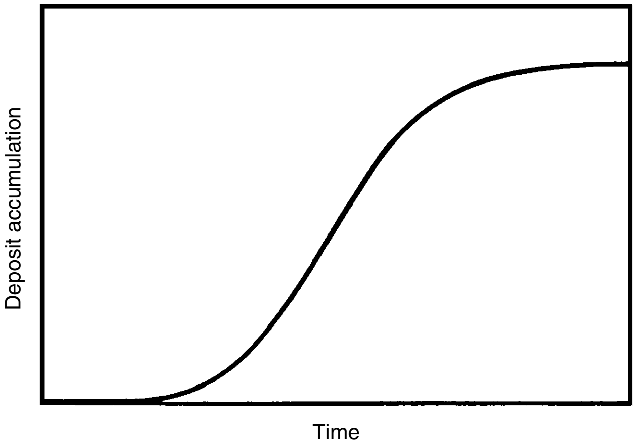

Figure 1. Idealized fouling curve.

Most bacteria flourish in an environment where the water pH is near 7. Variations affect the growth of biofilms, although most microorganisms can tolerate small changes in pH.

Algae

Algae require sunlight, carbon dioxide, and inorganic chemicals as their primary source of nutrients and energy for metabolism. Their natural habitat is attachment to rocks and stones in aqueous environments, or they may be "free floating" in lakes or reservoirs. Algae are larger than bacteria and exist as single entities or as filamentous colonies in an aqueous environment or attached to solid surfaces. In cooling water systems, they may be found where areas resemble those in nature that have access to sunlight, such as cooling tower basins, spray ponds, and serpentine coolers where the water, exposed to the atmosphere, flows over banks of horizontally mounted tubes. The formation of algal biofilms is initiated by the adsorption of water-soluble organic material, such as glycoproteins, and colonization by bacteria. Diatoms, unicells that have a symmetrical silica outer surface, are often early algal colonizers.

Algae themselves are not generally a problem in the enclosed parts of a cooling water circuit such as heat exchangers and pipelines, because of the lack of sunlight. The problem of algae growth in other parts of the system, however, is the production of organic debris that may give rise to blockage or be a source of nutrients for other microorganisms, such as bacteria that accumulate on heat transfer surfaces and in piping.

Fungi

Fungi require a fixed organic source of carbon. Their rigid cell wall limits them to being saprophytic on organic substrates or parasites living on higher forms of life, for example, so-called "athletes' foot" in humans. They lack chlorophyll, so that they cannot use photosynthesis in their metabolism.

In relation to cooling water systems, the nuisance value of fungi is not unlike that of algae. In sofar as they require a consumable substrate, they are to be found, for instance, on the wooden structures of older cooling towers. The attack of fungi on wooden structures involves enzymes (produced by the fungi cells) that open up the cellulose structure and make the structure liable to attack by other forms of microbial life. The presence of large quantities of living and dead material on the weakened wooden structure is likely to make it collapse. Modern cooling towers generally contain polymer packing that is resistant to fungal attack. The principal problem that fungi pose in cooling water circuits is the breakdown products and debris that arise from fungal growth. Operating problems may develop due to deposition on heat transfer surfaces and in pipelines, and by providing nutrients for microbial activity, particularly bacteria, as discussed earlier.

MACROFOULING OF SURFACES

Macrofouling is largely associated with sea or estuarine water involving the growth of macroinvertebrates. The fouling is usually confined to water intakes and culverts. Whitehouse et al. (5) summarized the conditions that support macrofouling of surfaces, including the continuous flow of seawater to provide oxygen and nutrients and reduced competition from algae and predators. Colonization of surfaces may be facilitated by bacterial biofilms (slime layers) already on the surface. The spectrum of species in the water varies with location and season.

Mussels

The growth of mussels is very much dependent on the season. Higher temperatures of summer facilitate growth, but at the lower winter temperatures, growth is restricted. Rapid growth, however, can occur at temperatures above about 10 °C. Following fertilization and a free swimming larval stage, metamorphosis occurs to produce a “spat.” Settlement onto a surface then occurs to provide a permanent adult site, where rapid growth can take place under suitable conditions. Settlement can be strongly affected by the water velocity across the surface; low velocities favor deposition and attachment. It is not practical to filter the water prior to the settlement process to remove the “spats,” because the small mesh size required would give rise to rapid “blinding” of the filter.

Barnacles

Barnacles are more of a problem in tropical regions than in more temperate zones. Planktonic larvae progress toward metamorphosis into small barnacles that can settle on surfaces under a higher water velocity than that for mussels. Blockage of filter screens is a common problem. Larvae can be carried forward into heat exchangers, where, if the velocity is relatively low, they may settle and develop to cause problems of blockage, pressure loss, and reduced heat transfer efficiency.

Hydroids

Hydroids are surface colonizers that facilitate the attachment of mussels. They are primitive creatures living in colonies of numerous microscopic units. There is a free swimming stage in development. The outer walls of hydroids are not calcified like barnacles and mussels, so their fouling potential is not great. Large accumulations, however, can severely restrict water flow.

Serpulid Worms

Calcareous tubes built by serpulid worms can cause fouling problems. Encrustations in pumps and valves can cause malfunction.

Other Organisms

There are many living organisms contained in estuarine and seawater that have not been listed but can cause severe operating problems in cooling water systems. The examples cited illustrate the general problems of macrobiofouling.

CONTROL OF BIOFILMS

It is essential to control biofilm growth in cooling water circuits particularly in heat exchangers, to maintain cooling efficiency and thus optimize costs. The two basic methods are chemical and physical.

Chemical Control

Chemicals, particularly chemical biocides that kill bacteria, have been used for many years. The action of the additive has essentially three phases:

1. adsorption onto the cell wall
2. penetration into the cell wall
3. chemical combination of the biocidal chemical and essential cell structures or components that directly affects cell metabolism or the integrity of the cell structure itself.

Chlorine has been the preferred biocide for many years on account of its availability and relatively low cost. Free chlorine reacts with water in the following way:

$$\mathrm{Cl_2 + H_2O \longrightarrow HOCl + HCl}$$

and

$$\mathrm{HOCl \longrightarrow H^+ + OCl^-}$$

Because it is a strong oxidizer, chlorine reacts with organic material in water. Many of these compounds are cancer forming, and chlorine can enter the food chain. It has, therefore an environmental risk, so its use is declining and in some places, it is not possible to discharge water that contains chlorine or its derivatives back into the environment from which it came without treatment. Other oxidizing biocides include hydrogen peroxide, ozone, and chlorine dioxide. The advantage of hydrogen peroxide and ozone is that they break down to water and oxygen.

There are many other chemical biocides available for the control of biofilm formation. In recent years, so-called “environmentally friendly” biocides have been developed that have a short life in aqueous solution and break down to innocuous by-products or nutrients for microorganisms that effectively disposes of these additives. Other chemicals that are used to control biofilm growth are biostats. These compounds reduce the activity of microorganisms, so that their influence is limited. Biostats may be included with appropriate biocides in proprietary mixtures for microbial control.

Physical Control

The use of physical techniques to control biofouling is not as widespread as the use of chemical additives. The principal reason for this is that chemicals are carried to all parts of the system, whereas this is not so for physical methods of control. Furthermore, the geometry of the cooling water system, particularly the heat exchangers, does not lend itself easily to the use of physical techniques.

One technique that has been successful in controlling biofouling in power station condensers is the so-called Tapproge system that involves circulating sponge rubber balls with the cooling water through the tubes of the condensers. The technology is suitable because the large number of tubes in a condenser are uniform in diameter. The balls are slightly larger in diameter than the internal diameter of the tubes, so that as the balls are forced through the tubes by the water flow, they are "squeezed" and wipe the inside surface of the tubes. The technique involves collecting balls, rejecting worn balls, and reinjecting acceptable balls. The effectiveness of the system depends on the availability of sufficient balls and the probability that balls pass through each tube reasonably frequently. Under ideal conditions, it has been estimated that each tube should receive 12 balls per hour (6). A potential drawback of the system is that balls may get stuck in the tubes or at a tube entrance on the tube plate, thereby causing a reduction in effective heat transfer area and an increase in pressure drop.

Potential future physical methods for biofouling control have recently been discussed (7). The use of ultrasound, the inclusion of wire-wound or spring-like inserts in tubes, and the circulation of robust polymer fibers are under development. The two former techniques depend, to some extent at least, on heat exchanger geometry and on increasing the removal forces acting on the biofilm generated by increased turbulence in the flowing water. The inclusion of polymer fibers in the flowing water, on the other hand, is more akin to the use of chemicals because the fibers are transported to all parts of the system by the water. The removal action is assumed to be from contact between the fibers and the deposit.

Ultraviolet light has been used to control biofilm growth, but the technique has severe drawbacks in cooling water systems. To be effective, the UV light source has to "see" the biofilm or the planktonic organisms in the circulating water. It is impossible, therefore, to control biofilm growth on heat transfer surfaces. It is possible, however, to pass the cooling water through a UV light unit that destroys organisms in the water. The problem that arises is that unless the kill is 100%, the remaining microorganisms can become colonizers of heat exchanger surfaces that are untouched and therefore are free to develop unwanted biofilms.

Treatment to modify the quality of surfaces likely to become fouled is a method of biofouling control. Electropolishing of stainless steel reduces fouling (8). The use of coatings to change the hydrophilicity of the surface has also been successfully used. Ion implantation has been effective in fouling control (9). The additional capital costs. imposed by these techniques and maintenance of the integrity of the treated surface are reasons why they are not used extensively in industry.

A more extensive discussion of cooling water and biofouling is to be found in (10).

BIBLIOGRAPHY

1. Fletcher, M. (1992). Bacterial metabolism in biofilms. In: *Biofilms—Science and Technology*. L.F. Melo, T.R. Bott, M. Fletcher, and B. Capdeville (Eds.). Kluwer Academic, Dordrecht, pp. 113–124.
2. Mozes, N. and Rouxhet, P.G. (1992). Influences of surfaces on microbial activity. In: *Biofilms-Science and Technology*. L.F. Melo, T.R. Bott, M. Fletcher, and B. Capdeville (Eds.). Kluwer Academic, Dordrecht, pp. 126–136.
3. Vieira, M.J., Oliveira, R., Melo, L.F., Pinheiro, M.M., and Martins, V. (1993). Effect of metallic ions on the adhesion of biofilms formed by *Pseudomonas fluorescens*. *Colloids Surf. B: Biointerfaces* **1**: 119–124.
4. Stoodley, P., de Beer, D., and Lewandowski, Z. (1994). Liquid flow in biofilms. *Appl. Environ. Microbiol.* **60**: 2711–2716.
5. Whitehouse, J.W., Khalanski, M., Saroglia, M.G., and Jenner, H.A. (1985). *The Control of Biofouling in Marine and Estuarine Power Stations*. CEGB Northern Region, UK.
6. Eimer, K. (1985). *Recommendations for the Optimum Cleaning Frequency of the Taprogge Tube Cleaning System*. Technical Report 85-26, Taprogge Gesellschaft mbH, Wetter.
7. Bott, T.R. (2001). Potential physical methods for the control of biofouling in water systems. *Chem. Eng. Res. Design* **79**: 484–490.
8. Mott, I.E.C. and Bott, T.R. (1991). The adhesion of biofilms to selected materials of construction for heat exchangers. *Proc. 9th Int. Heat Transfer Conf.* Jerusalem **5**: 21–26.
9. Zhao, Q. and Muller-Steinhagen, H. (1999). Influence of surface properties on heat exchanger fouling. In: *Proc. Int. Conf. Mitigation Heat Exchanger Fouling Its Econ. Environ. Implications*. T.R. Bott, A.P. Watkinson, and C.B. Panchal (Eds.). Banff, Canada, July 1999. UEF and Begell House, New York, pp. 217–228.
10. Bott, T.R. (1995). *Fouling of Heat Exchangers*. Elsevier Science, Amsterdam.

INDUSTRIAL COOLING WATER—CORROSION

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Corrosion is often a problem when metals are in contact with an aqueous environment. It may be defined as the deterioration and loss of metal due to some form of chemical attack. In general, it results from impurities in the water, which need only to be in trace quantities to initiate corrosion. Trace impurities can include gases dissolved from the atmosphere, particularly oxygen and carbon dioxide, that play important roles in the corrosion process. Small amounts of mineral salts in water can also become involved in corrosion reactions. Where the metal makes up an essential component of a structure, such as a bridge or equipment forming part of an industrial process, for example, a cooling water circuit, constant vigilance is required to maintain the integrity of the structure and the equipment involved. Corrosion is a complex phenomenon dependent on chemical and physical conditions within the particular system.

In general, corrosion is associated with iron and steel, although under certain circumstances, other metals and alloys may attacked. However, to illustrate the mechanisms of corrosion, reactions involving iron will be used.

The reddish-brown deposit that is generally evident when iron corrodes is the iron compound ferric hydroxide, usually mixed with ferrous oxide. It is produced by a sequence of electrochemical reactions in which a difference in electric potential develops between two different metals or between different areas on the same metal. The difference in potential enables electrons to flow from the positive to the negative regions which, is an electric current. Thus, there is a movement of electrons which affects the chemical nature of the surface, where they originate or the area to which the migrate, by localized electrochemical reactions. The mechanism is often referred to as "galvanic action." These centers of electrochemical activity, usually termed the "galvanic cell," have an anode and a cathode. Metal dissolution takes place at the anode. The overall corrosion process is facilitated by dissolved salts, usually inorganic, in the water, because they affect the electrical conductivity of the water. Water that has a high salt concentration is more conductive than water of a relatively low salt content. The basic migrations are shown in Fig. 1.

At the anode, electrons are released from the metal enabling it to dissolve in the water in ionic form.

$$\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2\mathrm{e} \quad (1)$$

where e represents an electron.

Electron flow through the metal constitutes an electric current. At the cathode, it is possible for electrons to take part in electrochemical reduction reactions.
Examples are

$$2\mathrm{H}^{+} + 2\mathrm{e} \longrightarrow \mathrm{H}_2 \uparrow \quad (2)$$

The H ion arises from the disassociation of water molecules which occurs to a small extent in water.

$$\mathrm{H_2O} \longrightarrow \mathrm{H}^{+} + \mathrm{OH}^{-} \quad (3)$$

$$2\mathrm{H_2O} + 2\mathrm{e} \longrightarrow \mathrm{H}_2 \uparrow + 2\mathrm{OH}^{-} \quad (4)$$

$$\mathrm{O}_2 + 2\mathrm{H_2O} + 4\mathrm{e} \longrightarrow 4\mathrm{OH}^{-} \quad (5)$$

As the combination of hydrogen ions takes place to form hydrogen gas, the depletion of hydrogen ions causes Equation 3 to move to the right, thereby releasing further OH$^-$ ions. The result is a significant increase in alkalinity, represented by the increased concentration of OH$^-$ ions. The presence of Fe and OH$^-$ ions can give rise to chemical reactions and hence relatively insoluble deposits such as ferrous hydroxide:

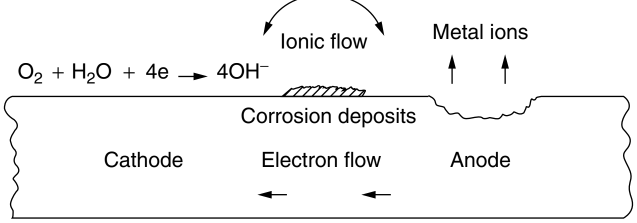

Figure 1. Electrochemical corrosion.

$$\mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} \longrightarrow \mathrm{Fe(OH)_2} \downarrow \quad (6)$$

Ferrous hydroxide itself can further react to give ferric hydroxide:

$$4\mathrm{Fe(OH)_2} + \mathrm{O_2} + 2\mathrm{H_2O} \longrightarrow 4\mathrm{Fe(OH)_3} \downarrow \quad (7)$$

Ferric hydroxide can react further:

$$2\mathrm{Fe(OH)_3} \longrightarrow \mathrm{Fe_2O_3} + \mathrm{H_2O} \quad (8)$$

Thus a mixture of corrosion products can be formed, and within the deposits, there may be inclusion of solids from the water, such as suspended particles comprised of clay, sand, and other mineral matter, along with microbial cells.

The character of the deposit can affect the continued rate of corrosion. For instance, if the deposit is porous, corrosion can continue. On the other hand, a dense impervious structure prevents ionic migration and thereby protects the underlying metal from further corrosion. The "oxide layer," as it is called, is often relied upon to provide protection and may be deliberately laid down for corrosion control.

Equations 2 to 5 demonstrate that hydrogen gas or hydroxyl ions are produced at the cathode, as a result of corrosion. If hydrogen and hydroxyl ions remain in the vicinity of the cathode, they represent a barrier that interferes with the diffusion of oxygen gas or hydrogen ions to the cathode that would enable further chemical reactions to take place. The barrier therefore acts as a natural corrosion inhibitor. The overall process is termed "polarization."

This barrier, however, cannot be relied on as an effective method of corrosion control because it is easily disturbed. In most situations, the water is flowing and the "flushing" that is created removes the hydroxyl ions and the hydrogen bubbles from the surface. Furthermore, because the water is likely to contain dissolved carbonates and carbon dioxide in ionic form that can produce hydrogen ions, the pH of the water is reduced. The chemical reactions involved are

$$\mathrm{H_2O} + \mathrm{CO_2} + \mathrm{CaCO_3} \longrightarrow \mathrm{Ca(HCO_3)_2} \quad (9)$$

$$\mathrm{Ca(HCO3)_2} \longrightarrow \mathrm{Ca}^{2+} + 2\mathrm{HCO}^{3-} \quad (10)$$

and

$$\mathrm{H_2O} + \mathrm{CO_2} \longrightarrow \mathrm{H_2CO_3} \quad (11)$$

$$\mathrm{H_2CO_3} \longrightarrow \mathrm{H}^{+} + \mathrm{HCO_3}^{-} \quad (12)$$

The increased concentration of H$^+$ ions allows reactions with the OH$^-$ in the barrier to form water, thereby in effect removing the barrier.

The discussion so far, has centered on the corrosion of iron, but other metals immersed in water can corrode and produce a measurable potential. The alkaline earth and alkali metals hold their outer shell of electrons rather loosely and have a greater potential difference than iron. On the other hand, so called “noble” metals such as gold produce very few electrons and therefore have relatively low potential. Those metals displaying lower potential, it could be assumed, corrode less extensively and less easily than those of higher potential.

The discussion has emphasized the importance of H^+ ions in the corrosion process. The pH of an aqueous solution is the negative $\log_{10}$ of the molar concentration of H^+ ions. The range of pH values is 0–14. Low pH (<7) signifies an “acidic” condition, whereas high pH (>7) represents alkaline conditions. The effect of pH on metals is dictated by the behavior of the metal oxide. If, for instance, a metal oxide is soluble under acidic conditions, the metal will exhibit a high corrosion rate under these conditions. Alternatively, if the metal oxide is soluble under alkaline conditions, $\text{pH} > 7$, the metal will corrode in contact with water. Some metals have oxides that are soluble in both acid and alkaline conditions. Zinc, tin, and aluminum fall into this group and are usually referred to as amphoteric metals. Metals that are insoluble at any pH are called “noble,” as already indicated.

Iron corrosion displays what might be considered inconsistent behavior. At low pH up to about 4, acidic conditions, the behavior is similar to that of an acid soluble metal. Between a pH of around 4 and up to about 11, the pH of the water has relatively little effect on the corrosion rate because oxygen depolarization is considered the principal influence on the corrosion process. Further increase in pH values reduces corrosion even further, the minimum is at a pH of around 12. At higher pH values, iron displays amphoteric behavior and corrosion again increases.

In industrial operations, notably cooling water applications, there are generally influences from the processing environment, in which the water is being used, for instance, the use of a biocide to control biofouling. Chlorine has been the preferred biocide to control microbial growth in cooling water systems for many years on account of its availability and effectiveness, but it can influence the corrosion of the cooling water system. Chlorine is soluble in water and reacts with it to give hypochlorous acid.

The chemical equation is

$$\mathrm{Cl_2 + H_2O \longrightarrow \underset{\text{Hypochlorous acid}}{HOCl} + \underset{\text{Hydrochloric acid}}{HCl}} \tag{13}$$

The acids ionize to give H^+ ions that reduce the pH and hence increase the potential for corrosion. The associated equations are

$$\mathrm{HOCl \longrightarrow H^+ + OCl^-} \tag{14}$$

and

$$\mathrm{HCl \longrightarrow H^+ + Cl^-} \tag{15}$$

Unwanted chemicals in the system may cause corrosion. For instance, ammonia may be introduced into cooling water from leaks of process fluids in the coolers of a chemical works. Ammonia can be highly corrosive to copper. The chemical reaction involved is

$$\mathrm{2Cu + 2H_2O + O_2 + 8NH_3 \longrightarrow 2Cu(NH_3)_4{}^{2+} + 4OH^-} \tag{16}$$

The cuprammonium ion $\mathrm{Cu(NH_3)_4{}^{2+}}$ is very soluble, and it can cause rapid deterioration of copper components in a system.

A common problem in cooling water systems is the accumulation of micro- and macroorganisms on surfaces, particularly on heat transfer surfaces. The metabolism of these organisms can give rise to modified local conditions that are often acidic, and thereby produce local corrosive conditions under the microbial deposit. If the attack on the metal is sustained, this can give rise to a corrosive condition known as “pitting.”

Some microbial growth can produce unique corrosion conditions. A microbial species known as *Desulfovibrio desulfuricans,* a sulfate reducing bacterium, gives rise to the production of hydrogen sulfide from the sulfates commonly found in water used for cooling purposes. Hydrogen sulfide dissolved in water lowers the pH and hence initiates corrosion. Hydrogen sulfide in solution in contact with iron or steel produces iron sulfide. The iron sulfide that is cathodic with respect to iron promotes galvanic corrosion.

Other Combinations of Conditions That Can Lead to Corrosion

When two dissimilar metals are in contact and are immersed in a salt solution, as described earlier, a potential difference can develop. This potential difference provides the opportunity for corrosion to occur, and this corrosion can be severe. The basic conditions for the interaction of two dissimilar metals are illustrated in Fig. 2.

Metal X has a lower electrode potential than metal Y. Ions migrate into the conducting water, and electrons flow across the junction of the two metals. Metal X is corroded at Z.

Immersion of the bimetallic couple in conducting water indicates only that corrosion is possible, but the rate of corrosion is governed by other external influences. The rate of corrosion, for instance, increases in proportion to the ratio of cathode to anode area. Generally, corrosion is also affected by other influences. Corrosion is the result of chemical reactions, so increased temperature accelerates corrosion. The velocity of the water across the corroding metal can exert an effect on the corrosion rate because it affects the resistance to the mass transfer of chemical components across the laminar sublayer.

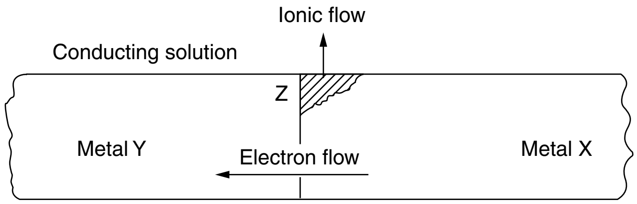

Figure 2. Corrosion at the junction of two dissimilar metals.

The metallurgy of the metal or alloy undergoing corrosion can also affect the extent of corrosion. Surface flaws such as scratches can become anodic to the rest of the metal. Anodic sites may also be established where there is stress within the metal at grain boundaries. Such a condition is often referred to as "stress cracking." So-called "caustic embrittlement" is considered a version of "stress cracking," and may result from the production of high concentrations of sodium hydroxide in the water in contact with the metal. Inclusion of metal particles that are not homogeneous with the principal metal in the system can also create a corrosion cell. For instance, brass is prone to this form of corrosion. Brass is an alloy of zinc and copper, if the zinc is removed from the surface of the metal, a porous copper layer remains that can establish corrosion cells. The process is usually referred to "dezincification." A combination of a corrosive environment and repeated working may result in early failure called "corrosion fatigue cracking." The fatigue is brought about by the repeated application of stress, such as in the tubes of a shell and tube heat exchanger that vibrate in response to operating conditions. If the protective oxide layer on the surface of the metal, discussed earlier, is subject to impingement of solid particles, or even bubbles traveling at high velocity in the water flow, the protective layer may be removed or not even formed, thereby allowing corrosion to occur.

CORROSION CONTROL

There are two principal ways in which corrosion of metal components can be eliminated or, at least, reduced by additives in circulating water. They include corrosion inhibitors and "controlled scaling." In general terms, the protection is achieved by positioning an electrical barrier on the metal that is under threat of corrosion, so that the electrical circuit is broken and the electron flow restricted. As indicated earlier, some systems have "natural" resistance to corrosion through the development of an impervious oxide layer on the metal surface that acts as an effective electrical barrier.

Corrosion, as described earlier, involves anodic and cathodic reactions. Chemicals that arrest or restrict these reactions halt or reduce corrosion. The terms anodic and cathodic inhibitors are used to classify the chemicals that are used for this purpose. Anodic inhibitors prevent or restrict electron flow (see Fig. 1), whereas cathodic inhibitors form a barrier at the cathode, restricting hydrogen and oxygen transport to the cathode surface. These are some chemical additives and their disadvantages:

Anodic Inhibitors	
Chromates	Generally not used now due to their toxicity
Nitrites	Nutrient for aquatic plant life
Silicates	Slow acting
Tannins	Nutrient for biological activity
Benzoates	Unreliable except perhaps for aluminum
Orthophosphates	Nutrient for aquatic plant life

Cathodic Inhibitors	
Zinc salts	Unlikely to be environmentally acceptable
Polyphosphates	Sludge forming and nutrient for aquatic plant life
Polyphosphonates/ molybdates	Require O_2 for effective protection; expensive.

So called "filming amines" that cover the entire surface of a metal liable to corrosion are used, particularly in the presence of steam condensate. An alternative is to apply an electrical current to the metal that is susceptible to corrosion to reverse the reactions described by Equations 2, 4, and 5, applying Le Chatelier's principle.

A more comprehensive discussion of corrosion in industrial cooling water can be found in Bott (1).

BIBLIOGRAPHY

1. Bott, T.R. (1995). *Fouling of Heat Exchangers*. Elsevier Science, Amsterdam.

INDUSTRIAL COOLING WATER—SCALE FORMATION

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Any source of naturally occurring water used of industrial cooling has been in contact with the earth, soil, and rock formations. As a result, soluble inorganic salts have been taken into solution that can give rise to "scaling" in industrial equipment. The phenomenon is apparent in domestic kettles that have been used to boil so-called "hard water." A whitish-brown deposit forms on the areas within the kettle that are subject to the highest temperatures, for example, the heating element in electric kettles. In cooling water circuits that usually employ water from natural sources such as rivers or lakes, deposition of inorganic salts, or "scaling" as it is often called, can represent a serious problem. The presence of these salts usually results in operating problems. The accumulation of deposits on heat transfer surfaces can lead to severe loss in cooling efficiency if not effectively controlled.

In general, there are two categories of salt present in water that is natural in origin, "normal" and "inverse solubility" salts. As the temperature of the water is increased, the solubility of the normal salt also increases, for example, sodium chloride. As the temperature of an inverse solubility salt solution is increased, the solubility of the salt decreases, and, if the solubility limit is exceeded, the salt begins to precipitate. Inverse solubility salts, for example, calcium carbonate, are usually sparingly soluble, whereas normal solubility salts have relatively high solubility. It will be seen from Table 1 that many common mineral salts display the properties of inverse solubility salts. They are often referred to as "hardness salts."

Table 1. Common Inverse Solubility Salts

Calcium	carbonate hydroxide phosphate silicate sulfate
Lithium	carbonate sulfate
Magnesium	hydroxide silicate

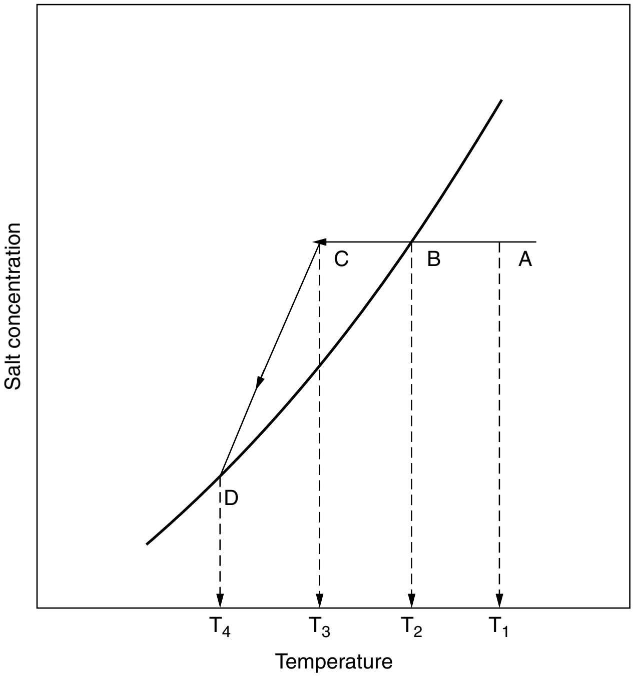

Figure 1. Cooling a normal solubility salt solution.

Whenever the temperature distribution changes in a water system containing dissolved salts, such as in an industrial cooling water system, the temperature sensitive solubility can affect successful operation. Deposition of inverse solubility salts is often one of the causes of operating problems in cooling water circuits, particularly on heat exchanger surfaces. The potential for scaling in industrial equipment is usually very high.

A solution that is in equilibrium with a soluble solid phase is said to be "saturated." The concentration in the water is the maximum that is possible at the given temperature. It is possible, however, under certain conditions, that as a saturated solution of an inverse solubility salt is raised slightly in temperature, precipitation is retarded, and the solution is said to be "supersaturated." Supersaturation can also occur with normal solubility salts. If the temperature of a saturated solution of a normal solubility salt is lowered slightly, a supersaturated solution may be produced.

Supersaturation is a necessary prerequisite for crystallization from a salt solution to occur. Its importance is illustrated in Figs. 1 and 2.

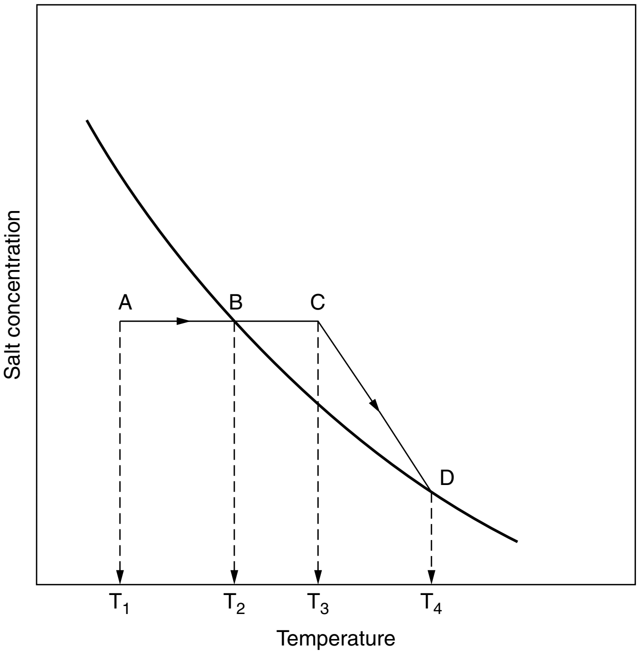

Figure 2. Heating an inverse solubility salt solution.

The curves in both figures represent the variation of saturated concentration with temperature. For a normal solubility salt, if the unsaturated solution represented by 'A' at temperature T_1 in Fig. 1. is cooled, that existing concentration will represent saturated conditions at the lower temperature T_2 at 'B'. Further cooling down to T_3 produces supersaturated conditions at 'C'. Supersaturation is represented by the temperature difference T_2-T_3, sometimes referred to as the "maximum allowable undercooling." 'C' represents a metastable condition; any disturbance such as the introduction of particles or crystals results in precipitation. If cooling (and precipitation) is continued, eventually a new equilibrium is reached at 'D' on the solubility curve, where saturation occurs at temperature T_4. Crystallization can occur either in the bulk or at the cold surface, through which heat is being withdrawn from the solution. The latter gives rise directly to deposit formation (scaling), and the crystallites produced in the solution may move toward the surface, under the influence of the hydrodynamics of the system, to be incorporated into the deposit on the surface.

The sequence of events, when an inverse solubility salt solution is heated is illustrated in Fig. 2. As the solution represented by 'A' is heated, it moves toward the saturation point 'B' on the solubility curve. As the temperature is further increased, point 'C' is reached where there is a degree of supersaturation and metastable conditions exist. The supersaturation is T_3-T_4. As the temperature is further increased, accompanied by a disturbance of the metastable condition, precipitation occurs, and the concentration of the salt in solution decreases till point 'D' is reached, representing equilibrium saturation conditions at temperature T_4. In a cooling water system, this could represent an operational problem in the coolers. In cooling operations, the highest temperature in contact with the coolant water is at the heat exchanger surface/water interface. Under these conditions, deposit formation, or "scaling," on the heat transfer surface can be expected. Furthermore, disturbance of the metastable supersaturation in the bulk water gives rise to crystallites that are likely, under the prevailing hydrodynamic conditions, to migrate toward the heat transfer surface with the further possibility of incorporation into the developing deposit.

In summary, the complex sequence of steps leading to scale formation is as follows: temperature changes that lead to supersaturation; disturbance of the metastable conditions, usually caused by solid particles, for instance, crystallites formed elsewhere in the system or particles of corrosion material that initiate the formation of crystallites, and ultimately crystals, either in the bulk water or at the heat transfer surface. Local hydrodynamic and temperature conditions affect the location of crystal and deposit formation.

Under constant heat flux, the presence of scale, a resistance to heat transfer, changes the temperature distribution across the heat transfer surface. These changes may affect the deposit structure and hence its strength, by reorienting the crystal lattice, with implications for the control of deposit accumulation. The degree of supersaturation may also be affected.

The previous discussion emphasizes that the key to scaling is the degree of supersaturation that is present, and it is likely that this will be different in different parts of the system. The following is a brief resume of the conditions that could lead to supersaturation; more detail is to be found in Bott (1).

Evaporation of water vapor from a solution, increases the salt concentration that could lead to supersaturation. The principal points in a system where this can occur is a cooling tower or a spray pond. It is here that the cooling water temperature is reduced for reuse by removing heat due to the latent heat required to vaporize some of the water. The "buildup" of dissolved salts is controlled by "blowdown," the removal of water containing relatively high concentrations of dissolved solids, to be replaced by "makeup" water that has the lower concentrations of the source water.

Mixing of different waters containing a common ion may lead to precipitation, the so-called "common ion effect" and attendant supersaturation. For instance, mixing a $Ca\ Cl_2$ solution with a solution of $Na_2\ CO_3$ may cause $Ca\ CO_3$ to precipitate if supersaturation occurs as a result.

Mixing of saturated or nearly saturated solutions may result in supersaturation and consequent precipitation.

Carbon dioxide, from the atmosphere dissolves in water in a cooling tower or spray pond. The chemical equilibria are

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

The bicarbonate ion can further ionize:

$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$

If the water is already saturated with dissolved $CaCO_3$ the additional CO_3^{2-} ions can produce supersaturation of $CaCO_3$, and crystallization of $CaCO_3$ is possible. Hydrogen ions are involved in the reactions, so the solution pH will also affect the extent of supersaturation (2).

Crystallization

Before crystallization can occur that might lead to scale formation, it is necessary to "seed" the solution to initiate the process; usually this is accomplished by minute particles. The process is generally referred to as "heterogeneous crystallization." The particulate solids may be foreign bodies, such as pieces of scale broken off the deposit upstream, corrosion products, or crystallites that have been spontaneously formed in solution. Suitable nucleation sites may also be present on surfaces such as heat exchanger surfaces within a cooling water system. It is possible that this process is responsible for the initial deposition that provides a structure onto which further crystallization can occur or into which crystallites and larger crystals can be accommodated. Spontaneous crystallization occurs without the need for seeding. The mechanism is not well understood, but it is considered that it is related to random clustering of molecules in suitable juxtaposition to allow a tiny crystal to form. Spontaneous crystallization, however, is unlikely to occur in industrial cooling water systems because of the almost universal presence of particulate matter that will initiate scaling before spontaneous crystallization can occur.

Depending on the prevailing conditions, it is possible for a robust crystal structure to be formed on solid surfaces, particularly on heat transfer surfaces, where the necessary supersaturation is present. The structure may be weakened, making removal easier, by the presence of impurities, such as particles, in the structure.

The factors and conditions that affect scaling may be summarized as follows (1):

System Variables

Total dissolved solids concentration

Concentration of particular species

Alkalinity/acidity defined as free alkali (e.g., $CaCO_3$) and free acid (e.g., H_2SO_4) expressed as mg/L.

pH

Temperature

Plant Factors

Residence time

Evaporation, that is, concentration effects

Changes in heat load that affect the temperature distribution across the heat transfer surface, thereby changing the surface/water interface temperature

Water velocity

The general design of the equipment may affect the deposition process.

SCALING CONTROL

The conditions and factors listed that affect the scaling process are generally inherent in any cooling water system and its associated processes. In most scaling problems, therefore, the operating conditions cannot be modified. Even in a medium-sized plant, due to the large volumes of water in the cooling water system, the amount of $CaCO_3$ present, even in small concentrations, will be large and may amount to several tonnes; this has to be kept in solution by suitable water treatment.

Due to the complex chemistry of cooling water containing dissolved salts, it is difficult to assess whether or not the water will be scale forming or corrosive. As a result "indexes" were proposed to provide guidance. If the pH of water saturated with $CaCO_3$ by contact with the solid salt is denoted pH_s and pH is the measured pH of the water in the system, Langelier (3) proposed that ($pH - pH_s$) could be used as an index to indicate whether the water would produce scale or be corrosive. If the Langelier index ($pH-pH_s$) is negative ($pH_s > pH$), it is assumed that the water would be corrosive. If on the other hand, the index is positive ($pH > pH_s$) the water is saturated in $CaCO_3$, and scale formation is a distinct possibility.

Ryznar (4) suggested an improved index, ($2pH_s-pH$). If the index is above 7, it is likely that the water would be corrosive. An index of 6 or lower suggests the possibility of scale formation.

Although these indexes have been used for many years in connection with water treatment in cooling circuits, there is some evidence that they are not altogether reliable because they are based on $CaCO_3$. Such a procedure ignores the complex water chemistry of associated cooling water systems and plant operating conditions.

Acid Treatment

The indexes discussed above suggest that a method of scale control could be the addition of acid, for example, sulphuric acid, to reduce the pH. There is a distinct risk, however, that severe corrosion may occur as a result of the acid treatment, so that in general, more sophisticated techniques are employed.

Water Softening (Removal of Hardness Salts)

Lime softening, ion exchange, and the use of membranes are potential methods for the control of scaling in industrial cooling water systems, but because of the large volumes of water to be treated, only lime treatment is used to any extent from this group of techniques. The more sophisticated techniques of ion exchange are far too expensive, except in closed cooling water circuits. Pretreatment with lime involves precipitation of carbonate hardness by hydrated lime, as calcium carbonate and magnesium hydroxide. An alternative is to pretreat with soda ash (Na_2CO_3) that precipitates other calcium salts in solution in addition to the carbonate. Soluble by-products in the form of sodium salts remain in solution.

Threshold Treatment (Sequestration)

When some chemicals are added to cooling water, even in relatively small quantities, they prevent the precipitation of alkaline salts and other scaling compounds, particularly calcium ions and manganese salts. Sometimes the result of the treatment is the production of sludge rather than scale that adheres to the heat transfer surface. The sludge can be removed from the system by suitable flushing. Phosphorous compounds are often used as sequestering agents. Table 2 provides some information on phosphorous compounds and their advantages and disadvantages for use with cooling water.

Crystal Modification

In the discussion of crystallization, it was stated that impurities included in the scale can reduce the cohesiveness of the crystal structure. It is possible, therefore, to effect scale control by adding so-called "scale modifiers" to cooling water. The action of these chemical additives does not prevent precipitation, as does threshold treatment, but simply reduces the opportunity for strong crystalline structures to form on heat transfer surfaces. The weaker structure of the scale makes it more susceptible to removal forces produced by the water velocity at the water/solid interface. Naturally occurring organic compounds, such as lignin or tannin, have been used for this purpose, but synthetic chemicals such as polycarboxylic acids are now more widely used as crystal modifiers. Polymaleic acid, for instance, produces a soft deposit with precipitating calcium carbonate that is easily removed.

Dispersants

It is possible to add a dispersing agent to the cooling water to keep the individual crystallites apart as they form in the water, and so reduce the opportunity of forming coherent crystal structure. Surface active agents on solid surfaces, such as heat transfer surfaces, may also hold the crystallites away from the surfaces, and so restrict scale formation. Dispersants that have been used for

Table 2. Organophosphorous Compounds Used as Sequestering Agents[a]

Compound Type	Advantages	Disadvantages
Polyphosphates	Hydrolysis to orthophosphate which reacts with calcium to form a sludge	Nutrient for microorganisms
Phosphonates	Effective against both alkaline and nonalkaline scaling conditions	If supersaturation levels are allowed to rise, uncontrolled precipitation may occur
Phosphate esters	Wide range available; biodegradable	Less effective than phosphonates
Phosphoncarboxylic	Similar to phosphonates	Some rise in supersaturation may be tolerated without attendant precipitation

[a] Reference 1.

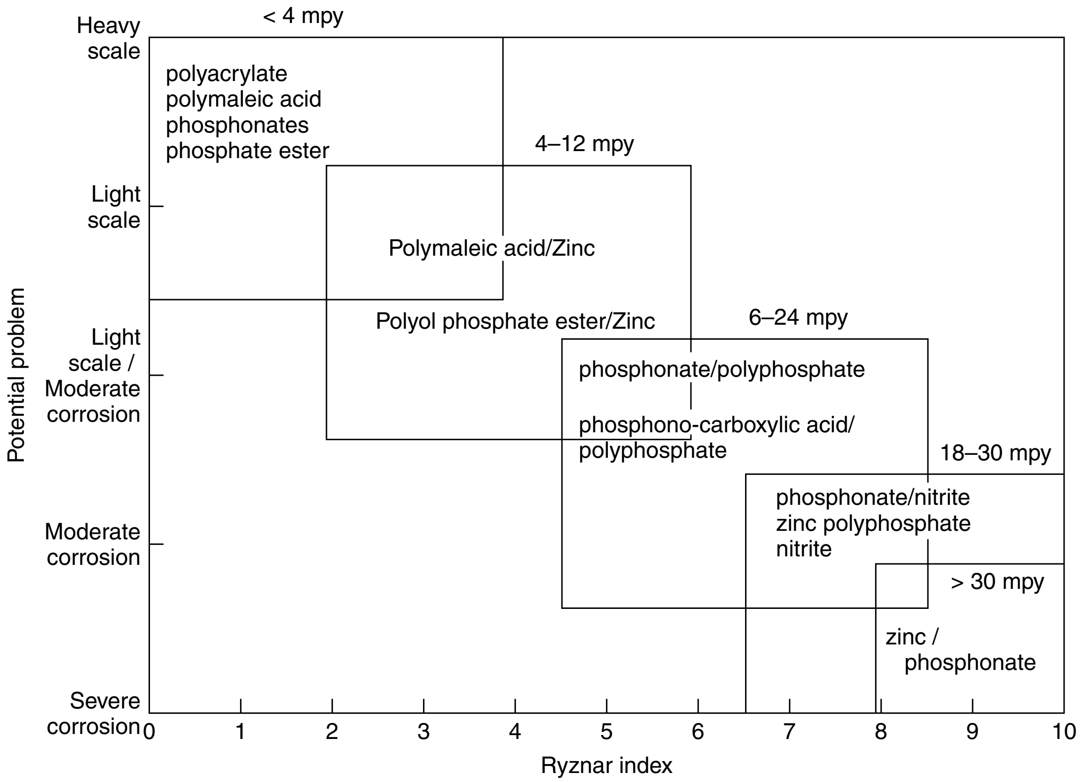

Figure 3. Scale and corrosion control based on the Ryznar index.

this purpose include organophosphorous compounds and polyelectrolytes.

General

Treatment programs for scale prevention are likely to include a range of chemical additives so that a number of techniques are working in parallel to control scale formation and also for corrosion control and biofouling mitigation.

Figure 3 is a diagram published some years ago that demonstrates how chemical additives may be used to control scaling and corrosion for different Ryznar indexes (5).

BIBLIOGRAPHY

1. Bott, T.R. (1995). *Fouling of Heat Exchangers*. Elsevier Science, Amsterdam.
2. Kemmer, F.N. (1988). *NALCO Water Handbook*. McGraw-Hill, New York.
3. Langelier, W.F. (1936). The analytical control of anticorrosion water treatment. *J. Am. Water Works Assoc.* **28**: 1500–1521.
4. Ryznar, J.W. (1944). A new index for determining the amount of calcium carbonate formed by water. *J. Am. Water Works Assoc.* **36**: 472–486.
5. Atkinson, A., Gerrard, A.F., and Harris, A. (1979). Development of additives to control inorganic fouling in industrial water systems. In: *Fouling Science or Art? Inst. Corr. Sci. and Inst. Chem. Engrs.* University of Surrey.

ECONOMICS OF INDUSTRIAL WATER DEMANDS

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This article examines what is known regarding the economic characteristics of industrial water use. Understanding the economic dimension of industrial water use is important for several reasons. First, in some countries, industrial water use is already an important part of total water use. Furthermore, in a number of countries, the proportion of total water use accounted for by industry is rising rapidly. Second, much of industrial water use results in significant alterations in water quality. Third, industrial water use differs from water use in other sectors because many firms recycle water and because many firms may choose their source of water supply.

INTRODUCTION

Manufacturing firms, mines and power generating plants typically withdraw water from the natural environment for three main reasons. First, water is applied in a production process. This includes cleaning and moving intermediate inputs as well as inclusion in final output (the production of beer). Second, water is used to cool

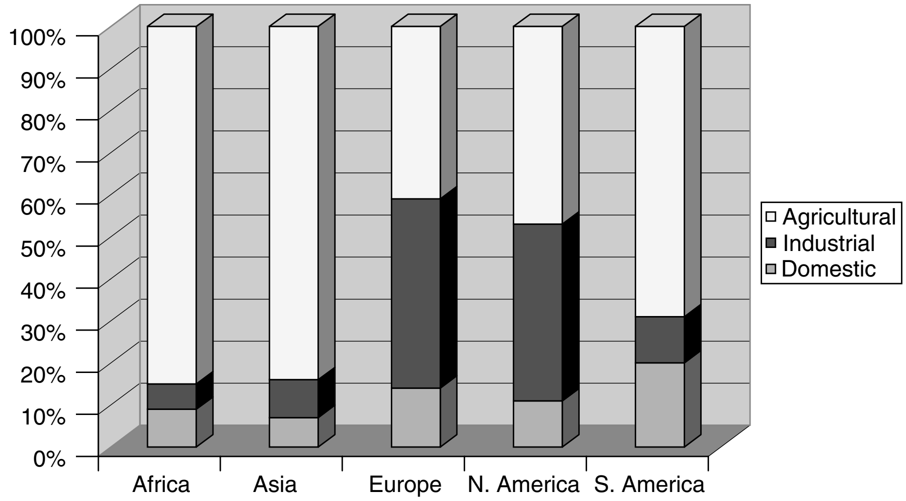

Figure 1. Sectoral shares in water use (1990) (1).

intermediate inputs (the production of petroleum-based fuels) or to produce steam (thermal electric generating plants). Third, water is used for a variety of miscellaneous purposes such as plant cleaning and personal sanitation.

The share of national water use accounted for by industrial water use (including water use in electrical power production) ranges from less than 5% in a number of low-income countries to more than 70% in a number of northern, high-income countries (1) (Fig. 1). Furthermore, in a number of countries experiencing rapid economic development and industrialization such as China, Indonesia and India, industrial water use's share is rising quite rapidly (2).

The next section of this article outlines briefly the economic theory that supports modeling industrial water use. The third section reviews the body of empirical industrial water demand models and the results that flow from this set of work. The last section concludes and provides suggestions for future research. Any brief survey must be selective in its coverage. A number of topics that are related to industrial water use are not discussed here. These include water-based commercial transportation, industrial wastewater discharges, and the valuation of industrial water use. These topics are covered in other articles found in this *Encyclopedia*. In addition, readers interested in a more detailed treatment of the issues surrounding the economic features of industrial water use may refer to Young and Gray (3), Stone and Whittington (4), Gibbons (5), and Renzetti (6,7).

The Economic Theory of Industrial Input Demands

Until recently, it was commonplace to assume that the amount of water required to produce a given quantity of output was fixed (8). In addition, aside from minor variations from differences in technology and the age of capital stocks, it was assumed that the ratio of water use to output was not sensitive to changes in the price of water or the prices of other inputs. In contrast, economists who believe that profit-maximizing firms' use of any input is sensitive to its own price, the prices of inputs, and the price of output have criticized this perspective. To see this, suppose that a firm's technology is represented by a production function $y = f(x_1, \ldots x_N)$ that shows that maximal amount of output (y) that can be produced from input quantities ($x_1, \ldots x_N$). Assuming that the firm faces a price of output (p) and prices of inputs ($w_1, \ldots w_N$) and that the firm seeks to choose output and input quantities to maximize its profits, then the firm's problem may be cast as the following:

$$\max_{\{y,x_i\}} p \cdot y - \sum_i w_i \cdot x_i, \quad i = 1 \ldots N$$

Carrying out this optimization yields the firm's profit-maximizing output supply and input demand equations (Ref. 7, chap. 4; 9):

$$y = g(p, w_1, \ldots w_N),$$
$$x_i = h(p, w_1, \ldots w_N), \quad i = 1 \ldots N$$

It is clear from this presentation that the demand for any input (including intake water) is a function of its own price, all other input prices, the price of output, and the firm's technology. Only in exceptional circumstances should it be expected that the ratio of water intake to output be invariant to prices. Economic theory predicts that both increases in the price of output and decreases in the price of intake water will increase the demand for water. The impact of changes in other input prices on the demand for water will depend on whether those inputs are substitutes or complements to intake water in the firm's production process. Economists typically report these types of relationships as an "elasticity." For example, the own-price elasticity of intake water demand is the change in the quantity of water intake used by the firm in response to a small change in the price of intake water (both changes are expressed in percentages). The strengths of all of these relationships (that is, the magnitude of the elasticities) is a matter for empirical investigation.

EMPIRICAL MODELS AND RESULTS

The main purposes for estimating or calibrating empirical models of industrial water use are to understand water's role in production processes; to examine the relationship between intake water, internal water recirculation, and other inputs; and to measure the sensitivity of water demands to prices. These models may be used to forecast water demands as well as predict the sensitivity of industrial water uses to policy measures aimed at promoting water conservation. There are two main obstacles standing in the way of this type of industrial water demand research. The first is the fact that much of industrial water intake is self-supplied rather than being supplied by a municipal or regional water utility. The result of this is that many industrial water users face either no price for their intake water or only an administrative price that bears little resemblance to the value of water. The second obstacle stems from the lack of data on industrial water intake, recirculation and discharge. Few countries regularly collect and report these data (9).

Despite these challenges, a number of researchers have considered the structure of industrial water demands. The modern literature concerned with industrial water demands begins with a major research effort undertaken by analysts at Resources for the Future (10–12). These studies are noteworthy for their careful application of economic principles and measurement techniques and combining of econometric and engineering methods to represent firms' water use patterns. Since that time, researchers have employed econometric and programming models to examine industrial water demands. Both of these approaches are discussed briefly here.

Initial econometric efforts use ordinary least squares to fit linear equations to plant-level data (13,14). The data included observations on the price of water, the quantity of intake water, and the level and type of output. Both authors report elasticities whose values vary by industrial sector and use of water. De Rooy finds that price and output elasticity estimates vary according to the use of the intake water: −0.894 and 1.212 (cooling); −0.354 and 1.359 (process); −0.590 and 1.243 (steam generation).

An important issue in these and subsequent studies concerns the specification of the price of intake water. For publicly supplied firms, industrial water prices are typically a combination of a connection fee and a complex rate schedule (9). When price is a function of quantity, this creates the possibility of introducing a simultaneity bias into the estimated demand equation. Ziegler and Bell (15) and Renzetti (16) address this issue by estimating demand equations using an instrumental variable technique.

An even more serious challenge arises from industrial water users who are self-supplied. In this case, there may be no external price for intake water. Self-supplied firms incur several types of cost for their water use. First, the firm incurs internal costs resulting from pumping, treatment prior to use (chlorination, descaling, etc.), and on-site storage. Second, the firm may face external costs arising from fees and charges set by government. Third, the firm may incur internal costs for water disposal such as treatment, removal of effluents, pumping, and on-site storage. It is very likely that information regarding the first and third sources of cost will not be publicly available and firms may not even collect this information themselves. This means that it is difficult to specify and measure the cost of an incremental increase in water intake. Grebenstein and Field (17) address this challenge by relying on water utility prices to proxy self-supplied firms' water costs, whereas Renzetti (16) relies on plant-level observations on water utility prices, government water charges, and internal water use costs to construct a proxy for the price of water.

A number of authors (16–19) have used a system of equations approach to estimate the industrial demand for water. This increases the efficiency of estimation and allows the authors to examine the relationship between water and other inputs. Each of the authors assumes that the technology of the manufacturing sector may be represented by a cost function that includes the prices of capital, labor, energy, materials, and water as well as the level of output, as explanatory variables. A system of input demands is then derived from the cost function and estimated. Babin, Willis, and Allen find that the own-price elasticity of intake water ranges from 0.0 to −0.66 and an estimate of −0.66 for all sectors combined. Water's relationship to other inputs also varies across sectors. Water is a substitute for capital in some sectors and is a complement in others. Renzetti (16) finds that water intake's price elasticities range from −0.153 to −0.589, depending on the sector. Water recirculation is seen as a substitute for intake for all industries. Industries that are heavy water users (paper and wood products, chemicals, petroleum, food and beverage) also are the most sensitive to price changes.

More recently, Dupont and Renzetti (20) take a different approach in examining industrial water demands. The authors incorporate water recirculation and technological change in their estimation model and examine the impact of water use regulations on water demands. Because self-supplied firms in Canada must obtain a permit before withdrawing water, the authors consider whether firms are free to choose the optimal quantity of intake water (as is assumed in deriving input demand equations). Two alternative models are estimated: one assuming that water intake is a variable input and the other assuming that water intake is fixed. Specification tests support the choice of modeling water as a variable input. Water intake is found as a substitute for energy, labor, capital, and water recirculation. The relationship between water intake and recirculation is stronger when water use is process-related rather than related to cooling and steam production. Technological change has been biased in the direction of increased water intake and decreased water recirculation.

An alternative to using econometric methods to model water demands is to use linear programming techniques. Linear programming is a technique that is employed to find optimal solutions to problems when the objective function is linear and constraints are expressed as linear inequalities. For example, the objective function may measure a firm's revenues, and the constraints may reflect production processes that relate combinations of input quantities to levels of output. The solutions to linear programming problems have several interesting features that differentiate them from the estimated econometric demand models discussed before. For example, input demand equations derived from linear programming models are typically piecewise, continuous and linear. Discontinuities in the demand equation correspond to the adoption of new production processes (such as the installation of a cooling tower that permits recirculation and reuse of cooling water). Simulations conducted by Calloway, Schwartz, and Thompson (21) demonstrate the significance of this feature. Their results indicate that for intake water prices anywhere below 3.2¢ (1971 US$) per 1000 gallons, a plant producing ammonia employs a water intensive 'once-through' cooling system. At 3.2¢ per 1000 gallons, however, the plant switches to recycling its cooling water, this reduces water intake by 95%, and further price increases do little to encourage further water conservation.

Thompson and Young (22), Singleton, Calloway, and Thompson (23), and Kindler and Russell (24) are representative of this approach. Thompson and Young (22), for example, use engineering data and linear programming techniques to examine water use in thermal power generating stations. They find that there are a number of options for conserving water intake and these options become financially feasible at differing water prices. In addition, the authors find that the power plants can be encouraged to reduce water intake through policy measures such as heat discharge taxes.

Firms that use water in their production processes must find some way to dispose of that water. Water quality regulations typically impose limits on the quantity and/or concentration of effluents that can be discharged. Some analysts argue that water quality regulations have been a driving force in compelling firms to reduce their emissions (25,26). Empirical evidence also suggests that economic forces are relevant. A number of authors (12,16,27) have examined the sensitivity of firms' water discharge decisions to economic factors such as sewage prices, discharge fees, and fines. For example, Renzetti (16) finds that, for the Canadian manufacturing sector as a whole, the price elasticity of water discharge is −0.9752.

The discussion thus far has concentrated on water use in the manufacturing sector. A limited number of studies have considered commercial and institutional water use. The limited amount of work done in this area suggests that this sector's water use is sensitive to water prices and the firm's level of output. Schneider and Whitlatch (28) estimate a series of demand equations to calculate price and income elasticities for several user groups, including commercial, industrial, government, and education. The account-specific price elasticities (following the order of user groups set out before) are −0.918, −0.438, −0.781 and −0.956. Given the diversity of water users in these sectors, generalizations regarding the nature of their water use is quite difficult.

Water use in the mining and electricity power production sectors also has received relatively little attention, maybe because mining water use in most countries is a small share of total estimated withdrawals (it is approximately 1% in the United States and Canada; (26). Despite mining's small share in total withdrawals, water use by mines can be important regionally if they are located in areas where water is scarce such as the American Southwest or the western provinces of China. Mining water use can also be important because of the water contamination that frequently results from mining operations. More attention has been paid to water use in electricity production. The primary concern here, however, has been in establishing the value of water in this use, as opposed to estimating water's role in this technology (29). Young and Gray (3), Gibbons (5), and Renzetti (7) survey the methods used to estimate the value of water use in electricity production.

CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

Industrial water use is important for several reasons: in a number of countries, it makes up a significant part of total water use; firms derive significant benefit from its use, it has the potential for causing substantial alterations in water quality, and it often involves decisions by the firm regarding the degree of internal recirculation to undertake. For these reasons, a number of researchers have sought to understand the economic character of industrial water use. The available empirical evidence indicates quite clearly that decision-making with respect to water does not differ significantly from that for other inputs. Thus, industrial water use is sensitive to its own price, the price of output, and other input prices. Future directions for research will include efforts to combine econometric and engineering process models of industrial water use. These approaches are quite complementary: process models are very detailed and satisfy materials balance constraints, and econometric models are based on a range of technologies and market prices. Another area that remains understudied is the set of factors that influence firms' decisions regarding whether (or how much) to recirculate water.

BIBLIOGRAPHY

1. World Resources Institute. (2000). *World Resources 2000–2001*. Oxford University Press, New York.
2. Biswas, A.K. (1997). Water development and environment. In: *Water Resources: Environmental Planning, Management and Development*. A.K. Biswas (Ed.). McGraw-Hill, New York.
3. Young, R.A., Gray, S.L., Held, R.B., and Mack, R.S. (1972). *Economic Value of Water: Concepts and Empirical Estimates*. Report to the National Water Commission, NTIS no. PB210356 (National Technical Information Service, Springfield, IL).
4. Stone, J. and Whittington, D. (1984). Industrial water demands. In: *Modeling Water Demands*. J. Kindler and C. Russell (Eds.). Academic Press, London.
5. Gibbons, D. (1986). *The Economic Value of Water*. Resources for the Future, Washington, DC.
6. Renzetti, S. (2001). Introduction. In: *Economics of Industrial Water Use*. S. Renzetti (Ed.). Edward Elgar, London, pp. 1–20.
7. Renzetti, S. (2002). *The Economics of Water Demands*. Kluwer Academic Press, Boston.
8. Giuliano, G. and Spaziani, F. (1985). Water use statistics in industry. Experiences from regional surveys and planning

studies in Italy. *Statistical Journal of the United Nations* **3**: 229–235.

9. Dinar, A. and Subramanian, A. (Eds.). (1997). *Water Pricing Experiences: An International Perspective*. World Bank Technical Paper No. 386, The World Bank, Washington, DC.
10. Bower, B. (1966). The Economics of industrial water utilization. In: *Water Research*. A. Kneese and S. Smith (Eds.). Resources for the Future, Washington, DC.
11. Löf, G. and Kneese, A. (1968). *The Economics of Water Utilization in the Beet Sugar Industry*. Resources for the Future, Washington, DC.
12. Russell, C.S. (1973). *Residuals Management in Industry: A Case Study of Petroleum Refining*. Resources for the Future, Washington, DC.
13. Rees, J. (1969). *Industrial Water Demand: A Study of South East England*. London School of Economics Research Monograph 3, London.
14. DeRooy, Y. (1974). Price responsiveness of the industrial demand for water. *Water Resources Research* **10**(3): 403–6.
15. Ziegler, J. and Bell, S. (1984). Estimating demand by self-supplying firms. *Water Resources Research* **20**(1): 4–8.
16. Renzetti, S. (1992). Estimating the structure of industrial water demands: The case of Canadian manufacturing. *Land Economics* **68**(4): 396–404.
17. Grebenstein, C. and Field, B. (1979). Substituting for water inputs in U.S. manufacturing. *Water Resources Research* **15**(2): 228–232.
18. Babin, F., Willis, C., and Allen, P. (1982). Estimation of substitution possibilities between water and other production inputs. *American Journal of Agricultural Economics* **64**(1): 148–151.
19. Dupont, D. and Renzetti, S. (1998). Water use in the Canadian food and beverage industry. *Canadian Journal of Agricultural Economics* **46**(2): 1–11.
20. Dupont, D. and Renzetti, S. (2001). Water's role in manufacturing. *Environmental and Resource Economics* **18**(4): 411–432.
21. Calloway, J., Schwartz, A., and Thompson, R. (1974). Industrial Economic Model of Water use and Waste Treatment for Ammonia. *Water Resources Research* **10**(4): 650–8.
22. Thompson, R. and Young, H.P. (1973). Forecasting water use for policy making. *Water Resources Research* **9**(4): 792–799.
23. Singleton, F., Calloway, J., and Thompson, R. (1975). An integrated power process model of water use and waste water treatment in chlor-alkali production. *Water Resources Research* **11**(4): 515–25.
24. Kindler, J. and Russell, C. (Eds.). *Modeling Water Demands*. Academic Press, London.
25. Brown, G. and Johnson, R. (1984). Pollution control by effluent charges: It works in the federal republic of Germany, Why not in the U.S. *Natural Resources Journal* **24**: 929–966.
26. Solley, W., Pierce, R., and Perlman, H. (1999). *Estimated Use of Water in the United States in 1995*. United States Geological Survey Circular 1200. Available: http://water.usgs.gov/watuse/pdf1995/html/.
27. Sims, W. (1979). The response of firms to pollution charges. *Canadian Journal of Economics* **12**(1): 57–74.
28. Schneider, M. and Whitlatch, E. (1991). User-specific water demand elasticities. *Journal of Water Resources Planning and Management* **117**(1): 52–73.
29. Gillen, D. and Wen, J.F. (2000). Taxing hydroelectricity in Ontario. *Canadian Public Policy* **26**(1): 35–49.

ELECTRIC GENERATING PLANTS—EFFECTS OF CONTAMINANTS

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INTRODUCTION

Environmental pollution incidents concerning electric generating facilities have often been widely publicized. Some examples of these include choking air emissions, catastrophic coal ash spills, temporary releases of radioactivity, and contamination of groundwater. In some cases, a direct threat to human health was the cause for concern. In the movie "Erin Brokovich," an activist (played by actress Julia Roberts) draws public attention to the contamination of groundwater by potentially toxic trace metals that have leached through a power plant ash disposal facility. Most of these spectacular pollution events, however, occurred before full, widespread implementation of major environmental statutes (e.g., Clean Air Act, Safe Drinking Water Act, Resource Conservation and Recovery Act, Clean Water Act), enacted by the U.S. Congress during the period 1970–1980. These statutes provide minimum (baseline) environmental protection requirements for the release of pollutants to air, water, and land. Although most states have implemented the requirements of these statutes for several years, concerns regarding pollution released from electric generating facilities still remain in some locations.

This article concerns contaminants released or discharged to the water environment by electric generating facilities. The focus of this article will be on contaminants originating from the combustion and use of fossil fuels. Releases from nuclear-powered facilities will not be considered, largely because the only significant contaminant released by these stations is heated water. The pathway by which power plant contaminants affect aquatic ecosystems may be either direct or indirect. Some pollutants emitted to the air by coal combustion facilities, for example, have the potential to degrade surface waters or affect human health. A general historical review of power plant environmental impacts and environmental control will be discussed, followed by an assessment of sources and effects of pollutants in the water environment.

Historical Review of Power Plant Generation and Contamination

In general, the historical pattern of environmental effects caused by electric generating facilities mirrors the extent and magnitude of fossil fuel (largely coal) combustion. More precisely, the efficiency and extent of pollution control technology in the mining, transport, and combustion of coal and coal-derived materials has been a significant determinant concerning the release of contaminants. The extraction and combustion of coal has a legacy of environmental degradation to air, land, and water. Ecological and human health effects from fossil fuel combustion, which occurred through the first half of the twentieth century, played a significant role in the public's demand for a cleaner environment. Most of these perturbations occurred in the coal-bearing Appalachian region, which is not to say that significant environmental degradation during the first 50–70 years of the twentieth century was limited to fossil fuel combustion; numerous other environmental problems (e.g., discharge of raw sewage, indiscriminant use of persistent pesticides, urban air pollution) affected many industrialized countries during this period. In short, the congressional adoption of the major environmental statutes during the 1970s was driven, at least in part, by the desire to mitigate the environmentally harmful effects of coal mining, transport, combustion, and waste disposal.

As a result of the oil embargo instituted by OPEC countries against the United States during the early to mid-1970s, a national policy of reducing United States dependency on foreign oil was instituted, which resulted in the unprecedented construction of coal-fired (and nuclear-powered) electric generating stations during the mid-to-late 1970s. An increased demand for coal began as the construction of more proposed coal-burning facilities was approved by government regulators. As greater and greater amounts of coal were burned, the magnitude of pollutants emitted (and waste disposed of) began to reach peak levels. During this period, several environmental concerns became widely publicized: acid rain, thermal pollution, particulate matter, acid mine drainage, groundwater contamination, and others. Ultimately, new federal laws and regulations were successful at reducing or mitigating the harmful effects of power plant contaminants.

During the past 30 years, the quality of ambient air and water has improved considerably. This success has resulted largely because of two factors: the adoption of more stringent ambient standards and the requirement to meet best available technology controls for each industry sector. The investment of pollution control technologies and process modifications made by the power industry has not been insignificant. New coal combustion facilities must meet "new source standards" for environmental controls. A new era of "clean coal" technologies is now being implemented. In 2002, combustion of coal (and coal-derived fuels) represented approximately 53% of the U.S. electricity demand (1). This high percentage is likely to remain for some time, as the domestic coal reserve is anticipated to last for about 200 years, considerably longer than reserves for oil and natural gas (2).

It is important to note that the process of coal combustion does not "create" new pollutants. Rather, the extraction and combustion of coal changes the forms, mobility, and environmental compartmentalization of natural constituents in coal. Coal mining mobilizes constituents that normally would be secured in geological strata. When coal is combusted, the natural constituents in this fuel (trace metal, radionuclide, and organic compounds) are transformed into volatile forms (air emissions) or concentrated in ash (solid waste) because of chemical reactions caused by high combustion temperatures.

Air Emission Contaminants

In terms of total mass of pollutants released to the environment, power plant air emissions far outweigh the amount of pollutants released to land and water. Table 1 indicates the types of contaminants released to the air during coal combustion and potential adverse effects on human health and terrestrial/aquatic receptors. Depending on site- and region-specific fate and transport processes, many contaminants emitted by fossil fuel combustion can eventually transfer to the aqueous (water) medium; contaminants such as mercury and selenium do have the potential to be bioaccumulated in surface water

Table 1. Typical Contaminants Released to the Air During Fossil-Fuel Combustion, and Potential Human Health and Environmental Effects

Contaminant Class	Representative Contaminants	Potential Human Health and Environmental Effects
Gases	CO, SO_2, SO_3, NO_2, O_3	Respiratory irritants; atmospheric warming; acidic wet deposition; eutrophication of surface waters; increased ozone and haze
Trace elements	As, Ba, Cd, Cr, Pb, Hg, Ni, Se, Tl	Respiratory irritants; bioaccumulation in crops; bioaccumulation in terrestrial and aquatic food webs
Radionuclides	Isotopes of U, Th, Ra	Radiation exposure via inhalation, dermal, or ingestion exposure routes
Carbonyl compounds	Formaldehyde, acetaldehyde	Respiratory irritants
Aromatic hydrocarbons	Dioxins, phenol	Potential carcinogenic effects; respiratory irritants; food chain bioaccumulation
Acids	Hydrofluoric acid, hydrochloric acid, sulfuric acid	Respiratory irritants
Fine particulates	Sulfur particulates	Respiratory irritants; eye and throat irritants

systems. Other power plant contaminants emitted by coal-fired power plants return to the soil or are sequestered in biomass (trees, grasses, crops). The potential of these sequestered contaminants to elicit adverse effects in the water environment is typically small or negligible.

In 1998, U.S. EPA issued a report to Congress on the levels, and associated health risks, of hazardous air pollutants (HAPs) emitted by utilities using fossil fuel combustion (3). A total of 67 pollutants were assessed by the agency. The report indicated that, for most toxic contaminants emitted to the air, the inhalation (respiratory) route of exposure was most important. Emissions of mercury from coal-fired utilities was the HAP of greatest potential health concern, because mercury is highly persistent and can bioaccumulate to potential harmful levels in foodstuffs (mostly fish and shellfish). Three HAPs were identified that pose potential health concerns, although considerable uncertainties remain: dioxins, arsenic, and nickel. Dioxin, like mercury, has the potential to accumulate in crops or food web compartments. The mass of dioxin emitted from power plants, however, is very small compared with other HAPs. U.S. EPA concluded that, for the majority of generating facilities studied, the cancer risk from inhalation exposure is estimated to be less than 1 in one million (1×10^{-6}).

Damage to aquatic ecosystems from the atmospheric drift and fallout (deposition) from industrial point sources has been well documented in certain geographic areas. Pervasive ecological damage (caused by deposition of several trace metals and resulting bioaccumulation) was documented in several lakes downwind of the Sudbury, Ontario smelter (4). Fossil-fueled power plants emit approximately 45 tons of mercury each year in the continental United States (5). The transport and fate of mercury emitted from coal-fired facilities is complex, however, and is driven largely by chemical speciation of mercury and local meterological conditions. Some studies have shown a close association between mercury emissions from a power plant and levels observed in proximate environmental compartments [e.g., (6)], whereas others have not [e.g., (7)].

Solid Waste and Water Contaminants

Although some contaminants emitted to air during fossil fuel combustion have the potential to deposit on surface water watersheds to levels that could cause adverse ecological effects, contaminants released from dry ash and aqueous (wet) ash disposal facilities have a greater potential to enter aquatic ecosystems because of the much greater proximity to surface waters and groundwater. Table 2 indicates the contaminants that are typically released to groundwater and/or surface waters as a result of solid and aqueous disposal of coal combustion byproducts.

Coal combustion results in voluminous amounts of ash, which must be disposed. Two types of ash predominate: fly ash and bottom ash. Fly ash (which represents about 80% of the total coal combustion waste) is composed of fine-grained particles that have a variable morphology and consist primarily of an amorphous glassy material. The elemental composition of fly ash is highly variable and directly related to compositional variations in the parent coals and to the operational characteristics of individual power plants. Some elements are concentrated (enriched) on fly ash particle surfaces. Some trace metals are particularly enriched on fly ash particles. Suloway et al. (8) reported that arsenic, selenium, antimony, and lead typically have concentrations in ash that are 2–10 times the concentration in parent coal samples. Depending on factors such as pH, some trace metals may desorb from the ash particles and become soluble in ash ponds (treatment facilities used to precipitate metals, salts, and other constituents prior to discharge). Fly ash leachates may be toxic to aquatic receptors, depending on the concentration and bioavailable fraction.

Table 2. Typical Coal Combustion Byproduct Contaminants Released to Groundwater and/or Surface Waters from Solid and Aqueous Disposal Facilities

Coal Combustion Byproduct Disposal Method	Typical Contaminants	Potential Groundwater/Surface Water Effects
Solid waste- dry fly ash disposal	Trace metals	Leachate may contaminate aquifer if impermeable liner has not been installed. Collected leachate may be discharged to surface waters
Solid waste—FGD Sludge Disposal	Salts (sulfate, chloride, calcium); some trace metals	Leachate may contaminate aquifer if impermeable liner has not been installed. Collected leachate may be discharged to surface waters
Fly ash and bottom ash—aqueous disposal	Trace metals; particulates; extreme pH	Direct toxicity to aquatic life if toxic (bioavailable) form predominates. Suspended particulates may precipitate on stream substrate or lake bottom. Proximal sediments may be toxic to aquatic life. Bioaccumulative metals may cause indirect food web effects (effects on top predators or aquatic-dependent wildlife)

Bottom ash is composed of heavier, agglomerated ash particles that are too dense to be carried in the flue gas. Bottom ash is typically gray to black in color, is quite angular, and has a porous surface structure. Normally, bottom ash is less enriched in trace metals and salts compared with fly ash.

Another type of power plant combustion byproduct that may affect surface waters or groundwater is flue gas desulfurization (FGD) material. FGD systems are installed at power plants to provide enhanced removal of sulfur compounds from flue gas, a process that involves the capture of sulfur gases with sorbents. Limestone (calcium carbonate), lime (calcium oxide), and ammonia are the most widely used sorbents. FGD wastes are typically enriched with various calcium and sulfur-based salts. If released from disposal facilities, these constituents can alter surface water ionic strength and, subsequently, cause ionic imbalances in aquatic life.

Contamination of groundwater is a concern if the affected aquifer is a source of drinking water. If ash disposal facilities are not placed on impermeable geological formations (e.g., clay) or not adequately enclosed with a synthetic liner, leachate materials (salts and/or trace metals) can infiltrate into nearby aquifers [e.g., (9, 10)].

EFFECTS OF CONTAMINANTS—WASTEWATER DISCHARGES

Cooling Water Contaminants

For power plants that use once-through cooling (ambient water withdrawn for heat transfer in the condenser pipes), a few contaminants may be added to the heated water at concentrations that may affect nearby aquatic life. On a periodic basis, condenser pipes are flushed with a strong oxidant (typically chlorine or bromine) to reduce biofouling buildup on the pipes. Biocides may also be used to directly kill small mollusks or other larger fouling organisms. Adverse effects to aquatic life have been demonstrated when chlorine is used for biofouling control [e.g., (11)]. In addition, synergistic effects have been observed when aquatic life is exposed to both chlorinated water and heated water, simultaneously.

Condenser pipes experience chemical corrosion over time. Thus, metals may slough off these pipes and, depending on the available dilution, can be present in potentially toxic amounts. Wright and Zamuda (12) measured elevated levels of particulate and dissolved copper downstream of a once-through cooled power plant in Maryland. These levels were clearly above ambient concentrations.

Chemicals may be deliberately injected into the condenser system to help prevent alloy metal corrosion. These chemicals can be toxic to aquatic life if the dosing regime is not adequately regulated.

Coal Ash Byproduct Contaminants

Some useful reviews of the chemical composition, toxicity, and environmental hazards of power plant ash have been published (13–15). The extensive review by Rowe et al. (15), in particular, provides excellent coverage of the chemical characteristics of coal combustion wastes and the range of documented toxicological and ecological effects caused by contaminants in these wastes. As the chemical characteristics of coal ash differ considerably because of the blend of coals burned, generalizations regarding the environmental hazards of coal ash wastes are only speculative. Site-specific assessments of final coal ash discharges (concentration, dissolved and particulate phases, mitigating characteristics) are needed to make definitive predictions of potential toxicity. Often, basic characteristics of the receiving waters (dilution capacity, buffering capacity, suspended solids concentrations) dictate whether *in situ* adverse effects actually occur.

Numerous studies have been conducted documenting the adverse effects of wet ash discharges. Table 3 summarizes the range of observed adverse effects caused by coal ash wastewater discharges, grouped by type of ecological aberration. See Rowe et al. (15) for a more comprehensive review of adverse effects from the discharge of coal ash combustion wastes to surface waters.

Table 3. Types of Adverse Ecological Effects Caused by Coal Ash Wastewater Discharges, with Selected Literature Examples

Ecological Effect	Selected Examples and Reference Citations
Direct toxicity of seepage/wastewater	Acidic, iron-enriched ash pond seepage caused direct mortality to fish (16)
Simplification/modification of invertebrate or fish community	Structural and functional modifications to stream invertebrates (17, 18)
	Tolerant invertebrates and fish species downstream of fly ash pond discharge (19, 20)
Sediment toxicity/metal accumulation	Elevated levels of metals in sediments influenced by fly ash pond discharge (21, 22)
Trace metal bioaccumulation	All food web compartments with elevated concentrations of some trace metals (21, 22)
	Elevated levels in specific fish tissues (23)
Physiological/biochemical/hematological aberrations	Several assays in affected fish significantly different compared to reference fish (24, 25)
Reproductive toxicity	Top predator fish in power plant cooling lakes (receiving coal ash inputs) showed reproductive toxicity due to selenium (26, 27)

REGULATORY CONTROLS—WASTEWATER DISCHARGES

Power plant wastewaters are currently regulated under technology-based national categorical effluent standards. These standards were promulgated in the Effluent Guidelines and Standards for the Steam Electric Power Generating Point Source Category in 40 CFR 423.12 in 1982 and 1983. These limitations include monthly and daily maximum limitations for pH, total suspended solids, oil and grease, and free chlorine (all regulated outfalls); maximum limitations for copper and chromium for boiler chemical cleaning wastes; and maximum chromium and zinc limitations for cooling tower blowdown. For all outfalls, no detectable amounts of PCBs are allowed. Most power generating facilities are able to comply with these categorical standards, as adequate treatment facilities can be designed well in advance of plant operation.

More problematic for power plant wastewater discharges, in terms of compliance, is the requirement to meet water quality-based effluent limitations (WQBELs). These limitations are based on numeric, not-to-exceed water quality criteria that often differ among states. Water quality criteria are estimates of pollutant-specific concentrations that would not cause adverse effects to aquatic life or humans (based on contact recreation or consumption of fish). In contrast to the fixed, categorical effluent limitations, WQBELs can change with time because water quality criteria change (often becoming lower in concentration, or more stringent). In many instances, power plant facilities have installed costly treatment systems to remove constituents (typically trace metals) in order to meet certain WQBELs.

Like other source categories, power plant wastewaters are subject to complying with whole effluent toxicity criteria and/or limitations. Whole effluent toxicity criteria are meant to protect against unacceptable toxicity in the aggregate wastewater discharge. Typically, discharges are assayed using standardized laboratory testing procedures. If effluent toxicity is high, a facility may be required to identify the causative toxicant and remove (or mitigate) the source of the pollutant.

SUMMARY

As an energy source, the combustion of fossil fuels has been a principal factor in the rapid industrialization of many countries during the twentieth century. The legacy of environmental degradation caused by coal combustion is well documented, from coal extraction activities (mining) to release of contaminants into the atmosphere. The adoption and promulgation of several major environmental statutes, however, has lessened the overall environmental impacts of coal combustion. New coal-fired power plants use coal that has low levels of sulfur, mercury, and other environmentally important constituents. The electric utility industry has made prudent investments in cost-effective pollution control technologies. The pressures to implement new, less polluting technologies will drive the industry to balance use of this abundant energy source with cost-effective environmental controls.

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BIBLIOGRAPHY

1. U.S. Department of Energy, Energy Information Administration. (2002). Electricity InfoCard. Accessed at http://www.eia.doe.gov/neic/brochure/elecinfocard.html.
2. Siegel, J.S. and Temchin, J.R. (1991). Role of clean coal technology in electric power generation in the 21st century. In: *Energy and the Environment in the 21st Century*. J.W. Tester, D.O. Wood, and N.A. Ferrari (Eds.). MIT Press, Cambridge, MA, p. 623.
3. U.S. EPA. (1998). Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress. EPA-453/R-98-004a. U.S. EPA Office of Air Quality, Research Triangle Park, NC.
4. Bradley, R. and Morris, J. (1986). Heavy metals in fish from a series of metal-contaminated lakes near Sudbury, Ontario. *Water, Air, and Soil Pollution.* **27**: 341–354.
5. EPRI. (2000). An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants. Technical Report 100608. EPRI, Palo Alto, CA, p. 6–1.
6. Smith, K. and Anderson, W. (1981). Distribution and accumulation of trace metals at a coal-fired power plant and adjacent cooling lake. *Illinois Natural History Survey Bulletin*. **32**: 691–730.
7. Pinkney, A., Logan, D., and Wilson, H. (1997). Mercury concentrations in pond fish in relation to a coal-fired power plant. *Archives of Environmental Contamination and Toxicology*. **33**: 222–229.
8. Suloway, J., Roy, W., Skelly, T., Dickerson, D., Schuller, R., and Griffin, R. (1983). Chemical and Toxicological Properties of Coal Fly Ash. Environmental Geology Notes 105, Illinois State Geological Survey, Champaign, IL, p. 22.
9. Cherkauer, D. (1980). The effect of flyash disposal on a shallow ground-water system. *Ground Water*. **18**: 544–550.
10. Simsian, G., Chesters, G., and Andren, A. (1987). Effect of ash disposal ponds on groundwater quality at a coal-fired power plant. *Water Res.* **21**: 417–426.
11. Giattina, J., Cherry, D., Cairns, Jr., J., and Larrick, S. (1981). Comparison of laboratory and field avoidance behavior of fish in heated chlorinated water. *Trans. Amer. Fisheries Soc.* **110**: 526–535.
12. Wright, D. and Zamuda, C. (1991). Copper contamination in the Patuxent River, Maryland. *Hydrobiologia*. **215**: 31–41.
13. Carlson, C. and Adriano, D. (1992). Environmental impacts of coal combustion residues. *J. Environ. Qual.* **22**: 227–247.
14. Theis, T. and Gardner, K. (1990). Environmental assessment of ash disposal. *Crit. Rev. Environ. Contr.* **20**: 21–42.
15. Rowe, C., Hopkins, W., and Congdon, J. (2002). Ecotoxicological implications of aquatic disposal of coal combustion residues in the United States: A review. *Environ. Monitor. Assess.* **80**: 207–276.
16. Coutant, C. et al. (1978). Chemistry and biological hazard of a coal ash seepage stream. *J. Water Pollution Control Fed.* **4**: 747–753.
17. Van Hassel, J. and Wood, K. (1984). Factors affecting aquatic macroinvertebrates below a fly ash pond discharge. *Freshwater Ecol.* **2**: 571–585.
18. Specht, W., Cherry, D., Lechleitner, R., and Cairns, Jr., J. (1984). Structural, functional, and recovery responses of

stream invertebrates to fly ash effluent. *Canadian J. Fisheries Aquat. Sci.* **41**: 884–896.

19. Cherry, D., Guthrie, R., Sherberger, F., and Larrick, S. (1979). The influence of coal ash and thermal discharges upon the distribution and bioaccumulation of aquatic invertebrates. *Hydrobiologia.* **62**: 257–267.
20. Reash, R., Van Hassel, J., and Wood, K. (1988). Ecology of a Southern Ohio stream receiving fly ash pond discharge: changes from acid mine drainage conditions. *Arch. Environ. Contam. Toxicol.* **17**: 543–554.
21. Cherry, D. and Guthrie, R. (1977). Toxic metals in surface waters from coal ash. *Water Resources Bull.* **13**: 1227–1236.
22. Reash, R., Lohner, T., Wood, K., and Willet, V. (1999). Exotoxicological assessment of bluegill sunfish inhabiting a selenium-enriched fly ash stream. In: *Environmental Toxicology and Risk Assessment: Standardization of Biomarkers for Endocrine Disruption and Environmental Assessment.* D. Henshel, M. Black, and M. Harras (Eds.). 8th Vol. ASTM STP 1364. American Society for Testing and Materials, West Conoshohocken, PA, pp. 423–445.
23. Lohner, T., Reash, R., Willet, V., and Rose, L. (2001). Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting a selenium-laden coal ash effluent. 1. Hematological and population level assessment. *Ecotoxicol. Environ. Safety.* **50**: 203–216.
24. Lohner, T., Reash, R., and Williams, M. (2001). Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting a selenium-laden coal ash effluent. 2. Tissue biochemistry and histochemical evaluation. *Ecotoxicol. Environ. Safety.* **50**: 217–224.
25. Lohner, T., Reash, R., Willet, V., and Fletcher, J. (2001). Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting a selenium-laden coal ash effluent. 3. Serum chemistry and fish health indicators. *Ecotoxicol. Environ. Safety.* **50**: 225–232.
26. Olmsted, L., Degan, D., Carter, J., and Cumbie, P. (1991). Ash basin effluents as a concern of fisheries managers: a case history and perspective. In: *Reservoir Fisheries Management: Strategies for the 80's*. G. Hall and M. Van Den Avyle (Eds.). American Fisheries Society, Bethesda, MD, pp. 261–269.
27. Baumann, P. and Gillespie, R. (1986). Selenium bioaccumulation in gonads of largemouth bass and bluegill from three power plant cooling reservoirs. *Environ. Toxicol. Chem.* **5**: 695–701.

ENERGY DISSIPATION

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Many process industries, such as oil refining or chemical manufacture, need to cool products or intermediate streams that may be either liquids or gases, before storage or further processing. To conserve heat and hence costs, it is usual to transfer as much heat energy as possible from an outgoing "hot" stream to an incoming cold stream or intermediate. However as the temperature of the "hot" stream is reduced, there comes a point where it is no longer economical or feasible to reduce the temperature of the stream to be cooled by further interchange of heat. As the temperature of the "hot" stream approaches the temperature of the incoming stream, the temperature driving force for heat transfer is reduced so that a relatively large heat transfer area is required to complete the cooling process. In general, naturally occurring water has a relatively low temperature and because there is so much of it in the world—in seas, lakes, rivers, canals, and boreholes—water is used as a universal cooling medium. The increasing world shortage of water, however, requires effective water management to conserve supplies and to protect the environment.

Apart from process industries, cooling is essential for efficient use of fuel for power generation. In the power industry, steam is usually made by combusting fossil fuel, biomass, or flammable waste, such as domestic refuse. The steam produced is used to power turbines, which drive electricity generators. It is possible to arrange for the exhaust steam from the turbines to be discharged at atmospheric pressure, but if the exhaust steam is condensed, the pressure drop across the turbine is increased so that additional energy from the steam can be converted into electrical energy. Heat removal from the steam that reduces the steam pressure is usually achieved in water cooled condensers, adding significantly to the overall efficiency of the power station in converting the chemical energy stored in the fuel to electrical energy.

The use of water for cooling purposes has several advantages. It is generally plentiful, although in some arid parts of the world it is not available in adequate quantities. Under these circumstances, air cooling is likely to be preferred. Water has a relatively high heat capacity and a relatively wide operating temperature range. It is easily transported around a cooling circuit by pumping. It is reusable, provided that its temperature, after use as a coolant, can be reduced and it is suitably treated to prevent operational problems that would otherwise occur.

COOLING WATER SYSTEMS

Three cooling water systems are used in industry: enclosed recirculating, open recirculating, and "once through" systems.

Enclosed Recirculating Systems

In the enclosed recirculating system, the water is totally enclosed and isolated from the atmosphere. In operation, the water takes heat from the process stream or condensing steam in a suitable heat exchanger and is then pumped through air blown coolers. Usually the tubes in these coolers are finned on the air side to improve the heat transfer from the water to the air stream. The air passes through the cooler by natural draft or is forced through by a suitable fan. The air may be drawn through the heat exchanger by a fan mounted on top of the exchanger, in which case it is known as an "induced draft" cooler. Alternatively, a fan mounted below the cooler is called a "forced draft" system. Provided that the water is suitably treated to avoid deposition and corrosion problems and the water quality is monitored frequently, the enclosed system can operate for long periods of time with a minimum of attention. The system is not common, however, at least in temperate zones, because of the additional capital cost involved, largely due to the fact that the heat is removed from the water as sensible heat. It is more usual to remove the heat gained by the cooling water by evaporating some of the water to the atmosphere in an open recirculating system. The removal of latent heat necessary to vaporize the water lowers the water temperature.

Open Recirculating Systems

It is possible to effect the necessary evaporation in a "spray pond." Here, water is sprayed into the atmosphere out of nozzles mounted on horizontal pipes. The pipes themselves are mounted in a concrete "pond." The evaporating droplets of water fall back into the pond for reuse in the recirculating system. The desired cooling can be achieved by adjusting the spray conditions.

In an open recirculating system, however, it is more usual to employ a cooling tower to evaporate some of the recirculating water, as illustrated in Fig. 1. In this technique, the water falls over suitable packing contained in the cooling tower. For many years, the packing in cooling towers consisted of a large number of wooden slats over which the water trickled as a film. The purpose of the packing was to maximize the contact area between the airflow and the water film. The use of wood was far from ideal because the damp wood and the favorable temperature conditions led to the growth of fungi on the packing and this, as well as the increased weight, tended to weaken the integrity of the wooden structure. Failure of the wooden structure was not uncommon in the past. In recent times, plastic materials that resist fungal growth have been used to fabricate packing. The use of these materials, molded to shape, has allowed more sophisticated designs of packing to be introduced, which maximize evaporation of water in the tower under given operating conditions.

It is usual to maintain the airflow by natural convection, as illustrated in Fig. 1. It is possible, however, to have special designs where the airflow is driven by a motorized fan, as described for the enclosed cooling system to create induced or forced circulation.

In the cooling tower, water is lost from the system by evaporation and what is known as "windage," as illustrated in Fig. 2. The windage is made up of droplets of water that leave the top of the tower and are often seen as a plume downwind from the tower. Water loss also occurs from any leakage from the system and from "drift loss" in the region of the cooling tower basin. The water used in open recirculating systems is usually taken from natural sources such as lakes, rivers, or canals and therefore contains dissolved solids in addition to biologically active material, such as microorganisms.

As water is removed from the system by evaporation, the concentration of the dissolved solids increases. Therefore, it is necessary to discard some of the recirculating water, usually back to the source, and replace it with "makeup" water from the source, which has a lower concentration of dissolved solids. The deliberate discharge of water is usually referred to as "blowdown." It may be continuous or intermittent, depending on the rate of buildup of dissolved solids. The "makeup" water (M) has to replace that lost from the system by all mechanisms and from Fig. 2,

$$M = E + W + L \tag{1}$$

A concentration factor n may be defined by

$$n = \frac{\begin{array}{c}\text{Dissolved solids concentration}\\ \text{in the blowdown water}\end{array}}{\begin{array}{c}\text{Dissolved solids concentration}\\ \text{in the makeup water}\end{array}} \tag{2}$$

In general n is in the range of 3–5, but it depends on the operating conditions in the cooling tower.

Blowdown B may be calculated ignoring windage and leakage water losses which are usually small compared with the evaporation, so that

$$B = \frac{E}{(n-1)} \tag{3}$$

Once Through System

In the once through system, water is taken from the source, passed through the system, and discharged back to the source without cooling. The technique reduces the capital cost of the installation, but there may be environmental problems associated with the temperature of the discharge water in relation to the temperature of the water source, a problem which is usually referred to as "thermal pollution." Local regulations may restrict the allowable thermal pollution of the natural source

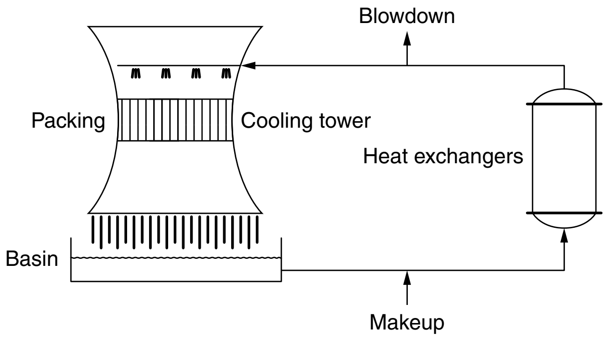

Figure 1. Recirculating cooling water system with cooling tower.

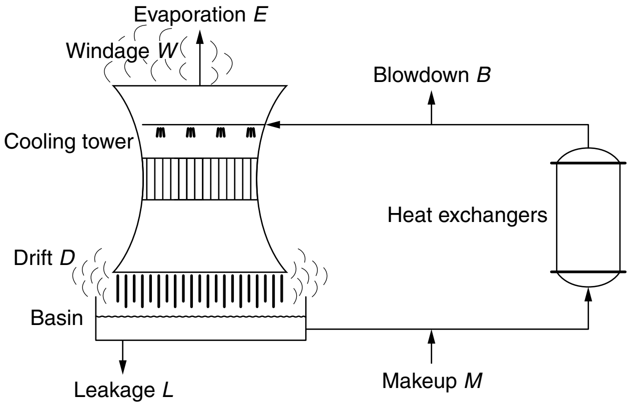

Figure 2. Water loss from a cooling tower circuit.

on account of its possible effect on the ecology of the water source.

Water Treatment

The origin of the water from a natural source in cooling water systems means that it can give rise to operating problems, generally associated with the heat transfer surfaces. Fouling may result from particulate deposition, microbial growth, or corrosion. These phenomena, the factors which influence them, and the methods available for control, are described elsewhere in this encyclopedia. Fouling is often controlled by chemical additives. Of general concern in open recirculating systems employing cooling towers or spray ponds is the presence of *Legionella* bacterium in the circulating water. Unless adequate precautions are taken, the bacterium may be present in the plume of water droplets, which leaves the top of the cooling tower or in the droplets above a spray pond. As a result, personnel who happen to be downwind of the tower or spray pond are susceptible to infection from the contaminated water. It is imperative for health and safety, quite apart from other considerations, to monitor the quality of the water within the system frequently and regularly.

CONCLUDING REMARKS

It is likely that the use of water for energy dissipation will continue in the future, but with greater emphasis on environmental protection and health and safety. It will increasingly be subject to regulation. To comply with the demands of legislators, the costs of operating the system are likely to be substantial. Effective management is necessary to keep the costs to a minimum.

WATER USE IN ENERGY PRODUCTION

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The United States uses far more water to produce energy and electricity than any other sector. A slight reduction in water use in the electricity sector would far outweigh other modes of saving—toilets using less water, low-flow shower heads,—in the household sector.

Most attention here will be devoted to thermoelectric and hydroelectric plants. Thermoelectric plants can be divided into fossil fuel—coal, oil, and natural gas—and nuclear. These constitute almost all the electricity producers in this country.

However, this may not always be the case in the future. Some government reports and projections have said that renewables—solar, wind, geothermal, ocean thermal—will be used more in coming years. The so-called Kyoto Protocol (unratified at this time) anticipates a decrease of thermoelectric plants (due to their emissions of carbon dioxide, a greenhouse gas) and increased use of renewables. For example, in Denmark now about 10% of its electricity is supplied by windpower.

Water use is usually defined and measured in terms of withdrawal or consumption. The former is what is taken, and the latter is that which is used up. Water withdrawal in energy production is much greater than consumption. In hydroelectric plants, far more water is used than in any other energy source. However, the amount of water consumed—that is, not available for further use—is a small fraction of the water used and is attributable to evaporation from lakes behind hydro dams. Energy consumption for thermoelectric plants is of the order of 2% of water used.

Some of the water used to produce energy becomes contaminated with pollutants. This aspect of energy production is not discussed in this article; it is treated in detail in other articles in this publication.

Units

Units in the discussion of energy water use are both English and metric. The graphs here use metric units. Where the original form is English, metric units follow in parentheses, using the conversion factor $1\ \text{m}^3 = 275$ gallons.

OVERALL WATER USE IN ENERGY PRODUCTION

More water is used for energy production than in any other sector in the United States, according to the Geological Survey (1). Of the 402,000 million gallons ($1460 \times 10^6\ \text{m}^3$) per day of withdrawals, 189,000 million (690×10^6), or 47%, was used in thermoelectric plants. Irrigation was second at 134,000 million gallons ($490 \times 10^6\ \text{m}^3$) per day.

During 2000, total U.S. net generation of electricity was $3{,}800 \times 10^9$ kWh (2). Of this, coal generated 1,967 (in the same units), or about 52%. This was followed by 754 from nuclear (20%), 612 from gas (15%), 273 from hydro (7%), 109 from petroleum (3%), and 84 from renewables (2%). Total fossil fuel electricity production was 2,688 billion kWh.

Of the renewables in the first six months of 2001, 0.37% of total production was from geothermal, 1.7% from biomass, 0.19% from wind, and 0.018% from solar (2).

CONVENTIONAL ENERGY SYSTEMS

Thermoelectric Water Use and Consumption

Most water withdrawn for thermoelectric power production is used for condenser and reactor cooling. Consumption of water was much less, at about 3,700 million gallons ($13.5 \times 10^6\ \text{m}^3$) per day, about 2% of the total amount of water withdrawn.

What is the rate of water withdrawal for the four types of thermoelectric plants noted before? Official data are divided into fossil fuel and nuclear (3). It is not clear how geothermal data are handled, but this forms only a small proportion of total electricity production. Fossil fuels have a total withdrawal of 135,000 million gallons ($490 \times 10^6\ \text{m}^3$) per day and consumption of about

2,800 (10×10^6 m^3) in the same units. For nuclear, the corresponding values are 54,500 (198×10^6 m^3) and 900 (3.3×10^6 m^3).

It would be of interest to determine (1) water use per unit of energy generated for each of the three fossil fuels—coal, gas, petroleum—compared to nuclear, (2) how the values varied within each type of energy, and (3) the relationship of water use to thermal efficiency of each type, but the data are not available in the official document.

However, the data above show that fossil fuels have a withdrawal of 67 m^3 per megawatt-hour (MWh) and consumption of 1.4 in the same units. For nuclear, the corresponding values are 97 and 1.6, respectively. The results are shown in Fig. 1. Hydroelectric values, to be discussed later, are also included.

Figure 1 uses a logarithmic scale because of the large amount of water use per unit of energy output for hydroelectricity. Values for water use in nuclear power are higher than for fossil fuels, primarily because of the lower thermal efficiency of the former. However, water consumption for both nuclear and fossil fuels are about the same. The ratio of consumption to water use for hydro, while not specified in official data, is much less than the approximately 2% for thermoelectric plants.

Two major documents dealing with water use in energy production in recent years, other than the Geological Survey document, are Gleick (4) and a German official publication (5). The values shown in the German document for thermoelectric plants using noncirculating water use (6), 160–220 m^3 per MWh, are somewhat higher than those in Fig. 1. Cooling water losses, or consumption, usually stay below 2% of water use, again in accordance with Fig. 1. The document also refers to small water requirements, in addition, of the order of 0.1 m^3 per MWh, for topping up the steam cycle, cooling the ashes, and operating certain types of flue-gas purification equipment (spray absorption, wet processes).

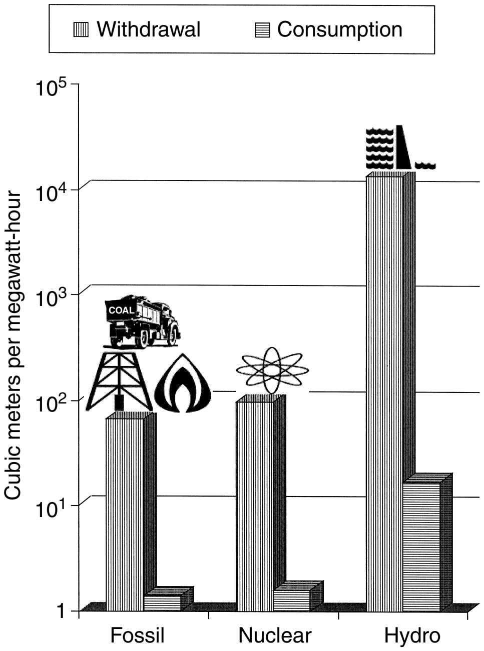

Figure 1. Water withdrawal and consumption rates for fossil fuels, nuclear and hydroelectricity, in cubic meters per MWh of electricity generated.

Reference 7 shows "consumptive water use" (taken to mean consumption as opposed to withdrawal) for the three main fossil fuels plus nuclear in m^3 per 10^{12} joules (thermal). Reference 7 considers many aspects of the fuel cycle, in addition to the generation phase, for each of the four major electricity sectors, that is, an attempt is made to estimate water requirements for the entire fuel cycle. This is in contrast to the Geological Survey and German documents, which concentrate on the generation phase. However, no indication is given in Ref. 7 about which of the components of water use for each technology is in widespread use.

For example, under nuclear, nuclear fuel reprocessing is shown as requiring about 50 m^3 of consumption per 10^{12} joules (thermal), the largest, by a factor of 2.5, of any of the nuclear components. But this aspect of nuclear technology is not in use in the United States.

Similarly, for the oil cycle, six possibilities are shown for enhanced oil recovery. The highest, micellar polymer, has the largest water consumption of any of the components for the four major technologies listed in the table. But it is not stated how common this technology is.

A later table (8) in Ref. 4 shows the average water consumption per megawatt-year for just the generating phase of the four major electricity sources. Results are then on the same basis as that of the official data. The values for fossil fuels with once-through cooling are comparable to those of Fig. 1, so they will not be repeated here. The results for coal and oil-fired generation are shown for both once-through cooling and cooling towers, although most fossil-fuel generation in the United States uses the former cooling method. Cooling towers consume about twice the amount of water of once-through cooling. The results in Ref. 8 for coal, oil, and gas are similar, so averaging over the three fossil fuels in Fig. 1 is reasonable.

Nuclear Power Water Use

Reference 3 states that nuclear plants use and consume somewhat higher amounts of water per MWh produced than fossil fuel plants. However, there are some proposed models of nuclear plants that will use and consume less. For example, the so-called MHTGR (modular high temperature gas reactor), due to its greater thermal efficiency, should require both less water use and consumption than other types of nuclear plants (9). At present, the MHTGR is not deployed in the United States.

In Ref. 8, only cooling towers are shown for nuclear generation, although most nuclear plants, like fossil-fuel plants, use once-through cooling. This produces a consumption value of about twice the official data, and tends to make nuclear look more water-consuming than is the case.

Hydroelectricity Water Use

Hydroelectricity produced about 6% of all U.S. electricity in the first 8 months of 2001. The proportion varies slightly from year to year, depending on rainfall, runoff, and other factors. In some countries, such as Canada and Norway, the proportion is much higher. Hydro is clearly a renewable system, but it is included in this section because it is conventional and widely used.

Water use for hydroelectric purposes is by far the largest of all U. S. energy sources, at 3,160,000 million gallons ($11{,}500 \times 10^6$ m^3) per day. This is about 2.6 times the total of the total annual runoff of the lower 48 states (10). This refers only to the withdrawal of water, the amount that passes through lakes and hydro dams.

Water is consumed, or evaporates, from the lakes behind dams. One set of estimates is from Ref. 11. The range of values for California dams is enormous, a factor of about 5,000 between the most water-conserving dams (measured in water consumption per MWh) and the most profligate. The variation will depend on such factors as the size of the lake, dam height and type, contours of the land, and outdoor temperatures.

For the United States, the average value is about three times that of the California average (12). The results are shown in Fig. 1. Average water consumption, per MWh, for hydro plants is about one-quarter the total withdrawal of fossil-fuel plants. If the most water-consuming dam had been used as a maximum for hydro, its value would have been greater than the entire water use for fossil and nuclear.

In 1995, 310×10^9 kWh of hydroelectricity were produced. This required 3,160,000 million gallons ($11{,}500 \times 10^6$ m^3) per day of withdrawals. So about 10 gallons (0.036 m^3) day, or 3700 gallons (13 m^3) per year, is required per kWh. The national average cost per kWh (enough to light a 100-watt light bulb for 10 hours) is about 8¢; so this implies that about 450 gallons (about 1.6 m^3) of water are required to produce about 1¢ of hydroelectricity value.

NONCONVENTIONAL ENERGY WATER USE

The key point in estimating water use and consumption by renewable energy systems was stated by the California Energy Commission (13): "In determining whether a particular fuel is 'clean' or not, consideration must be given to environmental impacts across the entire fuel cycle of the type of generation proposed (e.g., including fuel production, transportation, refinement, and generation)."

Renewable energy made up about 2% of all electricity production in the United States in the first 8 months of 2001. This fraction has changed only slightly in recent years. It has been widely claimed that this fraction will increase substantially in coming decades. Whether these claims are true can be verified only by the passage of time. Their present total water use is extremely small. All values presented here are only approximations. As more data are gathered, it is likely that many, if not all, of the values in this section will change. The German study (14) discusses the water implications of renewable energy sources, but nonquantitatively. It does make clear, however, that the entire fuel and energy cycle should be considered, not merely one aspect. This is also the implication of Reference 7.

Material Requirements for Energy Systems

To compare renewables with conventional energy systems in a consistent manner, the ratio of water use, both indirect and direct, per unit of energy or electricity output is required. The place to start is materials requirements for energy systems. The results of one calculation are shown in Fig. 2 (15).

Materials requirements for renewables, per unit of energy output, tend to be much higher than those for conventional energy systems. The main exception is hydro, but most of the requirements there are rock and earth, which require little water use. Solar and windpower generally are very dilute per unit volume compared to fossil and nuclear fuels. Thus considerably more collecting apparatus, again per unit energy output, is required. In turn, the collecting apparatus requires considerable material (and associated labor).

Water Use for Materials in Energy Industries

The next step is to estimate the water use for each of the materials shown in Fig. 2. For steel, the German study noted before estimates 5 m^3 per metric ton (16). This is in accordance with other estimates. On the other hand, "mini-mills generate up to 80 m^3 (of water use) per metric ton of steel product" (17). The value of 5, used here, may be different in non-Western countries. It is estimated that China requires 23–56 m^3 per ton (18).

For aluminum, one estimate is 1.5 tons of water (19) per ton of product. Another detailed look at the aluminum

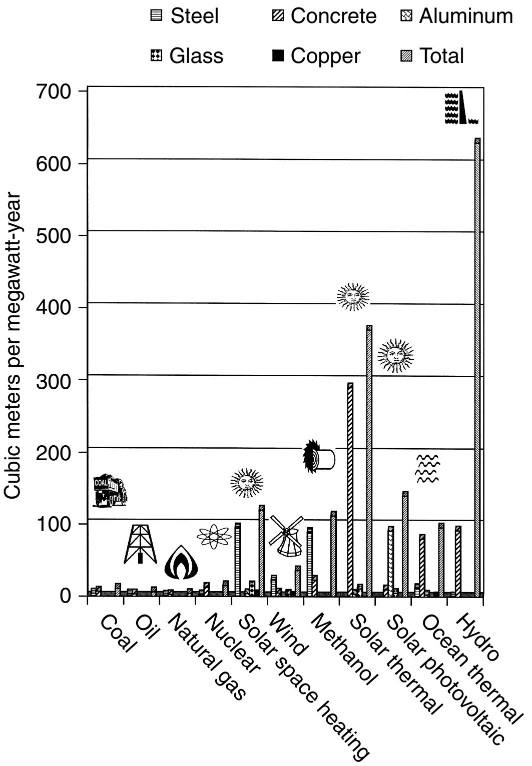

Figure 2. Material requirements for energy systems, per megawatt-year net output. Fuel—coal, oil, gas, and nuclear fuel—is not included.

industry suggests 5 m^3 of process water per metric ton of alumina and 1.88 m^3 of alumina per metric ton of aluminum. This then implies 2.6 m^3 of water per ton of aluminum, and this value is used here (20).

For copper, although water is undoubtedly used in its production, it proved difficult to obtain reliable data. For glass, "The average water consumption in a glass works should be less than 1 m^3/t of glass produced" (21). For cement, about 1–1.6 m^3 of water per metric ton of cement is required, depending on whether the dry or wet process is used (22). Concrete is one part cement to 6–8 parts other materials, so water use is adjusted accordingly.

Noted that values for water in materials production are likely use, not consumption. The data sources do not always make the distinction. The results for water use are as follows in m^3 per metric ton: steel, 5; aluminum, 2.6; copper, not available; glass, 1; cement, 1–1.6; and concrete, 0.1–0.25.

Indirect Water Use for Energy Systems

The indirect water use attributable to the materials used in all energy systems may be estimated by multiplying the values for specific materials in the preceding paragraph by the materials used per unit of energy output in Fig. 2. No values could be found for copper, so it is not included in the calculations. Its inclusion would change results only slightly. Minima and maxima of the results are shown as the bottom two components in the columns of Fig. 3.

Because of the wide differences between both components and the total of each column, the results are shown on a logarithmic scale. In each column, the lowest entry is for the minimum of indirect water use. The next highest entry is for the maximum of this component. Hydro has the highest amount of material use in Fig. 2, but almost all is rock and earth, assumed to have negligible water requirements. For coal-, oil-, and gas-fired, nuclear and hydro plants, values for direct water use are taken from Fig. 1. These are the next highest components of each column. Some technologies, such as solar photovoltaic, have negligible direct water use, so this component for their columns is blank. For solar thermal plants, an estimate of direct water consumption, as opposed to use, is available (23). It is assumed here that the ratio of water use to consumption for thermoelectric plants, approximately 50, also applies to this technology. Solar space heating, although included in Fig. 2, is excluded here because its output is thermal, not electrical.

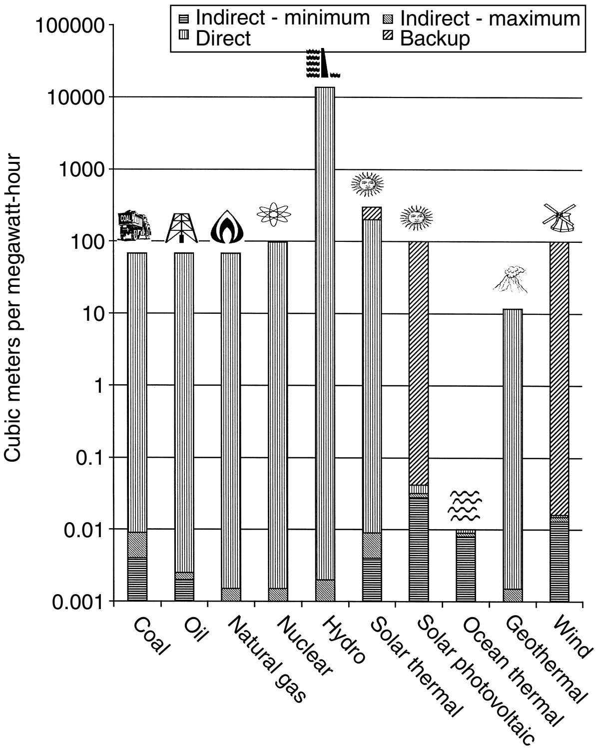

Figure 3. Water use per kWh output for conventional and renewable systems.

For geothermal, only values of consumption, not use, are available (23). Three values, for plants in the United States and New Zealand, have data, and the average was taken. It is likely that water use is higher than consumption for geothermal. One source states (24), "A geothermal plant produces much more wastewater than a coal-fired or atomic power plant," although no data on the proportion seem available. Backup water use, to be discussed in the next section, is shown for three energy systems.

Backup Energy and Electricity

Many articles dealing with renewable energy systems (other than geothermal and biomass) acknowledge the need for backup when the sun does not shine and the wind does not blow (25–29). The assumption is that consumers want reliable power, at least as reliable as present conventional systems. Given the fact that utilities are deluged with complaints after a power outage due to weather or other reasons, this is a reasonable assumption.

As a specific example of backup needed, consider Solar Two, one of the world's largest solar thermal plants. "During one stretch in the summer of 1998, the plant operated for 32 of 39 days", according to a U.S. Department of Energy Website dubbed "success stories" (30). Although this was only a demonstration project, in real life, consumers would be concerned about no power for 7 out of 39 days. Its average energy production was about 20% of its rating; fossil-fuel and nuclear plants routinely operate at 80% or more.

What proportion of backup is necessary? Estimates vary, depending on a host of factors: the variation of sunlight and wind, how much reliability is expected of renewable sources, whether the source is to be for peak power demands, and so on. Sørensen (31) notes that the "fuel-based supply system [for renewables] ... is a tenth of average load," that is, about 10% of conventional—fossil fuel, nuclear, and hydro in national proportions—electricity sources will be assumed as backup. Systems like geothermal, ocean thermal, and biomass require no backup because they produce energy continuously.

This proportion will change from one part of the country to another. For example, the proportion of hydro in the Pacific Northwest is higher than that in other parts. This would tend to make water use and consumption for backup higher there than elsewhere, on the basis of Fig. 1.

Backup would not apply to such renewable sources as biomass and geothermal, which produce power about as reliably as conventional energy systems. Using the values of Fig. 1 and the proportions of electricity production from fossil fuels, nuclear and hydro from earlier, an average national kWh of electricity would require 1.0 m^3 of water withdrawal and 0.0025 of consumption. Even though hydro is only about 7% of national electricity production, it generates about 95% of electricity water withdrawal and about half of water consumption. If an average backup of 10% is assumed, this implies 0.1 m^3 of withdrawal and 0.00025 of consumption per kWh of underlying energy attributable to backup.

SUMMARY

Most attention in water use and consumption has been focused on fossil-fuel and nuclear plants, though renewable energy systems, both present and in the future, can use considerable water when the entire energy cycle is considered. Hydro is classified as a renewable energy source by the Energy Information Administration and many other authors. It uses about 100 times the water and about ten times the consumption of thermoelectric plants, per MWh generated. Thermoelectric and hydro plants produce about 98% of all U.S. electricity. But hydro requires about 95% of all electricity water use and about half of electricity water consumption.

A number of conclusions can be drawn from Fig. 3. First, it clearly is important to take all aspects of the fuel or energy cycle into account when estimating water use and consumption. Second, hydro clearly has the highest water use (and consumption) of any major present or future energy electricity source. Third, although the material requirements estimated in Fig. 1 are useful, they affect overall results only slightly. Fourth, although Ref. 4 suggests that water use by most renewable energy sources will be negligible, Fig. 3 shows that this is not the case. Hydro and solar thermal rank the highest. Fifth, ranges of data are not shown in this figure except for water use associated with materials requirements, but remember that values in most cases are approximate and vary considerably. Sixth, ocean thermal (OT) apparently has the lowest water use of any of the technologies considered. OT uses considerable water in operation, but all of it is saline. Seventh, backup requirements make a considerable difference in water use for some renewable energy systems. Eighth, geothermal ranked second lowest of the systems, but its water use is probably underestimated in the graph, for the reasons explained in the caption.

In summary, to make rational decisions about which systems use more or less water, the entire fuel or energy cycle must be taken into account. Figure 3 shows the results of such calculations.

BIBLIOGRAPHY

1. Solley, W.B., Pierce, R.R., and Perlman, H.A. (1998). *Estimated Use of Water in the United States in 1995*. U.S. Geological Survey Circular 1200, US Government Printing Office, Offstream Use, Washington, DC.
2. Energy Information Administration (2001). *Electric Power Monthly*. November 2001. EIA, Washington, DC.
3. Ref. 1, op cit., *Thermoelectric Power.*
4. Gleick, P.H. (1994). Water and energy. *Annual Review of Energy and the Environment* **19**: 267–299.
5. German Federal Ministry for Economic Cooperation and Development (GFM). (1995). *Environmental Handbook*. Documentation on monitoring and evaluating environmental impacts, Vol. 2. Agriculture, Mining/Energy, Trade/Industry, GTZ GmbH, Eschborn, Germany.
6. Ref. 5, GFM, op. cit., Section 41.2.2.
7. Ref. 4, op. cit., Table 4, *Consumptive Water Use for Energy Production*.
8. Ref. 4, op. cit., Table 5, *Consumptive Water Use for Electricity Production*.
9. Neylan, A.J. Dilling, D.A., and Cardito, J.M. (1991). Environmental aspects of MHTGR operation. *Energy* **16**(1–2): 441–448.
10. Solley et al. op. cit., *Hydro Power*.
11. Ref. 4, op. cit., Table 7. *Average Annual Water Losses from California Hydroelectric Facilities*, in m^3 per 10^3 kWh per year.
12. Ref. 4, op. cit., Table 5.
13. California Energy Commission. (2001). *Energy Innovations Small Grant Program*.
14. Ref. 5, GFM, op. cit., Section 43, Renewable sources of energy.
15. Inhaber, H. (1982). *Energy Risk Assessment*. Gordon & Breach, New York, p. 36. Earlier versions of this study had some errors, which were removed by the time the book was published. About two-thirds of the book is devoted to responses to critics. One of the major critics of the original study later came to similar conclusions about the relative risk ranking of the technologies considered. This was noted by Watson (Watson, A.P. et al. (1983). *Health Implications of Unconventional Energy Production and Use, in Alternative Energy Sources*, Vol. 9, Policy/Environment, Hemisphere Publishing, Washington, DC, p. 249, who stated that “the conclusions of the two analyses [Inhaber’s and that of a major critic] are the same” [in terms of where the greatest health risks are]. A similar point is made by Sims (Gordon, H.E.S. (1990). *The Anti-Nuclear Game*. University of Ottawa Press, Ottawa, Canada) and others, too numerous to list here.
16. Ref. 5, op. cit., Section 49.2.
17. World Bank Group. (1998). *Pollution Prevention and Abatement Handbook*.
18. (1998). *Population Reports* **26**(1): 20.
19. Gleick, P.H. (2001). *Scientific American* **284**(2): 40.
20. (1997). *Energy and Environmental Profile of the US Aluminum Industry*. Energetics, Columbia, MD, pp. 29–30.
21. Ref. 5, GFM, op. cit., Section 48.2.
22. Ref. 5, GFM, op. cit., Section 46.2.
23. Ref. 4, op. cit., Table 5.
24. Found at http://www.geol.binghamton.edu/faculty/naslund/205.lect20c.html (Geology 205, Earthquakes and Volcanoes, Lecture 17, Geothermal Energy). The site was developed by H. Richard Naslund, Professor of Geology, State University of New York at Binghamton.
25. Cao, J. and Christensen, R.N. (2000). Modeling an integral dual solar/gas-fired generator for a water–lithium bromide absorption chiller. *Journal of Energy Resources Technology* **122**(4): 217–223. “Natural gas serves as the backup heat when the solar energy is unavailable or insufficient.”

26. Rhodes, R. and Beller, D. (2000). The need for nuclear power. *Foreign Affairs* **79**(1): 30–45. "A global solar-energy system without fossil or nuclear backup would also be dangerously vulnerable to drops in solar radiation from volcanic events such as the 1883 eruption of Krakatoa, which caused widespread crop failure during the "year without a summer" that followed."
27. Williams, R.H. (1990). Low-cost strategies for coping with CO_2 emission limits. *Energy Journal* **11**(4): 35. "Luz (solar thermal) units are hybrid systems with natural gas firing capacity added as backup" ... "PV systems (and wind systems as well) can be used in hybrid configurations with natural gas-based backup power, as in the case of solar thermal units."
28. Carta, J.A. and Gonzalez, J. (2001). Self-sufficient energy supply for isolated communities: wind-diesel systems in the Canary Islands. *Energy Journal* **22**(3): 115. "A wind-driven generator to convert wind energy to electrical energy, back-up diesel generators (for when there is no wind)."
29. Hansen, U. (1998). Technological options for power generation. *Energy Journal* **19**(2): 63. "The principal disadvantage of solar is the dependence on variable sunshine hours and the resulting short capacity utilisation as well as the need for energy storage and back-up systems."
30. Available: http://www.eren.doe.gov/success_stories/opt_solartwo.html.
31. Sørensen, B. (2000). *Renewable Energy: Its Physics, Engineering, Use, Environmental Impacts, Economy and Planning Aspects*. Academic, San Diego, CA, p. 676.

EVALUATION OF TOXIC PROPERTIES OF INDUSTRIAL EFFLUENTS BY ON-LINE RESPIROMETRY

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Industrial effluents often contain chemical compounds that have potential toxic properties which upon co-treatment with municipal wastewaters may affect the operation of a wastewater treatment plant. Respiration measurements, corresponding to the estimation of oxygen uptake rate (OUR) of living microorganisms, may be used to evaluate the toxic properties of industrial wastewaters, estimate their biological treatability, and predict the impact on the performance of a wastewatewater treatment plant. Several commercial on-line respirometric biosensors have been developed for monitoring various parameters such as carbon/nitrogen biological removal, anaerobic digestion, and activated sludge settling; these systems have common characteristics such as a simple measurement principle, low amount of chemicals required during their use, and the absence of a sample pretreatment step. On-line biosensors may be used as early warning tools in treatment plants, to protect plant operation and to increase efficiency, contributing to the development of toxicity management plans, especially in plants treating industrial wastes.

INTRODUCTION

The activated sludge process is considered today the most effective method for the biological treatment of wastewaters. The activated sludge process is based on the development of a heterogeneous microbial community in an aeration basin, which allows the system to be flexible with regard to considerable fluctuation in the influent wastewater composition. The activity and the concentration of the microorganism populations are crucial for the effective operation of the system, and the presence of certain toxic substances in increased concentrations in the influents may result in the reduction of microorganism activity. The effect of toxic substances on the more sensitive nitrifying bacteria is especially important, as these bacteria have a very low reproduction and growth rate (1,2). Toxic throughput is one of the major causes of the failure of biological treatment plants and results in noncompliance with discharge permit limits.

The operation of wastewater treatments plants has become an essential issue in European Union countries. According to Directive 91/271/EEC, all wastewaters in the territories of the European Union have to be collected and treated by appropriate methods prior to their discharge into a water receiver. In addition, municipalities with more than 15,000 inhabitants should have constructed and operated a wastewater treatment plant by the year 2000, whereas municipalities of more than 2000 inhabitants should have a secondary wastewater treatment plant by the end of 2005 to be able to discharge their wastewaters to a freshwater receiver. Furthermore, industrial wastewaters should be subjected to the same provisions as municipal wastewaters. In practice, industrial wastewaters are often discharged to a domestic collecting system and are fed to a municipal wastewater treatment plant for co-treatment. Thus, several municipal wastewater plants are receiving industrial wastewaters, which are often partially treated or even untreated; as a result, failure of the operation of municipal wastewater treatment plants is often attributed to the presence of certain compounds of industrial origin whose properties are potentially toxic to activated sludge microorganisms. Therefore, continuous monitoring of the potential toxic properties of influents is very important, prior to their introduction into the biodegradation process, to improve effluent quality, reduce operating cost, and increase reliability.

Conventional chemical analysis methods alone have been found inadequate for evaluating the toxic properties of wastewaters and for ensuring that the influents will not have significant effects on the receiving sewage works. Industrial wastewaters are characterized as complex mixtures of varying concentration of pollutants that may affect system performance. However, inhibitory metals and specific organic compounds may be detected in an industrial wastewater, but these data alone do not prove that the growth of bacteria and protozoa comprising the activated sludge biomass of the aeration basin will be suppressed. In addition, analytical chemical scans are very expensive and time-consuming and provide circumstantial evidence of the inhibitory nature of the waste. Furthermore, the toxicity of multicomponent mixtures to activated sludge microorganisms may differ from an additive response because synergistic or antagonistic interactions between mixture components may make the mixture more toxic than predicted by summing the effects of each individual toxicant (3). Consequently, an alternative method is necessary to evaluate the impact of industrial wastewaters on the performance of a domestic activated sludge treatment plant, based on assessing the toxicity of influents in a wastewater treatment plant.

TOXICITY ASSESSMENT OF INDUSTRIAL WASTEWATERS

Several biotests have been developed for evaluating wastewater toxicity to determine the toxic level of compounds to aquatic organisms. Test organisms that have been incorporated in bioassays include plants, invertebrates, fish, and microorganisms (4). Species that are widely used for determining the ecotoxic quality of freshwaters include (5,6): brook trout (*Salvelinus fontinalis*), Coho salmon (*Oncorhyncus kisutch*), bluegill (*Lepomis macrochirus*), channel catfish (*Ictalurus punctatus*), and invertebrates such as crayfish (*Pacifastacus leniusculus*) and Cladocera (*Daphnia magna, Daphnia pulex, Ceriodaphnia* spp.). In addition, marine species have been used for examining the ecological condition of seawater, including red algae (*Champia parvula*) and mysid shrimp (*Mysidopsis bahia*).

However, most of these bioassays are time-consuming and require scientifically skilled personnel and specific equipment. Moreover, the use of higher organisms, such as a fish, as a test species may be ethically undesirable. As a result, the development of an early warning system for monitoring the toxicity of influents is necessary. The last years of research has been directed to examinating of appropriate toxicity tests that are rapid, easy to operate, and inexpensive. Bacterial screening tests using microorganisms have been studied for their ability to assess the toxicity of wastewaters based on various principles such as microbial transformations, determination of microbial enzymes, and measurement of luminescent activity or respiration rate (5,7).

Most of the bacterial screening tests, such as the Microtox®, ToxAlert®, and the Mutatox® tests, which are used to detect cytotoxic and genotoxic agents, respectively, measure bioluminescence (8–10). The basic technology of these tests is using luminescent bacteria, specifically the strain *Vibrio fischeri*, to measure the toxicity of environmental samples. When properly grown, luminescent bacteria produce light as a byproduct of their cellular respiration. Cell respiration is fundamental to cellular metabolism and all life processes. Bacterial bioluminescence is tied directly to cell respiration, and any inhibition of cellular activity (toxicity) results in a decreased rate of respiration and a corresponding decrease in the rate of luminescence. The more toxic the sample, the greater the percentage of light lost from the test suspension of luminescent bacteria. Bacterial bioluminescence has proven a convenient measure of cellular metabolism and consequently, comprises a reliable sensor for measuring the presence of toxic chemicals in aquatic samples and for determining the toxicity of single compounds, mixtures of compounds, and industrial wastes (11). The particular strain was originally chosen for acute and chronic tests because it displayed high sensitivity to a broad range of chemicals.

The Microtox® acute test has been successfully used for a variety of environmental applications:

- wastewater treatment plant influent and effluent testing,
- toxicity reduction evaluations (TREs) and toxicity identification evaluations (TIEs), and
- assessment of soil contaminated with metals and energetic compounds.

However, the relevance of the information obtained by these bioassays is not considered essential for operating a municipal wastewater treatment plant, and continuous monitoring of the toxicity of industrial wastewaters is not achieved by such methods. Toxicity detected by *Vibrio fischeri* cannot always be associated with a biochemical cause that will exert the same activity reduction on the biomass culture in an activated sludge process (12). In general, toxicity assessment by Mictotox® may result in overestimating the acute toxicity effect on the biomass operating in a plant (13).

The key determinant in the response of a wastewater treatment plant is microbiological behavior. Thus, a proper estimate of the effect of toxic influents on an activated sludge unit should incorporate a system that closely mimics the conditions in the target plant because the response of a bacterial culture to a change in environmental conditions is highly dependent on the culture's physiological state, that is, it is determined by its growth history. Therefore, alternative techniques for on-line detection of toxicity relying on respirometric techniques, using activated sludge as the biological material, are considered the most suitable. Devices based on these techniques are easily operated, need minimum maintenance, and give fast and relevant responses (14–16). Respirometry was recognized many years ago as a key parameter for process control because it is a direct measure of the viability and activity of biological organisms. Therefore, respirometry plays an important role in detecting toxicity and in process control of wastewater treatment plants.

TOXICITY ASSESSMENT OF INDUSTRIAL EFFLUENTS BY RESPIROMETRIC TECHNIQUES

Respirometry is the measurement of oxygen uptake rates (OUR) of living biomass, such as activated sludge microorganisms, and can be used as an indicator of microbial activity in an aerobic biomass. On-line respirometry thus provides dynamic measurements of biological activity as well as a measure of the organic strength of a wastewater, which in turn gives an indication of the effective capacity of the system when sampled throughout the system.

Activated sludge is a flocculent mixture of microorganisms, mainly bacteria, which degrade multiple substrates to grow. The active organisms in the biomass of an activated sludge facility are contained in the solid phase and depend for growth on the carbohydrates, proteins, nucleic acids, and lipids contained in the influent to the plant. The organisms require dissolved oxygen to oxidize the organic food in wastewater and to provide organic carbon to synthesize the compounds necessary for reproduction. This oxygen consumption is referred to as respiration. Respiration is intimately linked to the growth of the activated sludge and to biodegradation.

In activated sludge heterotrophic bacteria which consume organic carbon, the carbon taken up is divided between that which is broken down in respiration and that which is built up into macromolecules for growth. The relationship between respiration, growth, and total carbon uptake (which equals biodegradation) is shown in Fig. 1.

By measuring the respiration rate (A), it is possible to calculate the amount of organic carbon (B) that is being used to provide energy. (A) can therefore be used to predict (B). Respiration rate (A) can also be used to predict the energy used in growth. It can be assumed that there is a proportional relationship between this energy and the amount of carbon being used for growth (C). (A) can therefore be used to predict (C). (B) + (C) equals the total carbon uptake, which equals the rate of biodegradation. Respiration rate (A) predicts (B) and (C), so it can be used to predict the rate of biodegradation. The situation in nitrifiers is simpler because the oxygen uptake rate provides a direct measure of ammonia biodegradation. These two mechanisms show the central role of the respiration rate (or more strictly, oxygen uptake rate, OUR) in the aerobic breakdown process.

In heterotrophic bacteria, toxic compounds in wastewater can inhibit either growth or respiration. Because of the tight linkages among respiration, growth, and biodegradation, it is obvious that if growth is inhibited, the requirement for energy decreases, and the respiration rate is reduced. Less carbon is required for respiration, so the rate of carbon uptake or biodegradation decreases. At the same time, the amount of carbon that is incorporated in growth is reduced. This also leads to reduced biodegradation. Conversely, if the toxic compound inhibits respiration, the amount of carbon for respiration is reduced, leading to reduced biodegradation. A decreased supply of energy from respiration results in a reduced growth rate and hence a lowered rate of carbon uptake or biodegradation. From this it can be seen that wherever the toxicity acts, there is inhibition of both the respiration rate and the rate of biodegradation. Nitrifiers are particularly prone to inhibition by toxic substances. Inhibition of either growth or the energy yielding oxidation reactions results in a decrease in both oxygen uptake rate and rate of uptake biodegradation of ammonia. The oxidative processes of respiration and nitrification that underlie the breakdown and removal of organic carbon and ammonia may be measured by respirometry, using specific biosensors.

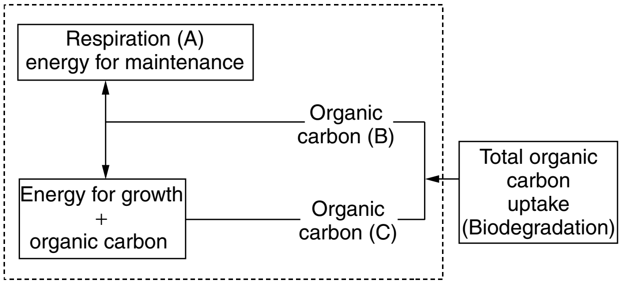

Figure 1. Relationship between respiration, growth, and biodegradation in heterotrophic bacteria.

Eight different types of respirometers have been developed, and in general they may be distinguished according to two criteria (17): (1) the phase where oxygen concentration is measured (liquid or gas) and (2) the method of liquid/gas introduction (flowing or static). Most respirometric methods are based on measuring the oxygen content in the liquid phase by using a dissolved oxygen (DO) probe. Static gas respirometers may be operated with a static or a flowing liquid phase. The static gas–static liquid respirometer is operated by withdrawing a sample of activated sludge from the aeration tank of a treatment plant, transferring it into a small reactor vessel, and then monitoring the decline of DO concentration by the time following a short aerated phase. The use of static gas–liquid respirometers is restricted due to potential problems from oxygen limitation. This type of respirometer, however, has the benefits of simple construction and measurement principle (18–20).

Flowing gas–static liquid respirometers, on the contrary, are continuously aerated and have the advantage that higher sludge concentrations can be used because there is a continuous input of oxygen, though oxygen limitation is unlikely (21). In this case, the oxygen transfer coefficient and the saturation DO concentration have to be known to calculate the respiration rate. Static gas–flowing liquid respirometers measure the DO concentration at both the inlet and the outlet of a closed respiration chamber (22). Aerated sludge is pumped continuously through the respiration chamber. The oxygen uptake rate is calculated by making an oxygen mass balance over the respiration chamber using the input and output DO concentration and the residence time in the vessel.

Several commercial biosensors have been presented for determining the toxicity of industrial effluents and assessing activated sludge plant performance, such as the Rodtox (Fig. 2a), the Stiptox (Fig. 2b), and the Manotherm. The Rodtox consists of a temperature controlled reactor vessel, which is filled with about 10 liters of activated sludge continuously aerated and stirred, while the dissolved oxygen concentration is monitored (21). Injection of a biodegradable calibration liquid in the reactor leads to a peak in the dissolved oxygen concentration. The total surface and the maximum height of the peak are proportional to the amount of BOD added, and the maximum slope of the respirogram is a measure of the activity of the activated sludge. The BOD of an unknown sample (short-term BOD, $\mathrm{BOD_{st}}$) is obtained by comparing the respirogram of the sample with that of the calibration liquid (23). Toxicity can be detected by comparing the peak of the calibration liquid before and after the addition of the sample. Stiptox is a toxicity analyzer with immobilized turbulent-bed biology where the microbes grow on the

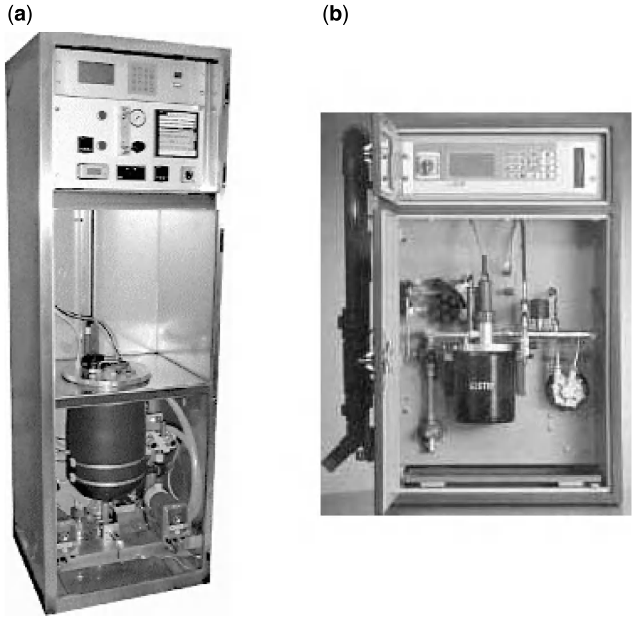

Figure 2. Commercial on-line toxicity biosensors: (**a**) Rodtox; (**b**) Stiptox.

inner surface of small hollow cylinders (24). Like the activated sludge of a treatment plant, the microbial population in the bioreactor is adapted to the conditions of the wastewater. As long as the wastewater is not toxic to the adapted biology, the organisms in the bioreactor take up dissolved oxygen. A toxic impact inhibits the respiration of the organisms, causing an increase in the dissolved oxygen level.

An alternative biosensor incorporating bacterial cells that can be used for rapid ecotoxicity analysis has been developed by Evans et al. (25). The amperometric biosensor device was called Cellsense and used ferricyanide, a soluble electron mediator, to divert electrons from the respiratory system of the immobilized bacteria to a suitable poised carbon electrode. The resulting current was, thus, a measure of bacterial respiratory activity, and the perturbation by pollutants could be detected within minutes as a change in the magnitude of the current.

In addition to carbonaceous removal, respirometric measurements are useful for monitoring nitrifying sludge activity and biological nitrogen removal. The interest in the nitrification capacity of activated sludge results from the higher sensitivity of nitrifiers to toxic compounds compared with heterotrophs (1). However, the main problem in measuring nitrifying capacity is separation of the nitrification oxygen uptake from the oxygen uptake for carbon substrate oxidation and endogenous metabolism. In general, batch experiments using activated sludge in the endogenous state may be used to determine nitrifying activity. In static gas–static liquid respirometers, the increase in OUR due to nitrification may be observed just after the addition of a certain amount of NH_4^+ (26). Respirometric methods consisting of pulse substrate additions to activated sludge cannot be used for estimating nitrification activity, as fresh substrate for both carbon oxidation and nitrification is continuously provided by the fresh wastewater entering the plant. Thus, selective nitrification inhibitors should be added; in this case, the experimental procedures consist of two subsequent phases. Initially, the total OUR of the sludge is measured, a nitrification inhibitor is added to the sludge, and OUR is measured again. The actual nitrification rate is then estimated by the difference between the two OUR values (20). Furthermore, respirometric experiments have been used to identify and quantify nitrogen nutrient deficiency in activated sludge processes (27). These methods may be applied to evaluate potential nitrogen nutrient deficiency and to estimate the amount of nitrogen required to remedy a nutrient deficiency in the sludge.

Respirometers have been used for detecting influent toxicity in wastewater treatment plants, using nitrifying bacteria as the indicating organisms, by the addition of specific nitrifying inhibitors (19,28). Nevertheless, specific techniques have been reported based on the implementation of bacteria from nitrifying enriched cultures containing no or little heterotrophic bacteria, where the addition of nitrification inhibitors is not necessary (19,28).

CASE STUDY: EXAMINATION OF INDUSTRIAL EFFLUENTS BY A RESPIROGRAPHIC BIOSENSOR

To evaluate the effect of industrial discharges on the performance of a municipal wastewater treatment plant, a biosensor (Rodtox, Kelma, NV) was installed in the industrial area of Thessaloniki, Greece. Several production plants are included in the Greater Industrial Area such as metal processing units, food industries, chemical-agrochemical, and pharmaceutical companies. Effluents from each process are partially treated on site and are discharged into a common pipe. Currently, industrial wastewaters are further treated in an industrial wastewater treatment plant; in the near future, industrial effluents will be fed to the Thessaloniki municipal wastewater treatment plant. The inhibition of the activity of activated sludge microorganisms due to the addition of industrial discharges to the respirometric biosensor, was estimated from the corresponding respirometric curves (21).

During the measuring period, activated sludge from the Thessaloniki municipal wastewater treatment plant was used as the biological material in the respirometric sensor. Activated sludge properties were considered as remaining almost similar during the monitoring time, as the wastewater treatment plant was fed by domestic wastewaters and its operation was maintained at constant conditions. In addition, the influence of the properties of activated sludge on the inhibitory results were periodically examined using calibration substances of known toxicity (solution of $ZnCl_2$), and slight differences were observed in the respirometric response. Similar results regarding the effect of the activated sludge origin have been already reported, underlying the insignificant influence of activated sludge on inhibition data (11).

Characteristic values measured in industrial wastewater samples are presented in Table 1. As shown in this

Table 1. Characteristic Values of Wastewaters from the Thessaloniki Industrial Area, mg/L

Parameter	Min	Max	Average
pH	7.1	8.3	7.6
BOD_5	71	2640	553
COD	155	4027	975
Ammonium nitrogen	2	317	62
Kjeldahl nitrogen	9	526	90
Total phosphorous	2	8	5
Suspended solids	148	376	249

table, industrial wastewaters in general were more polluted than municipal wastewaters; organic compounds reached up to 1000 mg/L COD. As a result, continuous monitoring of the toxicity of industrial discharges was very important to protect the co-treatment plant. Fluctuations in characteristic values could be attributed to seasonal variations, nontreated effluents, or effluents from processing units for which on-site wastewater treatment systems presented operating problems.

The short-term BOD of industrial wastewaters (BOD_{st}) and the corresponding inhibition of the respiration of activated sludge microorganisms during a 6-month period are shown in Figs. 3 and 4, respectively. High variation in both inhibition values and BOD_{st} was observed as a result of the complex nature of the samples. Short-term BOD values reached up to 3300 mg/L, and the corresponding inhibition values reached up to 98%, indicating that these wastewaters were toxic to the activated sludge microorganisms and could adversely affect the operation of the municipal treatment plant.

From the analysis of the relation between short-term BOD and inhibition of microorganism respiration during the particular period, it was concluded that the organic content of the industrial samples did not correlate directly with the toxicity of the samples. Samples of high toxicity, exceeding 35% inhibition, had BOD_{st} values ranging from low values up to 3000 mg/L. On the other hand, samples of low toxicity had a variation of organic loading from low levels up to levels exceeding 3000 mg/L. According to this observation, factors other than organic substances might affect the toxicity of the samples, such as inorganic compounds and especially metals and their speciation (29).

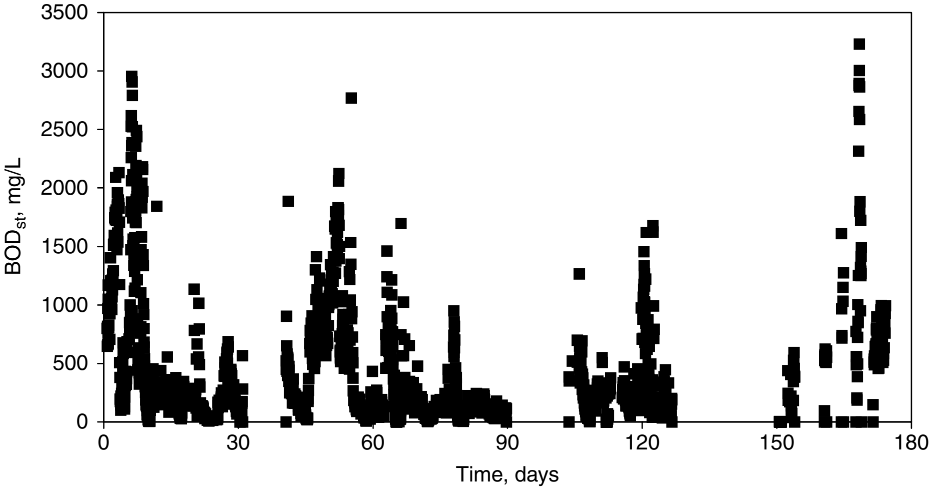

Figure 3. Short-term BOD values of industrial wastewaters, measured by an on-line toxicity meter.

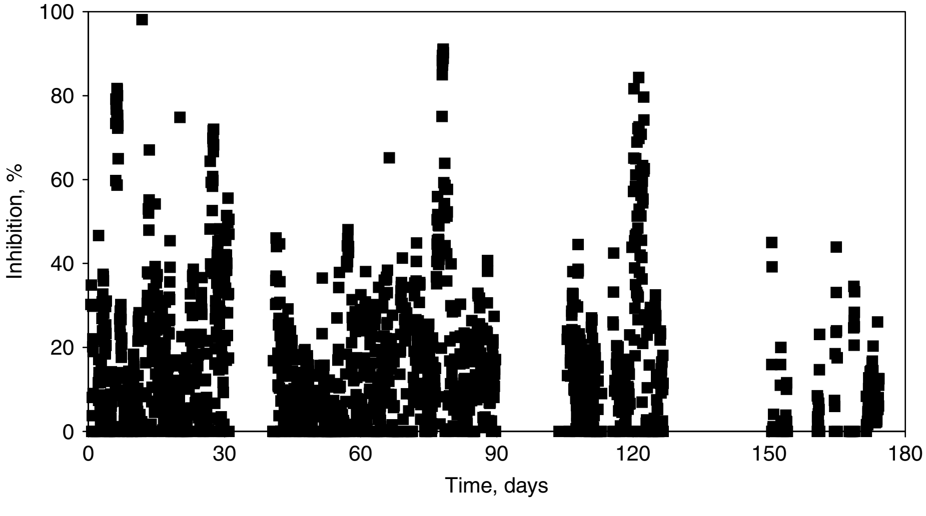

Figure 4. Inhibition of the respiration of active sludge microorganisms by the addition of industrial wastewaters.

Statistical analysis of the collected inhibition data was performed to obtain the daily toxicity distribution of industrial effluents; the characteristic values are shown in Table 2. In addition, the weekly frequency of toxicity values exceeding 35% inhibition is included in this table. As shown, the highest average toxicity values were observed on Saturday and Sunday, reaching about 18.5 and 20%, respectively. However, the maximum toxicity was observed on Tuesday evening. In addition, industrial effluents of high toxicity were supplied to the system on Thursdays and during weekends, corresponding to about 70% of the total number of values exceeding 35% inhibition. Furthermore, from the examination of the daily variation of inhibition values exceeding 35%, it was found that 63% of the peak inhibition values were observed during the night from 23:00 to 07:00. These results could be attributed to the reduced control of existing wastewater treatment systems in industrial plants, resulting in discharge of wastewater of low quality.

In conclusion, respirometry is an indispensable tool for assessing the biological treatability of industrial wastes separately and in combination with municipal wastewaters and for providing significant information about the impact of toxic effluents on the performance of a wastewater treatment plant. The benefit of on-line respirometric measurement is that it is a microcosm of the treatment facility and of what really affects process success. It shows the relative strength of the wastewater, how much treatment is needed, and the quality of the effluent produced.

Common characteristics of respirometric biosensors are the simple measurement principle, the low amount of chemicals required during their use, and the absence of a sample pretreatment step. Several biosensors have been developed to monitor various parameters such as biological removal of carbon and nitrogen, anaerobic digestion, and activated sludge settling characteristics that provide detailed information about important activated sludge processes. On-line respirometric biosensors may be used as early warning systems in influent toxic load detection, protecting the wastewater treatment plant from toxic shocks (30). Thus, their use in wastewater treatment plants supports the development of appropriate control strategies (31) to protect the efficient operation of a plant, to optimize system performance by better control of the treatment plant, and to improve effluent quality.

Table 2. Average Values and Daily Toxicity Variation of Industrial Discharges, %

Day	Min	Max	Average	Values Exceeding 35% Inhibition
Monday	0	79.7	13.7	10.7
Tuesday	0	98.1	7.7	0.9
Wednesday	0	64.4	8.4	2.8
Thursday	0	81.7	17.6	21.5
Friday	0	88.4	13.5	15.3
Saturday	0	91.1	18.5	23.9
Sunday	0	84.3	19.9	24.8

BIBLIOGRAPHY

1. Blum, D.J.W. and Speece, R.E. (1991). A database of chemical toxicity to environmental bacteria and its use in interspecies comparisons and correlations. *Res. J. Water Pollut. Control Fed.* **63**: 198–207.
2. Krois, P., Schweighofer, P., Frey, W., and Matsche, N. (1992). Nitrification inhibition—a source identification method for combined municipal and/or industrial wastewater treatment plants. *Water Sci. Technol.* **26**(5–6): 1135–1146.
3. Kungolos, A., Samaras, P., Kipopoulou, A.M., Zoumboulis, A., and Sakellaropoulos, G.P. (1999). Interactive toxic effects of agrochemicals on aquatic organisms. *Water Sci. Technol.* **40**(1): 357–364.
4. U.S. Environmental Protection Agency. (1991). *Technical Support Documents for Water Quality-Based Toxics Control*. EPA 502/2-90-001. Office of Water, U.S. EPA, Washington, DC.
5. Farre, M., Pasini, O., Carmen-Alonso, M., Casillo, M., and Barcelo, D. (2001). Toxicity assessment of organic pollution in wastewaters using a bacterial biosensor. *Anal. Chim. Acta* **426**: 155–165.
6. Farre, M. and Barcelo, D. (2003). Toxicity testing of wastewater and sewage sludge by biosensors, bioassays and chemical analysis. *Trends Anal. Chem.* **22**(5): 299–310.
7. Anderson, K., Koopman, B., and Bitton, G. (1988). Evaluation of INT-dehydrogenase assay for heavy metal inhibition of activated sludge. *Water Res.* **22**(3): 349–353.
8. Chen, C.Y., Huang, J.B., and Chen, S.D. (1997). Assessment of the microbial toxicity test and its application for industrial wastewaters. *Water Sci. Technol.* **36**(12): 375–382.
9. Chen, C.Y., Chen, J.N., and Chen, S.D. (1999). Toxicity assessment of industrial wastewater by microbial testing method. *Water Sci. Technol.* **39**(10–11): 139–143.
10. Dos Santos, L.F., Defrenne, L., and Krebs-Brown, A. (2002). Comparison of three microbial assay procedures for measuring toxicity of chemical compounds: ToxAlert® 10, CellSense and Biolog MT2 microplates. *Anal. Chim. Acta* **456**: 41–54.
11. Dalzell, D.J.B., Alte, S., Aspichueta, E., de la Sota, A., Etxebarria, J., Gutierrez, M., Hoffmann, C.C., Sales, D., Obst, U., and Christofi, N. (2002). A comparison of five rapid direct toxicity of pollutants to activated sludge. *Chemosphere* **47**: 535–545.
12. OECD Method 209. (1987). Activated sludge, respiration inhibition test. In: *OECD Guidelines for Testing of Chemicals*. OECD, Paris, France.
13. Ricco, G., Tomei, M.C., Ramadori, R., and Laera, G. (2004). Toxicity assessment of common xenobiotic compounds on municipal activated sludge: Comparison between respirometry and Microtox®. *Water Res.* **38**: 2103–2110.
14. Vanrolleghem, P.A., Kong, Z., and Coen, F. (1996). Full-scale on-line assessment of toxic wastewaters causing change in biodegradation model structure and parameters. *Water Sci. Technol.* **33**(2): 163–175.
15. Ubay, E., Sozen, S., Orhon, D., and Henze, M. (1998). Respirometry analysis of activated sludge behaviour-I. Assessment of the readily biodegradable substrate. *Water Res.* **32**(2): 461–475.
16. Gutierez, M., Etxebarria, J., and de las Fuentes, L. (2002). Evaluation of wastewater toxicity: Comparative study between Microtox® and activated sludge oxygen uptake inhibition. *Water Res.* **36**: 919–924.
17. Spanjers, H., Vanrolleghem, P., Olsson, G., and Dold, P. (1996). Respirometry in control of the activated sludge process. *Water Sci. Technol.* **34**(3–4): 117–126.

18. Drtil, M., Nemeth, P., and Bodik, I. (1993). Kinetic constants of nitrification. *Water Res.* **27**: 35–39.
19. Gernaey, K., Bogaert, H., Massone, A., Vanrolleghem, P., and Verstraete, W. (1997). On-line nitrification monitoring in activated sludge with a titrimetric sensor. *Environ. Sci. Technol.* **31**: 2350–2355.
20. Gernaey, K., Vanderhasselt, A., Bogaert, H., Vanrolleghem, P., and Verstraete, W. (1998). Sensors to monitor biological nitrogen removal and activated sludge settling. *J. Microbiological Methods* **32**: 193–204.
21. Vanrolleghem, P.A., Kong, Z., Rombouts, G., and Verstraete, W. (1994). An on-line respirographic biosensor for the characterization of load and toxicity of load and toxicity of wastewaters. *J. Chem. Technol. Biotechnol.* **59**: 321–333.
22. Vanrolleghem, P. and Spanjers, H. (1994). Comparison of two respirometric principles for the determination of short-term biochemical oxygen demand. *Proc. 49th Ind. Waste Conf.*, May 9–11, Purdue University, West Lafayette, IN, pp. 177–188.
23. Kong, Z., Vaerewijck, M., and Verstraete, W. (1996). On-line stBOD measurement and toxicity control of wastewaters with a respirographic biosensor. *Environ. Tech.* **17**: 399–406.
24. Teutscher, M. and Grosser, J. (1994). Experiences with on-line toxicity analysers in municipal and industrial waste water treatment plants. *Eur. Symp. Biol. Resort Continuous Monitoring Water Qual.*, October 13–14, Nancy, France.
25. Evans, M.R., Jordinson, G.M., Rawson, D.M., and Rogerson J.G. (1998). Biosensors for the measurement of toxicity of wastewaters to activated sludge. *Pest. Sci.* **54**: 447–452.
26. Nowak, O. and Svardal, K. (1993). Observations on the kinetics of nitrification under inhibiting conditions caused by industrial wastewater compounds. *Water Sci. Technol.* **28**(2): 115–123.
27. Ning, Z., Patry G.G., and Spanjers, H. (2000). Identification and quantification of nitrogen nutrient deficiency in the activated sludge process using respirometry. *Water Res.* **34**(13): 3345–3354.
28. Aivasidis, A., Hochscherf, H., Rottman, G., Hagen, T., Mertens, M.T., Reiners, G., and Wandrey, C. (1992). Neuere Konzepte zur Prozessuberwachung und—regelung bei der biologischen Stickstoffelimination. *Abwassertechnik* **42**(5): 48–55.
29. Akio, I. and Earnest, G.F. (1996). Speciation of chromium (III) in activated sludge. *Water Sci. Technol.* **68**(3): 301–310.
30. Temmink, H., Vanrolleghem, R., Klapwijk, A., and Verstraete, W. (1993). Biological early warning systems for toxicity based on activated sludge respirometry. *Water Sci. Technol.* **28**(11–12): 415–425.
31. Copp, J.B. and Spanjers, H. (2004). Simulation of respirometry-based detection and mitigation of activated sludge toxicity. *Control Eng. Pract.* **12**: 305–313.

POLYCYCLIC AROMATIC HYDROCARBONS

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Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds that have two or more fused aromatic rings. They have relatively low solubility in water and are highly lipophilic. The term polycyclic organic matter (POM) defines a broad class of compounds that generally includes all organic structures that have two or more fused aromatic rings. Polycyclic organic matter has been identified with as many as seven fused rings and, theoretically, millions of POM compounds could exist; however, only about 100 species have been identified and studied, and typically only a small fraction of them are regularly tested for as part of emissions measurement programs (1). Any effort to quantify emissions of POM relies on the group of compounds or analytes targeted by the test method employed. The EPA has defined these eight major categories of compounds in the class known as POM (2).

- polycyclic aromatic hydrocarbons (PAHs);
- aromatic hydrocarbons that contain nitrogen in a heterocyclic ring;
- aromatic hydrocarbons that contain a carbon–nitrogen double bond (C=NH);
- aromatic hydrocarbons that contain a one-ring carbonyl divalent group (C=O), also known as quinones; contain two-ring carbonyl divalent groups;
- carbonyl arenes that contain hydroxy groups and possibly alkoxy or acyloxy groups;
- oxa arenes are aromatic hydrocarbons that contain an oxygen atom in a heterocyclic ring; thia arenes are aromatic hydrocarbons that contain a sulfur atom in a heterocyclic ring; and
- some polyhalo compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), may be considered POM although they do not have two or more fused aromatic rings.

PAHs, the focus of this article, include naphthalene, phenanthrene, anthracene, fluoranthene, acenaphthalene, chrysene, benz[*a*]anthracene, cyclopenta[*cd*]pyrene, benzopyrenes, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, coronene, and some alkyl derivatives of these compounds. The structural representations of some of these PAHs are presented in this section (Fig. 1).

There are other naming divisions used also. If two or more benzene rings share pairs of carbon atoms resulting in fused aromatic rings, they have been known as polycyclic aromatic hydrocarbons (PAHs) and polynuclear aromatic compounds (PNAs). The PNA classification is more general and includes heterocyclic aromatic compounds (as discussed above in the EPA definitions). The rings constituting PAHs contain only carbon (3). PAH nomenclature is based on 35 IUPAC-prescribed compounds and naming sequences described in detail elsewhere (3).

Most POM compounds are solids that have high melting and boiling points and are extremely insoluble in water. The PAHs are primarily planar, nonpolar compounds whose melting points are considerably higher than 212 °F (100 °C). Phenanthrene, whose melting point is 214 °F (101 °C) and benzo(c)phenanthrene, whose melting point is 154 °F (68 °C) are two exceptions. The molecular weights,

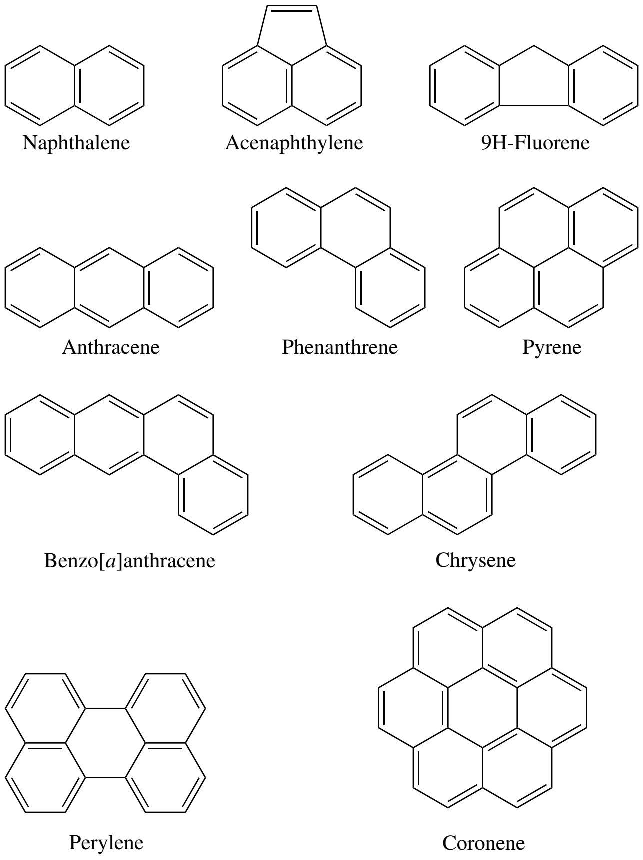


Figure 1. PAH structural representations.

melting points, and boiling points of selected PAH species are listed in Table 1.

The vapor pressures of POM compounds vary depending on the ring size and the molecular weight of each species. The standard vapor pressures of pure PAH compounds vary from 6.8×10^{-4} mmHg for phenanthrene to 1.5×10^{-12} mmHg for coronene (4). Table 1 includes vapor pressures at 25 °C for selected PAHs. Ultraviolet absorption spectra are available for many POM compounds. Most polycyclic aromatic hydrocarbons absorb light at wavelengths found in sunlight (>300 nm) and are believed to be photochemically reactive by direct excitation.

The chemistry of POMs is quite complex and differs from one compound to another. Most of the information available in the literature concerns polycyclic aromatic hydrocarbons. Generally, PAHs are more reactive than benzene, and reactivities toward methyl radicals tend to increase with greater conjugation. Conjugated rings are structures that have double bonds alternating with single bonds. Conjugated compounds are generally more stable, but they are more reactive toward free radical addition (6). For example, in comparison to benzene, naphthalene and benz(a)anthracene, which have greater conjugation, react with methyl radicals 22 and 468 times faster, respectively.

PAHs undergo electrophilic substitution reactions quite readily. An electrophilic reagent attaches to the ring to form an intermediate carbonium ion; to restore the stable aromatic system, the carbonium ion then gives up a proton. Oxidation and reduction reactions occur to the stage where a substituted benzene ring is formed. Rates of electrophilic, nucleophilic, and free radical substitution reactions are typically greater for PAHs than for benzene.

Environmental factors also influence the reactivity of PAHs. Temperature, light, oxygen, ozone, other chemical agents, catalysts, and the surface areas of particulates onto which the PAHs are adsorbed may play a key role in the chemical reactivity of PAHs.

The principal formation mechanism for POM occurs as part of the combustion process in many different types of sources. A secondary formation mechanism, primarily represented by naphthalene production and use categories, is volatilization of lightweight POM compounds. However, the combustion mechanism is much more significant in overall POM formation, and it also much more complex.

Most PAHs that have low vapor pressure in the air are adsorbed on particles. Dissolved in water or adsorbed on particulate matter, PAHs can undergo photodecomposition when exposed to ultraviolet light from solar radiation. In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides, and sulfur dioxide, yielding diones, nitro- and dinitro-PAHs, and sulfonic acids, respectively.

Table 1. Physical Constants of PAHs[a]

PAH	Mol. wt.	Solubility (μg/L)	Vap. Pressure at 25 °C (mmHg)	Log K_{ow} (Log K_{oc})	Henry's Law Constant,[b] atm-L/mole	MP °C	BP °C
Naphthalene	128.2	12,500 to 34,000	1.8×10^{-2}	3.37	4.5	80.5	218
Acenaphthylene	152.2	3420	10^{-3}–10^{-4}	4.07 (3.40)	0.24	96.2	279
Fluorene	166.2	800	1.64×10^{-5}	4.18 (3.86)	0.074	116	295
Anthracene	178.2	59	2.4×10^{-4}	4.5 (4.15)	1.8×10^{-3}	217	340
Phenanthrene	178.2	435	6.8×10^{-4}	4.46 (4.15)	—	100	340
Pyrene	202.1	133	6.9×10^{-7}	4.88 (4.58)	0.013	153	360
Benz[*a*]anthracene	228.3	11.0	1.1×10^{-7}	5.63 (5.30)	1.2×10^{-3}	160	435
Chrysene	228.3	1.9	5.3×10^{-9b}	5.63 (5.30)	6.7×10^{-4}	252	448
Perylene	252.3	2.4	—	6.21	—	274	500
Coronene	300.3	0.14	1.5×10^{-11}	7.36	1×10^{-6}	438	525

[a] Reference 5.

[b] Polycyclic aromatic hydrocarbons (PAHs) database in alphabetical order, http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/00alphabet.html.

PAHs may also be degraded by some microorganisms in the soil (7,8).

PAHs are formed mainly as a result of pyrolytic processes, especially incomplete combustion of organic materials during industrial and other human activities, such as coal and crude oil processing, natural gas combustion, including heating, combustion of refuse, vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization. There are several hundred PAHs; the best known is benzo[*a*]pyrene (BaP). In addition, a number of heterocyclic aromatic compounds (e.g., carbazole and acridine), as well as nitro-PAHs, can be generated by incomplete combustion (7).

Examination of a number of drinking-water supplies for six PAHs (fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, BaP, benzo[*ghi*]perylene, and indeno[1,2,3-*cd*]pyrene) indicated that the collective concentrations generally did not exceed 0.1 μg/L. The concentrations of these six PAHs were between 0.001 and 0.01 μg/L in 90% of the samples and higher than 0.11 μg/L in 1%. Concentrations of BaP in drinking water range to 0.024 μg/L (9).

PAH compound treatment depends upon the end user requirements. Some of the criteria are provided in Table 2. From a treatment perspective, it is only practical to target the objective at the criterion or detection limit (DL), whichever is smaller. In some instances, the practical quantitation limit (PQL) would be the target. Some of the standards shown in Table 2 require values below the PQL (e.g., for benzo [*a*] anthracene $0.013 < 0.044 < 0.13$).

Napthalene and other PAHs by extension are classified as aromatic compounds because they exhibit some of the properties of benzene. Napthalene has the required structure of an aromatic compound (6). It contains six-membered rings, and the atomic orbitals show that the structure can provide π clouds that contain six electrons, as shown in Fig. 2. As illustrated, ten carbons lie at the corners of two fused hexagons. Each carbon is attached to three other atoms by σ bonds. The bonds result from the overlap of trigonal sp^2 orbitals, so all carbon and hydrogen atoms lie in a single plane that has π electron clouds above and below forming a shape like fused toroids by the overlap of p orbitals (6).

Table 2. PAH Detection Limits and Criteria

PAH	Detection Limits[a] DL, μg/L	PQL,[b] μg/L	Drinking Water, μg/L	Surface Water, μg/L
Naphthalene	1.8	18		
Acenapthylene	2.3	23	1200[c]	2700[c]
Acenapthene	1.8	18		
Fluorene	0.21	21	400[d]	
Phenanthene	0.64	6.4		
Anthracene	0.66	6.6	3000,[d] 9600[c]	110000[c]
Fluoranthene	0.21	2.1	400[d]	
Pyrene	0.27	2.7	960[c]	11000[c]
Benzo [*a*] anthracene	0.013	0.13	0.044[c]	0.49[c]
Chrysene	0.15	1.5		
Benzo [*b*] fluoranthene	0.018	0.18	0.2,[d] 0.044[c]	0.49[c]
Benzo [*k*] fluoranthene	0.017	0.17	0.044[c]	0.49[c]
Benzo [*a*] pyrene	0.023	0.23	0.2,[d] 0.7,[e] 0.044[c]	0.49[c]
Dibenz [*a*, *h*]-anthracene	0.03	0.3	0.044[c]	0.49[c]
Benzo [*g*, *h*, *i*] perylene	0.076	0.76		
Indeno [1,2,3-*cd*]-pyrene	0.0043	0.43	0.044[c]	0.49[c]

[a] U.S. EPA Method 8310.

[b] Practical quantitation limit = 10 × detection limit (DL).

[c] State of Virginia, ftp://ftp.deq.state.va.us/pub/watqual/tox/appc.pdf.

[d] State of Wisconsin, http://www.dhfs.state.wi.us/eh/ChemFS/pdf/pah.pdf.

[e] World Health Organization, http://www.who.int/water_sanitation_health/GDWQ/Summary_tables/Tab2b.htm.

PAH compounds, like other aromatic compounds, are resonance hybrids or resonance structures. The following Kekulé diagram illustrates the resonance equilibria (Fig. 3). Unlike benzene, all carbon–carbon bonds are not the same length. However, from a general approach, naphthalene and other PAH compounds are expected to have many of the typical aromatic properties, especially those relating to the π bond and resonance.

Two of the reactions discussed in Morrison and Boyd, (6) including oxidation (Fig. 4) and reduction (Fig. 5), reduce the bond order in PAHs. These can be helpful for researchers and designers in determining some of the potential reactions and treatment in water and possibly solid media. It is also speculated that PAH compounds can be treated via high-energy chemistry (e.g., UV/H_2O_2) to reduce toxicity. This may be assisted by using surfactants because, as previously discussed, PAHs are not very soluble in water and prefer a solid phase. This is discussed after the classical naphthalene reactions.

The first reaction reduces the bond order. The product may or may not be toxic, but the use of chromium is excluded, because it is a listed toxic metal. The second reaction has been commercialized in a different form known as the aqueous electron. However, due to the energetic sodium metal, this is not used for aqueous liquids (10).

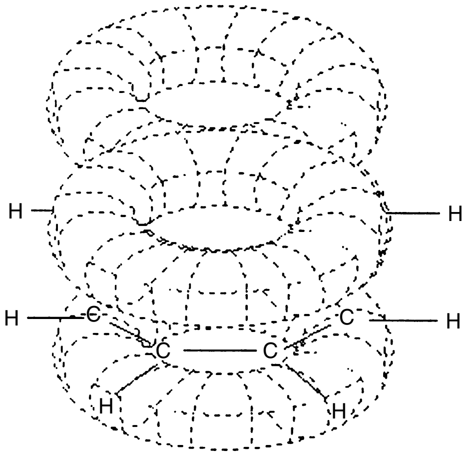


Figure 2. Napthalene π clouds.

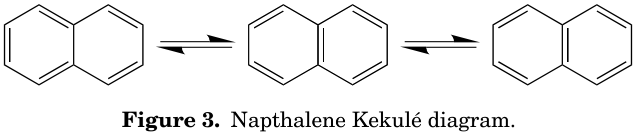


Figure 3. Napthalene Kekulé diagram.

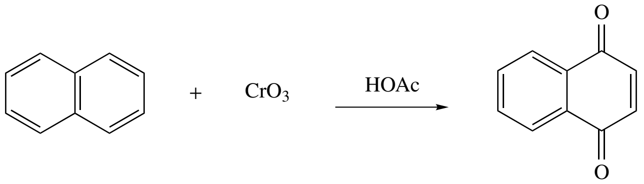


Figure 4. Oxidation using chromate.

A possible reaction path for naphthalene is shown in Fig. 6. This shows that naphthalene produces an aldehyde-ring compound that would be expected to undergo further additions thereby destroying the ring structures and likely forming complex aldehydes.

However, PAHs are sparingly soluble, so only the small amount in the aqueous phase would be removed, and the equilibrium would shift from the solid, if present, to maintain the solubility until there is no appreciable PAH left. It may be possible to use a surfactant to promote solubility and enhance this reaction. This requires evaluation because there are UV interferences, including phosphates, hydroxyl scavengers, and precipitates, all common in waters, that can impact the feasibility of this technology. The section on organic treatment discusses some of these technologies (11).

Because of low volatility, PAH compounds are not generally good candidates for removal by air stripping. The stripping factor (11) shows that quite large quantities of air are required:

$$\frac{G}{L} = \frac{R}{H} \tag{1}$$

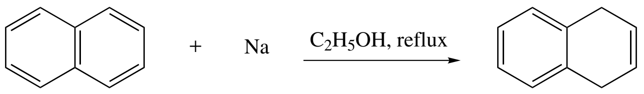
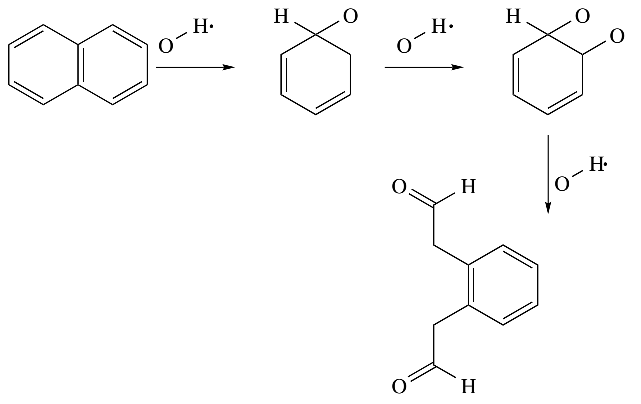


Figure 5. Reduction by sodium in alcohol.



[2-(2-Oxo-ethyl)-pheny]-acetaldehyde

Figure 6. Possible reaction mechanism using UV/H_2O_2.

Using the highest H for Napthalene in the above and a break-even $R = 1$,

$$\frac{G}{L} = \frac{1}{4.5\ \text{atm} - \text{L/mole}}{}^{*}0.0823\ \text{L} - \text{atm/mole/K}^{*}298\ \text{K} = 5.45$$

Assuming a flow of 10 kg/min, the air rate would need to be 54.5 kg/min or 42 standard m^3/ min. This is feasible, but it represents excessive air requirements and becomes unrealistic for the other PAH compounds shown in Table 1.

Frequently, estimates of the air, water, and solid phase concentrations are desired. Assuming that the components of the phases are in equilibrium, the fugacities are equal (12).

$$f_{i,\text{gas}} = f_{i,\text{liquid}} = f_{i,\text{solid}} \tag{2}$$

Therefore, the gas and solid fugacities can be equated with the liquid fugacity. The result for a closed system (e.g., a closed vessel at atmospheric pressure) is

$$x_L = \frac{x}{K_D S + HV + L} \tag{3}$$

$$x_S = \frac{xK_D}{K_D S + HV + L} \tag{4}$$

$$x_V = \frac{xH}{K_D S + HV + L} \tag{5}$$

To illustrate the hydrophobic tendencies and also explain the meaning of K_{ow} in Table 1, the above values are calculated for fluorine. K_D is found from K_{oc} and f_{oc} (13):

$$K_D = K_{\text{oc}}{}^{*}f_{\text{oc}} \tag{6}$$

The octanol–water partition coefficient is a measure of the distribution of an organic compound between water and octanol. It is a general measure of a compound's hydrophobic tendencies. High values indicate hydrophobicity; low values indicate hydrophilic tendencies and hence higher solubility, for example, in alcohol.

K_{oc} can be found by a relation of the sort:

$$\ln K_{\text{oc}} = a \ln K_{\text{ow}} + b \tag{7}$$

However, the value listed for fluorine is log (K_{oc}) = 3.86 so that $K_{\text{oc}} = 7,240$ L/g. Assuming that the organic fraction of the solid is 1% ($f_{\text{oc}} = 0.01$), the solid phase has 10 g, the liquid phase and gas phases are 1 L each, and adding $x = 10$ mg,

$$K_D = K_{\text{oc}}\, f_{\text{oc}} = 72.4$$

$$x_L = \frac{10\ \text{mg}}{72.4\ \text{L/g}^{*}10\ \text{g} + 0.074\ \text{L} - \text{atm/mole}/(0.0823\ \text{L} - \text{atm/mole K}^{*}298\ \text{K})^{*}1\ \text{L}^{*}0.082 + 1\ \text{L}}$$

$$x_L = 0.0138\ \text{mg/L}$$

$$x_S = \frac{10\ \text{mg} \times 72.4\ \text{L/g}}{725} = 1\ \text{mg/g}$$

$$x_V = \frac{10\ \text{mg} \times 0.00302}{725\ \text{L}} = 4.17 \times 10^{-5}\ \text{mg/L}$$

This estimate demonstrates conclusively that PAH compounds are distributed preferentially on solids containing organics. In addition, the solids do not necessarily need to contain organics. However, the presence of the organic fraction ensures high distribution on the solid phase.

If there is no solid, then the fluorine will split into the water phase and a separate PAH phase consisting of nearly pure fluorine,

$$10\ \text{mg} = 0.8(\text{mg/L}) \times L(L) + x\text{mg}$$

or $x = 9.2$ mg in a separate phase with a distinct vapor pressure of 1.64×10^{-5} mmHg. Therefore, the presence of a solid has a very large effect on the distribution between the phases and must be considered in treatment strategies.

Granular activated carbon (GAC) is an excellent technology for removing PAH compounds from water due to its demonstrated isotherms. Freundlich adsorption isotherms available for PAH compounds show that K's vary from 115 for acenapthalene to 376 for anthracene (14). The article in this Encyclopedia on organic treatment (11) provides examples of removing benzene that has a poor Freundlich isotherm, $K = 1.0, 1/n = 1.6$. Removal of PAH compounds using GAC would require far less carbon than that for benzene and be much more efficient.

High-energy chemistry processes for bond reduction and detoxification of PAHs are potentially feasible processes. High-energy chemistry is defined as

$$E > \kappa T \tag{8}$$

This energy is not supplied in the form of heat but through the impact either of an electron, ion, atom, molecule, or photon or by application of electric, magnetic or other fields (15). PAHs are expected to be less refractory (i.e., more reactive toward free radicals) than benzene. As previously discussed, the main problem for these processes is low solubility. However, some of them (e.g., Fenton's reagent) do not depend on light transmittance and can be readily implemented (11).

NOMENCLATURE

a	Constant
b	Constant
E	Energy ML^2/t^2
f	Fugacity Pa
f_{oc}	Fractional organic carbon in solid
G	Gas rate in stripping $M/t/L^2$
H	Henry's law constant
K	Freudlich isotherm coefficient (capacity constant) mg/g*$(L/mg)^{1/n}$
K_D	Distribution coefficient, L/M
K_{oc}	Organic-carbon distribution coefficient, L/M
K_{ow}	Octanol–water distribution coefficient, L/M
L	Liquid phase or liquid rate in stripping, $M/t/L^2$
$1/n$	Freundlich bonding constant
R	Stripping factor
S	Solid phase
x	Concentration, M/L^3
V	Vapor phase
κ	Boltzmann's constant J/K

BIBLIOGRAPHY

1. U.S. Environmental Protection Agency. (1980). *POM Source and Ambient Concentration Data: Review and Analysis*. EPA Report No. 600/7-80-044, Washington, DC.
2. U.S. Environmental Protection Agency. (1975). *Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter (PPOM)*. EPA Report No. 600/6-75-001, Washington, DC.
3. Watts, R.J. (1998). *Hazardous Wastes: Sources, Pathways, Receptors*. John Wiley & Sons, New York.
4. U.S. Environmental Protection Agency. (1978). *Health Assessment Document for Polycyclic Organic Matter*. EPA Report No. 2/102, External Review Draft. Research Triangle Park, NC, pp. 3–1 to 3–47.
5. Neff, J.M. (1979). *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates and Biological Effects*. Applied Science, Essex, UK.
6. Morrison, R.T. and Boyd, R.N. (1978). *Organic Chemistry*, 3rd Edn. Compounds. Allyn and Bacon, Chap. 30.
7. WHO. (1987). Polynuclear Aromatic Hydrocarbons (PAH). *Air Quality Guidelines for Europe*. Copenhagen, World Health Organization Regional Office for Europe, pp. 105–117.
8. Agency for Toxic Substances and Disease Registry. (1994). *Toxicological Profile for Polycyclic Promatic Hydrocarbons (PAHs): Update*. US Department of Health and Human Services, Public Health Services, Atlanta, GA.
9. IARC. (1983). *Polynuclear Aromatic Compounds. Part 1. Chemical, Environmental and Experimental Data*. Lyon, International Agency for Research on Cancer. (IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 32).
10. Ashworth, S.C. (1998). *K Basin Sludge Polychlorinated Biphenyl Removal Technology Assessment*. HNF—3095 DOE Information Bridge. Available: http://www.osti.gov/bridge/.
11. Ashworth, S.C. (2004). *Hydrocarbon Treatment Techniques*. IW71.
12. Thibodeaux, L.J. (1979). *Chemodynamics*. Wiley-Interscience.
13. Hemond, H.F. and Fechner, E.J. (1994). *Chemical Fate and Transport in the Environment*. Academic Press.
14. Pontious, F.W. (1990). *Water Quality and Treatment*, 4th Edn. McGraw-Hill, New York.
15. Bugaenko, L.T., Kuzmin, M.G., and Polak, L.S. (1993). *High-Energy Chemistry*. Ellis Horwood PTR Prentice-Hall.

HYDROCARBON TREATMENT TECHNIQUES

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There are various criteria concerning hydrocarbons for water needs. Some water users have little concern for dissolved hydrocarbons (e.g., agriculture), and some have strict standards (e.g., drinking water). In general the presence of organic compounds, including hydrocarbons, in water can lead to a buildup of biofilms. Biofilms can be problematic in many situations including drinking water, cooling water, recirculating water, and water used for various other industrial processes. During biofilm formation, the first substances on the surface are not bacteria but trace organics (1). Almost immediately after the clean pipe surface comes into contact with water, an organic layer deposits on the water/solid interface (2). These organics form a conditioning layer that neutralizes excessive surface charge and surface free energy that may prevent a bacteria cell from approaching near enough to initiate attachment. In addition, the adsorbed organic molecules often serve as a nutrient source for bacteria.

Though there are many criteria, the thrust of this article is on the treatment, including the removal and destruction of hydrocarbons for whatever purpose. It is assumed in this article that the hydrocarbons are dissolved in water, so that technologies such as incineration or decantation will not apply. The focus will be on water-phase separation and destruction. No economic evaluation is considered. In reality, the trade-offs would need to be considered, for example, waste disposal costs, electrical cost, and materials.

BACKGROUND

In general, water from natural sources will lead to poor cooling performance unless adequate steps are taken to remove hydrocarbon contaminants (3). The extent of the problem, however, will depend on the quality of the raw makeup water. The deposits that occur on heat exchanger surfaces are complex and are likely to include particulate matter, crystalline salts, corrosion products, and biofilms. It is necessary to counteract this problem of deposition onto surfaces to maintain heat exchanger effectiveness.

The shape and structural arrangement of a biofilm growing in a flowing fluid will influence the mass transfer characteristics of the biofilm system as well as the drag force exerted on individual biofilm structures (4). If the biofilm is a highly compliant material, the shape will vary through the growth cycle of the biofilm and also due to variations in fluid shear stress (5). Fluctuations in biofilm shape will also affect the hydrodynamic drag that in turn will influence the detachment rate and pressure losses in a flowing system. In addition, it is thought that biofilm viscoelasticity may explain the large pressure drops observed in biofilm fouled pipes (6).

There are also regulatory standards for certain waters (e.g., drinking water and water discharged to aquifers and bodies of water). Some of these that might apply include the Safe Drinking Water Act (42 U.S.C. 300f et seq.), Clean Water Act (33 U.S.C. 1251 et seq.), Resource Conservation and Recovery Act (42 U.S.C. 6901 et seq.), and a host of others. Many of them provide standards for organic compounds including hydrocarbons in effluents and source waters.

The above are a few reasons for removing organic compounds but there are others, including the pharmaceutical and semiconductor industries that have specific needs and criteria in this regard.

TREATMENT

Separation

Separation is the process of removing a compound from one phase to another (e.g., activated carbon adsorption). One of the simplest methods for separating volatile hydrocarbons and other organic compounds from water is air stripping. An example is benzene, a ring molecule shown in Fig. 1.

A typical stripper is a packed system using Raschig rings or other packing that provides high surface area, as shown in Fig. 2.

Descending water containing dissolved benzene enters the top of the column and is distributed to flow through the packing. The air enters at the bottom contacts the descending water, and the benzene transfers from the water to the air, an interphase mass transfer operation. The clean water is used for the purposes required, and the air is ejected to the atmosphere, regulations permitting, or treated accordingly (e.g., vapor-phase activated carbon).

The driving force for mass transfer is the gradient from the water to the air. At the interface, it is normally assumed that the interfacial water concentration and the air partial pressure are in equilibrium. If the amount of dissolved organic in the water is small enough (water mole fraction not appreciably different from 1.0), equilibrium is expressed using Henry's law (7). Henry's law is a special case of the following relation for gas–liquid

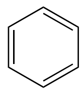

Figure 1. Benzene molecule.

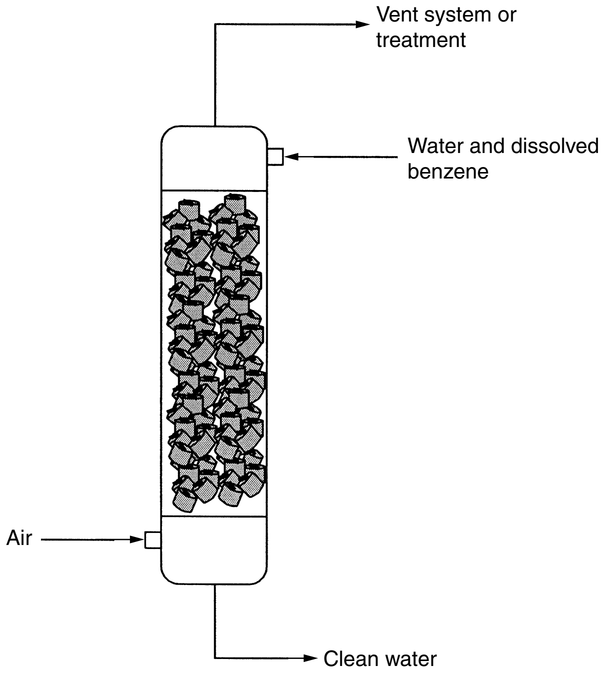

Figure 2. Packed-bed air stripper.

thermodynamic equilibrium[a]:

$$y_i \phi_i P_T = x_i P^{vap} \gamma_i$$

$$p_i = \frac{P^{vap}\gamma_i}{\phi_i} x_i = H x_i$$

Or the partial pressure of i equals Henry's constant times the liquid mole fraction of i where H (Henry's constant) is constant for small mole fractions in the liquid phase. The rate of mass transfer is based on using Henry's constant. For a dissolved gas, there are two resistances, gas-phase and liquid-phase. The mass transfer (F) flux is

$$F = K_L(C_B - C^*) = K_G(p^* - p_B)$$

The C^* and p^* above are virtual properties; C^* is the concentration in equilibrium with the bulk pressure if there were a liquid present. Similarly, p^* is the partial pressure that would be in equilibrium with the bulk liquid. Figure 3 illustrates these relations. Because C^* is not known, p_B/H is substituted for it. Similarly, C_BH is substituted for p^*. This is the easiest form as all that needs to be known are the bulk liquid concentration and bulk partial pressure.

The mass transfer based on individual coefficients is (see Fig. 4)

$$F = k_G(p_i - p_B) = k_L(C_B - C_i)$$

By combining these and using Henry's Law, the following is determined for the overall mass transfer coefficients either one can be used:

$$K_L = \frac{1}{\dfrac{1}{Hk_G} + \dfrac{1}{k_L}}$$

$$K_G = \frac{1}{\dfrac{1}{k_G} + \dfrac{H}{k_L}}$$

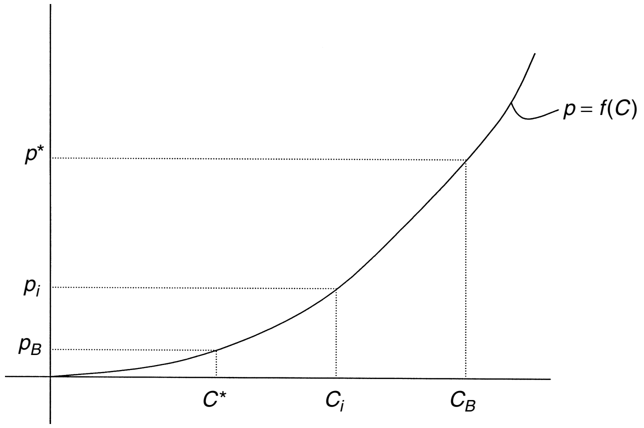

Figure 3. Stripper concentration and partial pressure relations.

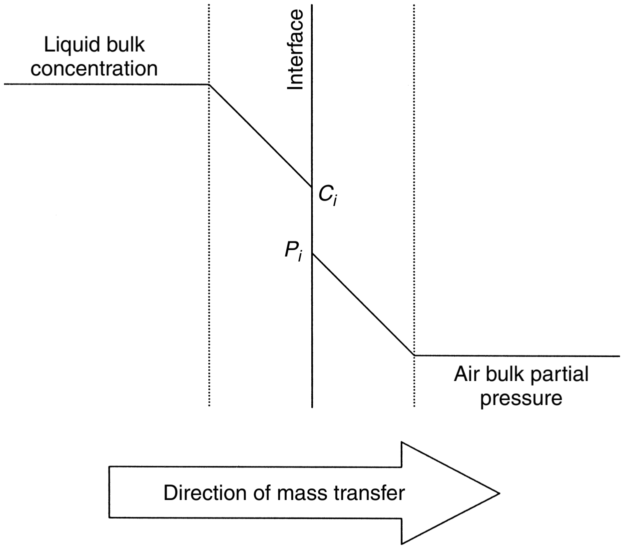

Figure 4. Interphase mass transfer.

There are many references that cover this thoroughly (8,9,11) but if Henry's Law applies, the height of a stripping column is

$$h = HTU * NTU$$

$$HTU = \frac{L}{K_L a}$$

$$NTU = \frac{R}{R-1} * \ln \frac{C_i/C_o * (R-1) + 1}{R}$$

$$R = \frac{HG}{L}$$

Using benzene as an example with an MCL of 5 μg/L, the height will be determined to achieve this starting with 50 μg/L and the data in Table 1. This would take a stripper approximately 5 m high (15–20 ft) to meet the MCL for benzene.

The R parameter is called the stripping factor and must be greater than one ($R > 1$) for stripping to be feasible. As observed by its definition, a small H can be somewhat overcome by a large G/L. The trend is such that volatile materials are easy to strip, whereas the semivolatiles and large organic compounds that have low vapor pressures are difficult to strip.

Adsorption

The use of activated carbon for organic removal from a water source or effluent is another very common and useful separation process. There are two types in use, granular and powdered. Only the granular type is discussed here; the powdered type is covered in other sources (10). Normally, the system is designed so that water flows into the top of the column and exits the bottom, as shown in Fig. 5.

Some methods for multicomponent adsorption are available. One is the multicomponent Langmuir that doesn't always give good predictions (11). There has also been some work on multicomponent systems (2). Some

[a] a Actually, $H_i \equiv \lim_{x_i \to 0} \frac{f_i^L}{x_i}$

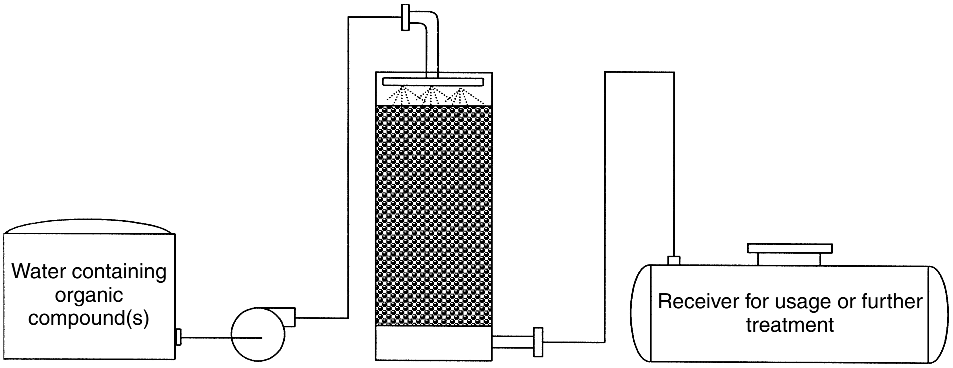

Figure 5. GAC system.

Table 1. Data for Air Stripping Benzene

Given Data	Values
C_i, μg/L	50
C_o, μg/L	5
G, m^3/m^2/h	1000
H, atm L/mg	5.52E−05
H, Dimensionless	1.80E−01
K_{L_a}, hr^{-1}	10[a]
L, m^3/m^2/h	20
Flow, gpm	10
Calculated	
R	9.00
HTU, m	2
NTU	2.47
h, m	4.94
A, m^2	0.11
D, m	0.38

[a] This was an assumed value. Note that K_La is a combined, overall liquid mass transfer coefficient where a is the surface area to volume ratio of the packing and is usually measured or estimated as a single quantity. It is found similar to the K_G and K_L and there are correlations for it in many references, e.g., 8–10.

computer software is available for sizing but is limited to 8–10 components. Vendors also have programs and rule of thumb methods available. Freundlich isotherms for many of the compounds are readily available, and hence, this method is used for single organic compounds. The Freundlich isotherms are sometimes used for scoping multicomponent systems. However, the Freundlich method is not amenable to multicomponent systems. Therefore, it is assumed that they are additive, each compound adsorbs independently of the others without competition. Column dynamic testing of the actual liquid is preferred for multicomponent systems.

The Freundlich isotherm is explained by

$$q_e = KC_e^{1/n}$$

The additive type of method assumes that the organic compounds adsorb in layers; the strongest bonding molecules profile toward the top of the equilibrium zone, and the less strongly bonded toward the bottom (K is related to capacity, and $1/n$ is related to bonding strength). This is shown ideally in Fig. 6. It shows that the organic compounds that have the highest affinity for GAC profile toward the top of the column and those of low affinity profile toward the bottom. Hence, breakthrough of benzene would occur first if in a multicomponent system.

The procedure is to determine the amount of GAC for a component individually via the method of Snoeyink (Pontius 1990) (11) and determine the amount of GAC required. Using benzene again at 50 μg/L (it does not have a very favorable isotherm),

$$q_{e,Benzene} = 1 * 0.05^{1.6} = 0.0083 \text{ mg/g}$$

The amount of water per GAC, according to Snoeyink is,

$$Y = \frac{q_e}{C_i - C_o} * \rho_{\text{GAC}} = \frac{0.0083 \text{ mg/g}}{0.05\text{–}0.005 \text{ mg/L}} * 500 \text{ g/L}$$
$$= 92 \text{ gal/galGAC}$$

The amount of GAC is then the volume to be treated/Y. For 1000 gallons this is

$$\text{GAC} = \frac{1000}{92} = 11 \text{ gal}$$

or 11 gallons of GAC per 1000 gallons treated.

To avoid immediate breakthrough, the bed length must be greater than the mass transfer zone (MTZ). The MTZ is calculated from column dynamic tests as

$$\text{MTZ} = L\frac{t_s - t_b}{t_s}$$

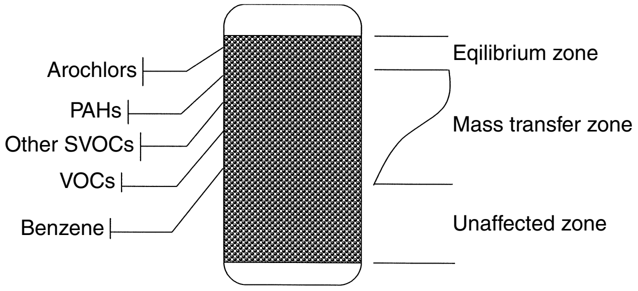

Figure 6. Zones in a GAC column.

The most important GAC adsorber design parameter is contact time, most commonly described by its empty bed contact time (EBCT) (11), V/Q. The empty bed contact time (EBCT) is an important design parameter in GAC column design. The range for 47 plants was 3–34 minutes, and the median was 10 minutes (Pontius 1990)(11). Longer contact times are normally used for highly concentrated solutions, so this design uses the value of 5 minutes. Based on this, the minimum column volume is

$$V_{\text{column}} = EBCT * Q = 5 \text{ min} * 10 \text{ gpm} = 50 \text{ gal}$$

A typical hydraulic loading is 3–4 gpm/ft^2. Using 10 gpm, the area is 2.5 ft^2. The height is

$$h = \frac{50 \text{ gal} * \text{ft}^3/7.48 \text{ gal}}{2.5 \text{ ft}^2} = 2.67 \text{ ft}$$

Destruction

The final technologies discussed for removing organic compounds from water are destruction/reaction techniques based on high-energy chemistry. High-energy chemistry is defined as

$$\text{E} > \kappa\text{T}$$

So-called advanced oxidation technology is a subset of high-energy chemistry that uses free radicals to oxidize the target compound. All of these processes work by generating free radicals followed by attack on the target's bonds by the free radicals. All of these processes are commercially available. However, some of them have certain restrictions on their use (e.g., nitrates, liquid only,). The following are some of the processes comprising advanced oxidation.

The UV/H_2O_2 process consists of a chemical reactor (batch or flow-through) that uses UV light to produce free-radical hydroxyls (Fig. 7)

$$H_2O_2 + h\nu \rightarrow OH\cdot$$

The free radicals extract electrons from the target and create a free radical target product. The ensuing mechanism is a chain reaction eventually degrading the target to CO_2 and H_2O and other simple, less regulated compounds. The overall reaction can usually be modeled by first-order kinetics. The design relation used for this type of reactor is the EE/o, the electrical energy per volume per order of magnitude (in kwh/1000 gal/order). This relationship provides all of the information required to determine efficiency (i.e., once known, any efficiency can be obtained by adjusting the power).

There are several similar systems that produce free-radical hydroxyls, including

- UV/ozone
- ozone/peroxide
- Fentons' reagent
- UV-vis/Peroxide

It has been speculated that UV is required for some compounds like polychlorinated biphenyls (PCBs), to activate the bonds, and OH^- is required to react with the activated bonds (i.e., synergism) (13).

For some compounds (e.g., NDMA), direct irradiation of organic pollutants by high-intensity UV light provides a significant destructive pathway. The target compounds degrade after absorbing UV light. The target must strongly absorb UV.

The hydrated electron is a very strong reducing agent that can react with halogenated alkanes and alkenes. The hydrated electron interacts with the chlorine–carbon bonding electrons and provide energy to break the bond and demineralize the target. There are several commercially available processes involving reduction via aqueous electrons. The aqueous electron is produced by several mechanisms including nuclear and high-energy processes, photochemistry, and chemical. Some processes require transferring high-energy electrons through thin films of water because the free path or linear energy transfer (LET) is small for electrons (high voltage process).

The baseline process is a UV-catalyzed process. The chemical added that is shown is a proprietary catalyst. The catalyst interacts with UV light shown by the energy arrow that produces the aqueous electron (e^-_{aq}). An example of this production reaction is

$$\text{Fe(CN)}_6^{-4} + h\nu \rightarrow \text{Fe(CN)}_6^{-3} + e^-_{\text{aq}}$$

The aqueous electron then interacts with the chlorine–carbon bond producing chloride ion and a free radical chlorinated aromatic:

$$e^-_{\text{aq}} + C_{12}H_5Cl_5 \rightarrow C_{12}H_5Cl_4^- + Cl^-$$

The free radical goes on to extract electrons from another molecule, and a chain reaction usually occurs. The rate constants for reductions are normally quite large. This process is particularly well suited to compounds not amenable to advanced oxidations, for example, CCl_4. The UV-induced process is commercially available (e.g., Calgon Advanced Oxidation Technologies).

Supercritical water oxidation, sometimes known as hydrothermal waste processing, uses the solvating traits of water in its supercritical state to destroy liquid organic wastes. As water is heated beyond its critical temperature (374.1 °C) and critical pressure (250 Mpa-s, about 3219 psi), the density of the water drops dramatically (typical operating densities are 0.15–0.2 g/cm^3). These changes in density and hydrogen bonding make organics highly soluble, and inorganic substances become nearly insoluble. The organic material is dissolved in an oxygen-rich environment where conversion occurs rapidly due to the high temperature of the process. Under such high pressure and temperature, organic materials are rapidly decomposed by oxidation at removal efficiencies of 99.9999% or greater.

Ultrasound can induce unusual high-energy chemistry through the process of acoustic cavitation, the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation can occur in both clouds of collapsing bubbles (multi-bubble cavitation) or with high symmetry for isolated bubble (single-bubble cavitation, SBC). Multi-bubble cavitational collapse produces localized, transient hot spots with intense local heating (approx > 5000 K), high pressures (>2000 atm), and short lifetimes (sub-microsecond) in an otherwise cold liquid. From hydrodynamic modeling of this cavitational collapse, it has been estimated that both the heating and cooling rates are in excess of 1010 K/s. Acoustic cavitation is a unique means of creating high-energy chemistry, easily and inexpensively. Aqueous sonochemistry produces, supercritical water conditions on a microscopic scale. In this regime of temperature and pressure, the sonochemistry of water is an extreme limiting case of supercritical phenomena and is closely related to hydrothermal oxidation. For example, the ultrasonic irradiation of water produces a variety of extraordinarily reactive species (including OH^-, H^+, and HO_2^-) that can decompose many organic compounds.

The last design example is treating benzene-contaminated water to the same degree as the previous two examples using UV/H_2O_2. Figure 7 illustrates a schematic batch test reactor. Benzene has an EE/o = 2–5 kWh/1000 US gal/order (14). Therefore, the dosage of UV required in a flow-through system at 10 gal/min is (using 5 for the worse case) and the industry design relation (14):

$$\begin{aligned}&\text{Power(kWatt)}\\&= \frac{5\ \text{kWh} * 10\ \text{gal/min/order} * \log_{10}(50/5) * 60\ \text{min/hr}}{1000}\\&= 3\ \text{kW}\end{aligned}$$

So a UV lamp of 3 kW is sufficient to meet the requirement. Of course, if the flow rate were 100 gpm, it would require 30 kW, and so on. There will be economic trade-offs, electrical power costs, and chemical costs.

It is highly useful at this point to consider reaction kinetics and reactor design as there are some unusual features for this type of reactor. For a batch system, as shown in Fig. 8, the material balance and first-order reaction are

$$\frac{dC}{dt} = -kC$$

$$\ln\left(\frac{C_i}{C_o}\right) = kt$$

The first-order reaction coefficient is inversely proportional to the EE/o:

$$k = \frac{\ln 2 * P(kW)}{V * \text{EE/o} * \log 2}$$

The power for a batch reactor is then the same used for the industry design equation (14):

$$P(kW) = \frac{\ln(C_i/C_o) * V * \text{EE/o} * \log 2}{\ln 2 * t}$$

In a plug flow reactor (see Fig. 8), a material balance on a differential volume element yields:

$$QC - Q(C + dC) - kCdV = V\frac{dC}{dt}$$

At steady-state,

$$\ln\frac{C_i}{C_o} = k\frac{V}{Q}$$

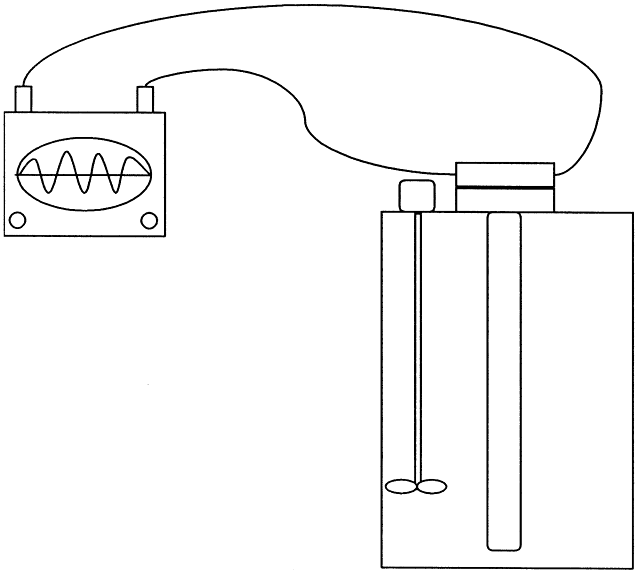

Figure 7. Batch reactor with lamp and agitator.

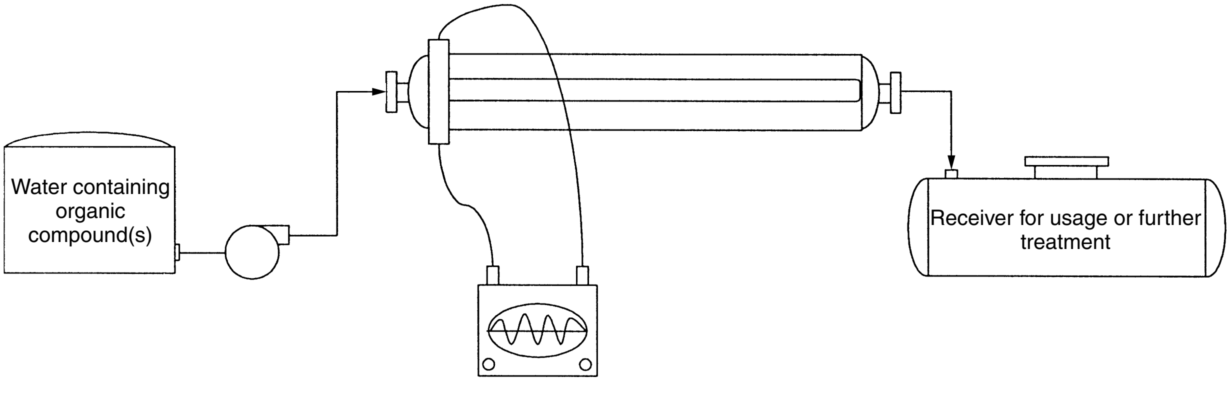

Figure 8. Plug flow UV system.

The power, based on this k, is then the industry design equation (14).

$$\mathrm{P(kW)} = \frac{\mathrm{EE/o} * \log 2 * Q * \ln(C_i/C_o)}{\ln 2}$$

For a continuously stirred reactor (CSTR), the steady-state material balance yields

$$\frac{C_i}{C_o} = \frac{kV}{Q} + 1$$

This does not yield the industry design equation. The answer to this seemingly paradoxical result is that the plug flow design applies, regardless of the reactor type for flow-through reactors. This is so because the reaction must be in the vicinity of the lamp surface; a solute in a CSTR must, at some time in its residence history, approach the lamp sufficiently close. This is one reason that flow-through reactors require appropriate design to obtain turbulence.

Nomenclature

A	Cross sectional area
C_B	Bulk liquid concentration
C_e	Equilibrium concentration
C_i	Inlet concentration
C_o	Outlet concentration
$C*$	Fictitious concentration in vapor phase
D	Diameter
EE/o	Electrical energy/1000 gallons/order
F	Mass transfer flux
G	Gas mass velocity
H	Henry's Law constant
$h\nu$	Photon energy
HTU	Height of a transfer unit
k	1st order reaction coefficient
K	Freundlich constant (related to capacity)
K_G	Overall mass transfer coefficient based on gas
K_L	Overall mass transfer coefficient based on liquid
k_G	Gas phase mass transfer coefficient
k_L	Liquid phase mass transfer coefficient
K_{L_a}	Overall liquid phase mass transfer coefficient
L	Liquid mass velocity, length of column
NTU	Number of transfer units
$1/n$	Freundlich exponent (related to bonding strength)
P	Power
P_T	Total pressure
p_B	Bulk gas partial pressure
p_i	Partial pressure at interface
P^{vap}	Pure component vapor pressure
$p*$	Fictitious pressure in liquid phase
q_e	Quantity adsorbate/adsorbent
Q	Liquid flow rate
R	Stripping factor
t_b	Breakthrough time
t_s	Saturation time (influent = effluent)
V	Volume
x_i	Liquid phase mole fraction
y_i	Gas phase mole fraction
γ_i	Activity coefficient
κ	Boltzmann's constant
ϕ_i	Fugacity coefficient

BIBLIOGRAPHY

1. Edstrom. (2002). Available: http://www.edstrom.com/Resources.cfm?doc_id=23.
2. Mittelman, M.W. (1985). Biological fouling of purified-water systems: Part 1. *Bacterial Growth and Replication, Microcontamination* **3**(10): 51–55, 70.
3. Bott, T.R. (1998). Techniques for reducing the amount of biocide necessary to counteract the effects of biofilm growth in cooling water systems. *Applied Thermal Engineering* **18**(11).
4. Stoodley, P., Lewandowski, Z., Boyle, J.D., and Lappin-Scott, H.M. (1999). Structural deformation of bacterial biofilms caused by short-term fluctuations in fluid shear: An *in situ* investigation of biofilm rheology. *Biotechnology and Bioengineering* **65**(1).
5. Boyle, J.D., Dodds, I., Stoodley, P., and Lappin-Scott, H.M. (1997). Stress management in biofilms. In: *Biofilms: Community Interactions and Control*. J.W.T. Wimpenny, P.S. Handley, P. Gilbert, H.M. Lappin-Scott, and M. Jones (Eds.). BioLine, Cardiff, UK, pp. 15–22.
6. Picologlou, B.F., Zelver, N., and Characklis, W.G. (1980). Biofilm growth and hydraulic performance. *J. Hydraul. Div. Am. Soc. Civ. Eng.* **106**(HY5): 733–746.
7. Prausnitz, J.M., Lichtenthaler, R.N., and de Azevedo, E.G. (1986). *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, Englewood Cliffs, NJ
8. Perry, R.H. and Green, D.W. (1984). *Perry's Chemical Engineers' Handbook*, 6th Edn. McGraw-Hill, New York.
9. Treybal, R.E. (1987). *Mass-Transfer Operations*. McGraw-Hill, New York.
10. Perrich, J.R. (1981). *Activated Carbon Adsorption for Wastewater Treatment*. CRC Press, Boca Raton, FL.
11. Pontius, F.W. (1990). Adsorption of organic compounds. *Water Quality and Treatment*. 4th Edn. McGraw-Hill, New York.
12. Khan, A.R., Al-Bahri, T.A., and Al-Haddad, A. (1997). Adsorption of phenol based organic pollutants on activated carbon from multi-component dilute aqueous solutions. *Wat. Res.* **31**(8): 2102–2112.
13. Ashworth, S.C. (1998). *K Basin Sludge Polychlorinated Biphenyl Removal Technology Assessment*. HNF–3095 DOE Information Bridge. Available: http://www.osti.gov/bridge/.
14. Calgon Carbon Corporation. (1996). *Advanced Oxidation Technologies Handbook* **1**(1): MI-AOT-10/96.

USE OF ANAEROBIC-AEROBIC TREATMENT SYSTEMS FOR MAIZE PROCESSING PLANTS

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After the discovery of the American continent by the Spaniards in the fifteenth century, corn (*Zea mays*), an indigenous plant from Mexico, spread all over the world and became a staple food for many human groups. However, the traditional ways of eating the many products derived from this cereal in Mexico, inherited from the Mayan, Aztec, and other Mexican indigenous groups, were not disseminated until the last 20 years. Due to globalization, one of these maize products, "tortillas," is now an extremely popular food that can be found in most countries of the world. "Tortillas" are a sort of unleavened bread in circular form that, due to a mild flavor, can be combined with vegetables, meats, pulses, etc. They are the bread equivalent to "chapattis" for the people from India and "falafel" for the people of the Middle East (Fig. 1).

The traditional production of "tortillas" involves a Precolumbian technique, known as "*nixtamalization*," derived from the Aztec words *nextli* = lime ashes and *tamalli* = cooked corn dough. This ancient process, almost as old as corn domestication and cultivation, is a time- water- and energy-consuming technique (Fig. 2). Modernization of the traditional process to produce cornmeal instead of dough to lengthen its shelf life as well as some other changes for mass production have been introduced in the last 50 years. However, these changes affect the sensory characteristics of "tortillas," mainly "rollability," "sturdibility," and softness, so it has been a common practice among large-scale producers to introduce some chemical additives to make the new "supermarket tortillas" desirable from the sensory point of view. Unfortunately, from the nutritional point of view, it has not yet been proved that these additives do not affect the health of consumers. Some innovative processes that maintain these desirable nutritional and sensory characteristics, and at the same time, reduce energy and water consumption, and most importantly, processing time, have also been developed and started to be used (2–5). However, the traditional plants (more than 100,000 small-scale and 25 large-scale in Mexico) are still in operation, so methods to treat and stabilize the wastewater generated in the traditional process (so-called "nixtamal" mills that process around 0.5 to 4 metric tons maize per day) or in its industrial modifications (so-called precooked cornmeal or masa-harina factories that process from 100–1,000 metric tons maize per day) and contain appreciable amounts of soluble and insoluble organic matter (Table 1) have also been developed. These methods are based on anaerobic and aerobic systems, and the interesting issue is that by-products from the treatment can be further used, giving added value to these treatment processes.

The biological processes developed were screened out after testing at laboratory level. These processes are commonly used in biological wastewater treatment, such as activated sludge, aerated lagoons, facultative lagoons, low and high rate anaerobic reactors, etc. (7). Figure 3 shows the method developed for treating the wastewater from maize alkaline processing to produce "tortillas," particularly for those factories that process considerable amounts of corn. After primary settling to recover broken maize pieces and peelings, the anaerobic process is carried out to transform most of the biodegradable dissolved matter in the wastewater into methane-rich biogas. This is followed by the aerobic process that polishes the treatment, removes the traces of sulfide and other undesirable compounds in treated water, and converts the remaining biodegradable matter into protein-rich biomass. A tertiary treatment using activated carbon or any organic adsorbent will render recyclable water for the process. The water absorbed by corn is added as makeup freshwater to the overall process. The recycling of the by-products generated is shown in Fig. 3. The amount of methane from biogas obtained from the anaerobic treatment of the wastewaters is 9.6–16.8 m^3 per metric ton of maize processed (considering 5 m^3 of wastewater produced per metric ton maize at a conversion of 80% of the dissolved biodegradable matter into biogas). If this gas contains roughly 80% methane, the yield of this energy-rich gas is 7.7–13.48 m^3 methane per metric ton of maize processed. This methane-rich biogas may be washed and compressed to be used as a secondary source of energy during the lime-cooking of corn grains (nixtamalization). The amount of biomass and suspended solids obtained may be processed by extrusion to form pellets or flakes for fish feedstuff, considering the mass balances from the aerobic and anaerobic processes is of 23 kg SS and 10.6 kg biomass per metric ton of maize cooked. These biomass and suspended solids pellets or flakes proved comparable

Figure 1. (**a**) Modern "tortilla" making machine. (**b**) Traditional "tortilla" hand-making (1).

Operating conditions	Nixtamalization	
	Traditional	Modern
Processing time, h	20	8
Water consumption, water:grain ratio	6:1	3:1
Wastewaters	5:1 (high BOD_5)	2:1 (DBO_5 extremely high)
Energy consumption	1 (basis)	0.75

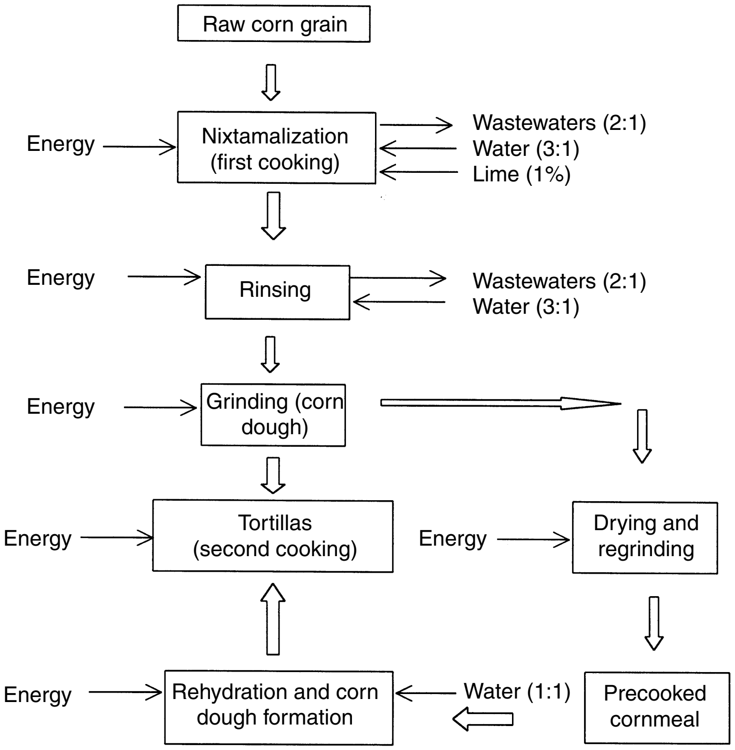

Figure 2. Diagram of the traditional nixtamalizatiȯn process (2).

Table 1. Maize Lime-Cooking (Nixtamalization) Wastewater Average Composition[a]

Characteristics	Average Values	UE Normativity[b] for Surface Water
Suspended solids, kg/m^3	2.4–4.6	0.025 (25 mg/L)
Dissolved organic carbon, kg/m^3	3.0–5.0	—
Biochemical oxygen demand (5 days, 20 °C), kg/m^3	1.5–3.0	<0.007 (7 mg/L)
Chemical oxygen demand (dissolved), kg/m^3	7.5–11.0	0.030 (30 mg/L)
Nitrogen (Kjeldahl), mg N/L	80–270	0.003
Phosphates, mg PO_4^{-3}/L	7–18	0.0007
pH Value	10–14	5.5–9.0
Color	Dark yellow	Colorless

[a] Reference 6.

[b] European Community: 16/6/75 (after physical and chemical treatment including desinfection).

to that for commercial feedlots for carp and other edible fish (8).

The reactors most suitable for this type of carbonaceous wastewater are those that develop active biofilms, particularly because the biomass formed tends to show more cohesion and separates more easily from the liquid phase by sedimentation. For the anaerobic step, packed bed anaerobic reactors or upflow anaerobic sludge blanket reactors are those that render the highest conversion into methane-rich biogas at the lowest hydraulic residence times between 24 and 48 hours. For the aerobic step, rotating biological reactors are excellent for transforming the soluble remaining biodegradable dissolved and colloidal organics into an easily settleable aerobic biomass. The energy consumption for the rotational speed needed is very low, and the area occupied by the reactors is also very small. Figure 4 shows the system to be used in cornmeal factories. Both systems, the anaerobic and the aerobic, are compact and easy to operate. The saving in water and energy consumption, wastewater disposal costs, and the sale of biomass for fish protein-rich feedlots make the treatment and recovery process economically feasible. The

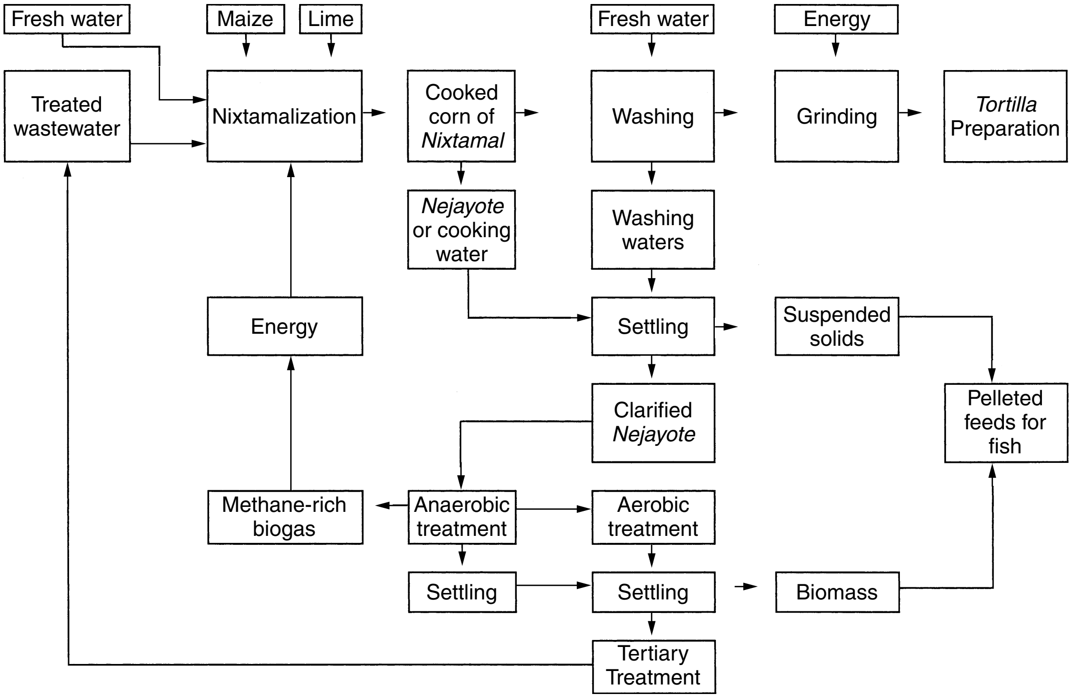

Figure 3. Wastewater treatment for maize alkaline cooking process for "tortilla" preparation ("*nixtamal*", "*nejayote*", Aztec derived words from ***nextli*** = lime ashes, ***tamalli*** = cooked maize dough, ***ayotl*** = broth, watery solution).

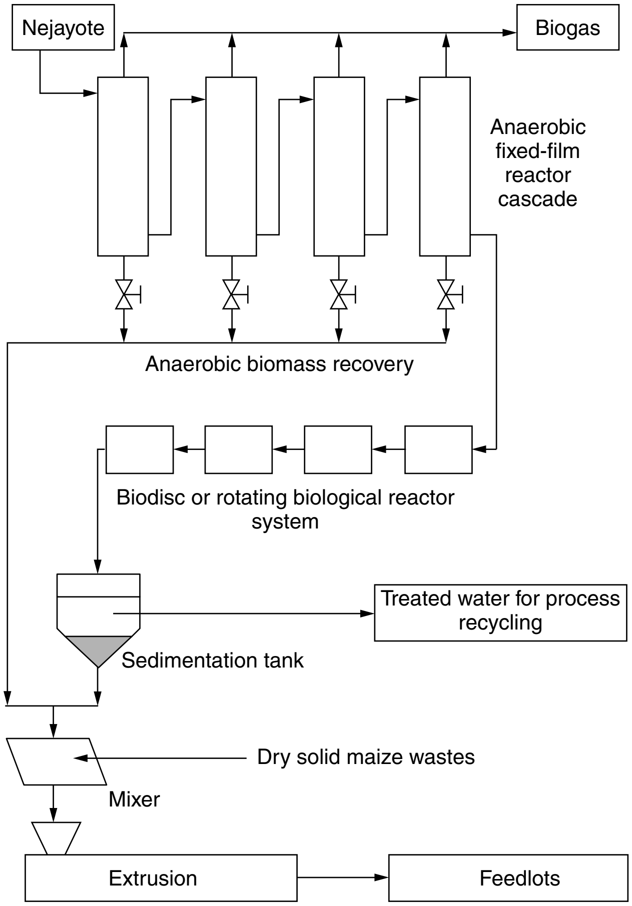

Figure 4. Wastewater treatment in a precooked cornmeal factory that uses a combined anaerobic-aerobic treatment system (7).

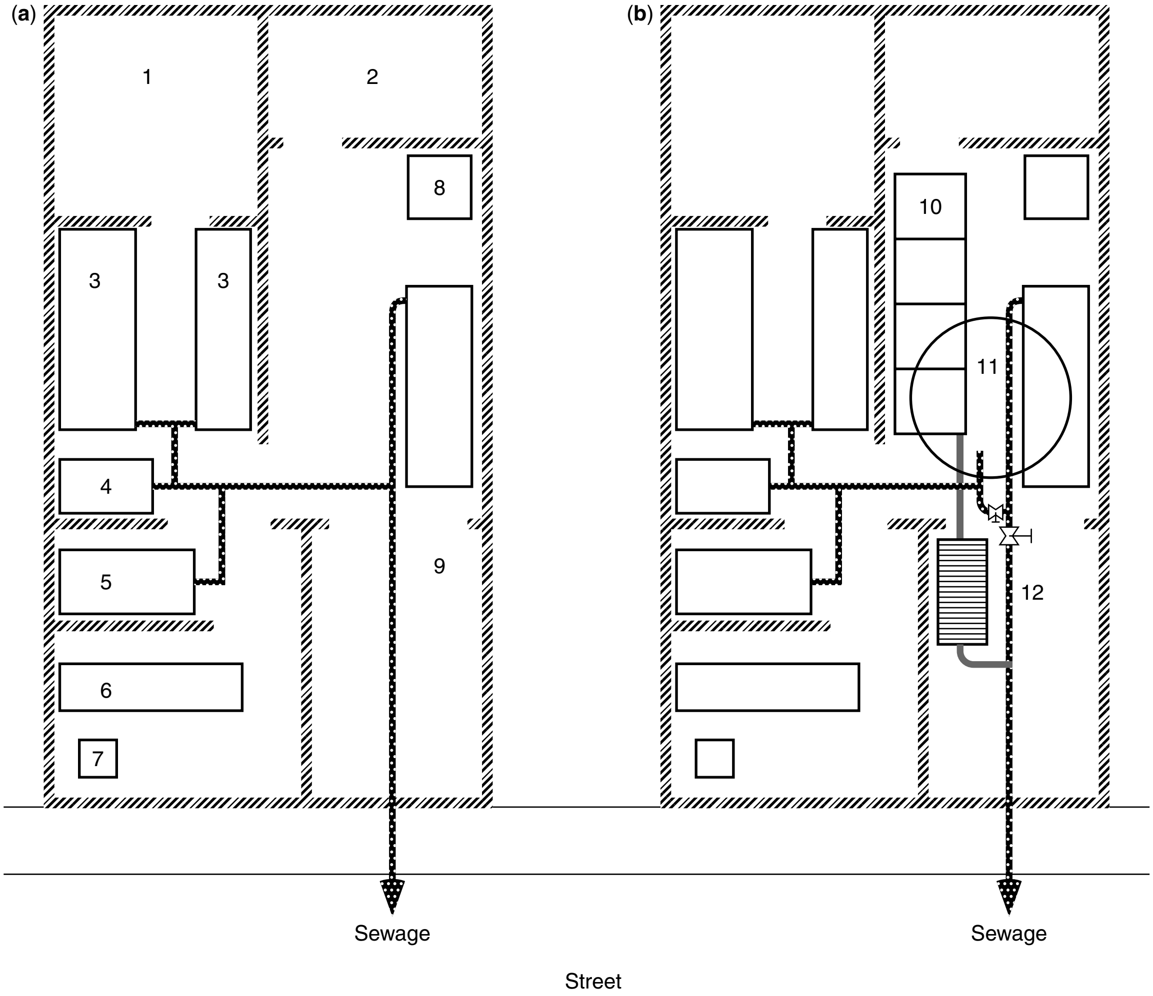

Figure 5. Wastewater treatment in a corn traditional mill (7). (**a**) Unimproved mill: (1) grain storage, (2) boiler, (3) nixtamalization tanks, (4) wash water tank, (5)stone grain mill, (6) selling shelf, (7) scales, (8) water reservoir, and (9) lime and corn solid waste storage room. (**b**) Changes for introducing the aerobic wastewater treatment system that includes an (11) underground settling tank with a sludge pump attached to the bottom exit pipe that sends the sludge to a (12) filter press, and the filtered wastewater to a (10) rotating biological reactor.

turnover rate is 1.5 years, that is, the money invested in the wastewater treatment plant together with the accessories to recover biogas and biomass and to reuse them is recovered in 18 months.

Due to the size of nixtamal mills, it is not so economical to install an anaerobic-aerobic process for treating their wastewaters (between 2.5 to 20 m^3). An aerobic system is then used for these small establishments (Fig. 5). The solid material collected from the filter press can be fed directly to small farm animals and, although the protein cannot be directly assimilated by the animals, it does not damage them. In this case, partially treated wastewater is sent to the municipal sewer system. Finally, it should be mentioned that this combined anaerobic-aerobic process may be applicable to wastewater from other food industry sectors, particularly to those that contain carbonaceous substances. When proteinaceous wastewater is to be degraded, the wastewater may be anaerobically treated, but the gases must be washed to remove the sulfur compounds separated from protein matrices before using the biogas as a combustion or fuel source. Hydrogen sulfide is extremely corrosive and toxic, but once dissolved in water, may be used by aerobic organisms to be reconverted into biomass protein.

BIBLIOGRAPHY

1. Bonfil, G. (Ed.). (1984). *SEP Cultura: El Maíz, Fundamento de la Cultura Popular Mexicana*. Museo Nacional de las Culturas Populares. G.V. Editores, S.A. México D.F. México.
2. Durán-de-Bazúa, C. (1972). *Report on Novel Technologies: Application of the Extrusion Process for the Production of Mexican Traditional Corn Foods*. University of California, Berkeley, College of Nutritional Sciences, Berkeley, CA.
3. Durán-Domínguez, M.C. (1978). *Procedure for Cooking Corn by Extrusion/Procedimiento Para Cocer Maíz or Extrusion*. Patent 172126. April 7. Dir. Gral. Invenciones y Marcas. Dept. Patentes. Secretaría de Patrimonio y Fomento Industrial, México D.F. México.

4. Durán-Domínguez-de-Bazúa, M.C. (1992). *Procedure for Cooking Cereals and Other Grains (Legumes and Oilseeds) by Alkaline Extrusion/Procedimiento para Cocer Gramíneas (Cereals, Leguminosas y Oleaginosas) por Extrusion Alcalina*. Patent requested on May 13. Dir. Gral. Invenciones y Marcas. Dept. Patentes. Secretaría de Patrimonio y Fomento Industrial, México D.F. Mexico.
5. Durán-Domínguez-de-Bazúa, M.C., Sánchez-Tovar, S.A., and Solís-Fuentes, J.A. (2002). *Procedure for Cooking Grains (Cereals, Legumes, and Oilseeds) and Agroindustrial by-Products by Alkaline Extrusion/Procedimiento Para Cocer Gramíneas (Cereals, Leguminosas y Oleaginosas) y Subproductos Agroindustriales por Extrusion Alcalina*. Patent requested on November 16. Instituto Mexicano de la Protección Industrial, México D.F. Mexico.
6. Durán-de-Bazúa, C. and Hartmann, L. (1979). *Produktion Von Biomasse aus Prozessabwaessern Der Lebensmittelindustrie*. Internationales Seminar, Universität Karlsruhe, 7 IIBB-UNIKA, Karlsruhe, German Federal Republic.
7. Durán-Domínguez-de-Bazúa, M.C. (1987). Effluents of the food industry in México: Environmental impacts on soil and water resources and possible solution using the biotechnological approach. Case problem: The corn industry. In: *Global Bioconversions*. Vol. II, Chap. 4. CRC Press, Boca Raton, FL, pp. 75–119.
8. Durán-Domínguez, M.C., Pedroza-Islas, R., Rosas-Vázquez, C., Luna-Pabello, V.M., Sánchez-Zamora, A., Capilla-Rivera, A., Paredes-Gómez, L., Valderrama-Herrera, S.B., and Vázquez-Cedeño, I. (1991). Producción de alimentos para peces: Utilización de subproductos del tratamiento de aguas residuales. In: *Premio Nacional Serfín El Medio Ambiente*. J.J. De Olloqui (Ed.). Futura Eds., Villa Nicolás Romero, Méx., Mexico, pp. 79–106.

BONDING OF TOXIC METAL IONS

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Worldwide environmental problems are becoming more and more acute. It is known that many specific industrial wastewater streams with large flows contain toxic metals in concentrations up to 500 mg/L, which have to be removed prior to water recycling, indirect discharge into a sewage system, or direct discharge into surface waters. Some examples are (1) rinse water in metal working enterprises, containing Cu, Ni, Zn, Sn, Cd, Pd, Ag, Al, Au, Cr, Mo, etc.; (2) rinse water in the semiconductor industry, containing Cu, Sn, Pb, Sb; (3) wastewater from the copper industry, containing As, Se; (4) other types of water in which the presence of toxic metals causes problems; (5) drinking water from ground water contaminated with As; and (6) mine water contaminated with different toxic metals (e.g., U, Ra, As).

When discharged directly into rivers, polluted wastewater poses a great risk to the aquatic ecosystem, and discharge into a sewage system negatively affects biosludge activity and leads to contamination of the sludge to be disposed of. As a result of the standards specified in the Water Resources Act, which was amended in 1986, industry takes precautions against these risks by treating dangerous components in a partial stream before mixing with other types of wastewater. So, research was focused, among others, on the development of highly selective bonding agents (often denoted as BA) with fast reaction kinetics for removing heavy metal ions (Fig. 1a). The latter may lead to better use of the capacity of bonding agents, resulting in smaller units and low residual concentrations of toxic metals in treated water streams, to comply with individual standards for water reuse or discharge—sorption kinetics constitutes another article in this *Encyclopedia of Water*.

In addition to zeolites (1,2), other typical materials extensively used are apatites (3,4) and various iron sorbents (5,6). These BA materials are broadly classified in three classes: carbon sorbents (active carbons, activated carbon fibers, molecular carbon sieves, fullerenes, heterofullerenes, nanomaterials), mineral sorbents (silica gel, activated alumina, oxides of metals, hydroxides of metals, zeolites, clay minerals, inorganic nanomaterials) and others (synthetic polymers, composite sorbents, mixed sorbents, etc.).

A review paper on bonding agents recently presented to a conference (7) also mentioned new types such as mesoporous materials and chelating resins and their potential applications to metal bonding from aqueous solutions. It also presented the equilibrium sorption capacity for metal ions of certain sorbents and stated that the functionalized silica materials have shown higher uptake capacity than that of other materials found in the literature. An inherent disadvantage of these materials is their low loading capacities and relatively small metal ion binding constants.

To circumvent these limitations, promising heavy metal sorbents have been prepared by coupling chelating ligands (e.g., thiol, amine, or crown ether functions) to support matrices consisting of inorganic oxides (e.g., silica, alumina, or clay) or organic polymers (e.g., polystyrene, cellulose, or polymethyl-methacrylate). Such functionalized materials have relatively high metal ion loading capacities and strong binding affinities for selected metal ions. This performance can be attributed to the presence of the surface-bound ligands, which can be specifically tuned to accommodate the selective sorption of targeted metal ions. Although superior in performance to conventional ion exchangers, functionalized matrices remain relatively inefficient because only a fraction of the immobilized ligands is accessible for metal complexation. The discovery of mesoporous metal oxide molecular sieves (by Mobil researchers) and organoceramic sorbents has given rise to new prospects for sorbent and catalyst design (7).

The knowledge of the governing chemical state of the metal ion to be removed is a prerequisite, so that any new development is based on a solid scientific

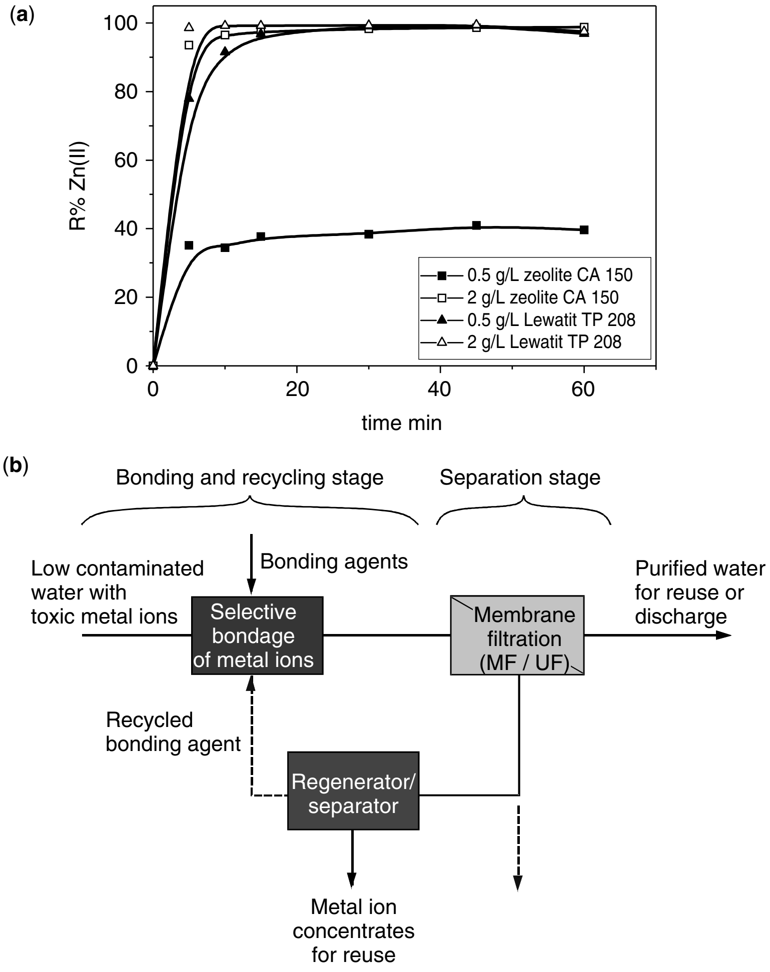

Figure 1. (**a**) Removal of zinc (50 mg/L, pH 6) by an ion exchange resin and zeolites for comparison (unpublished data). (**b**) Membrane separation of bonding agent/metal complexes for wastewater (METASEP project). Reprinted with gratitude from Reference 10.

foundation (8). The impact of chemical speciation is important in any process, including adsorption, ion exchange, or precipitation. These often act together, and the dominance of one specific is often hard to distinguish without careful chemical measurements and advanced analytical techniques. Identifying the bonding mechanism of metals on the agent/sorbent used is significant because, for example, the mechanism could dictate the mobilities of the species in their existing environment.

A new treatment process aimed at water and metal reuse was developed for the selective separation of heavy metals from wastewater to reduce costs and mitigate the environmental impact of wastewater pollutants (9). One of the variants, divided into three stages (shown as Fig. 1b), was the separation of BA-metal complexes by cross-flow microfiltration/ultrafiltration from wastewater that has metal concentrations less than 50 mg/L. This project was a contribution to the key action of European Union "Waste water treatment and re-use," in the 5th Framework programme.

The use of iron-based bonding materials, such as goethite and akaganéite, was successful because they are inexpensive, easily synthesized, suitable for both cation and anion sorption, and present low risks of adding a further pollutant to the system. Typical results are presented in Fig. 2; the sorbents had high surface area and defined pore size distribution. The synthesis of these materials involved hydrolyzing aqueous solutions of ferric salts followed by membrane purification and freeze drying (6). Sorption, in general, depends on the solution pH and its ionic strength. These macroscopic observations were used to differentiate between the kind of adsorption, physical or chemisorption (13). Other additional indications were obtained by examining the influence of temperature during equilibrium experiments and/or calculating (from the van't Hoff equation) the change of the respective enthalpy.

Table 1. Information about Industrial Effluents[a]

Wastewater from	Metal Targeted	Cationic	Anionic	Cleaning	Recovery
Open pit copper mine	Cu	X		X	X
Copper foil production	Sb, Cu	X	X	X	X
Groundwater	As (as AsF_6^-)		X	X	
Copper production	Se, As		X	X	

[a] Reference 10.

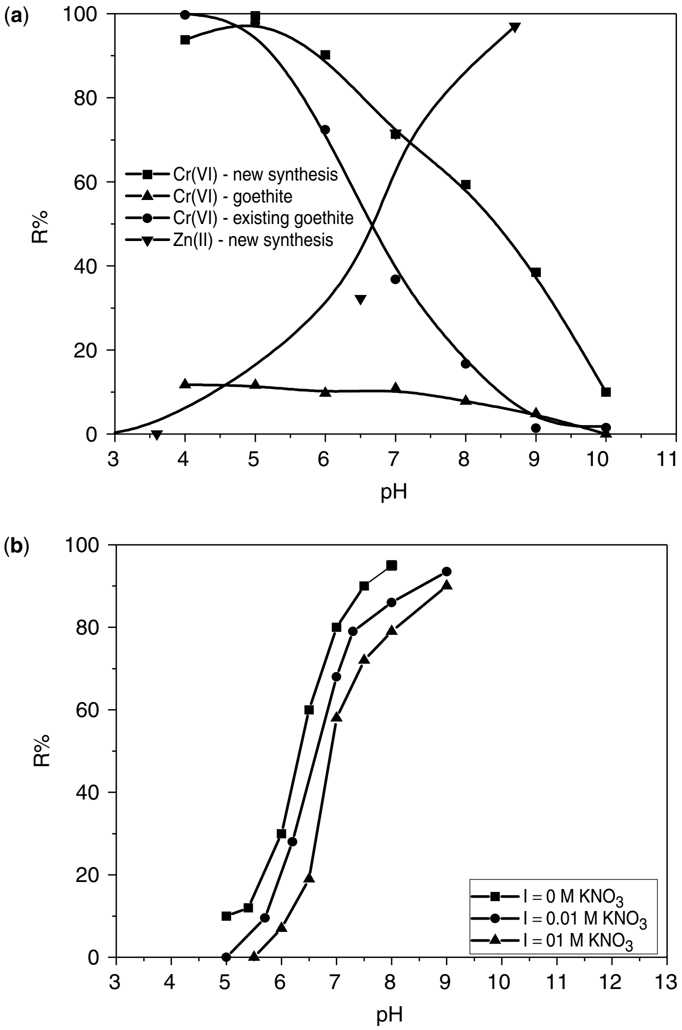

Figure 2. (**a**) Sorption of chromates (10 mg/L) and zinc ions (50 mg/L) by various goethite adsorbents, as a function of solution pH (1 g/L goethite, 2 h contact time). Reprinted with permission from Reference 11; copyright (2004) Scientific Journals. (**b**) Effect of pH on the adsorption of cadmium onto akaganéite for different values of ionic strength. Reprinted with permission from Reference 12; copyright (2004) Technical Faculty and Copper Institute, Bor Serbia.

The stability of a suitable bonding agent should be evaluated in a real process, for chemical and physical stability as well as losses in the proposed flowsheet. The selected industrial effluents in the aforementioned research project (e.g., METASEP) are presented in Table 1.

An effective mode of a sorption process is based on a fixed-bed contactor configuration (14). The sorption bed has to be porous to allow the liquid to flow through with minimum resistance but allow the maximum mass transfer into the particles—see also the article on Sorptive filtration in this *Encyclopedia*. Another possibility for this solid/liquid separation stage of loaded ultrafine material, as adsorbents and ion exchangers are, constitutes flocculation, as examined for goethite (Fig. 3a). The dynamics of flocculation were studied by a technique based on measuring the fluctuations of transmitted light in flowing dispersions.

An alternative for metals removal is *in situ* production, for instance, of ferric hydroxide (see Fig. 3b), which could be also conducted by electrocoagulation. Specifically, adsorbing colloid flotation is the process that involves removing a solute from an aqueous solution by adsorption on, coprecipitation with, or even occlusion in a carrier floc, often produced from ferric or aluminum salts by hydrolysis and solution pH modification. The aggregate, including the metals, is usually then floated after the addition of a suitable surfactant or collector (11).

The combination of flotation following sorption downstream (termed sorptive flotation) for metal cation removal by ion exchange materials, as the synthetic zeolites (of MAP type), gave promise for an improved metal separation process (16). A disadvantage of this is the application of surfactants, as flotation collectors; this represents an enormous demand, as flotation also applied in mineral processing, is currently met by numerous chemicals, mainly petroleum-based, hence, substances that are usually toxic to the environment and nonbiodegradable. For this reason, the successful application of biosurfactants was investigated (17).

Regeneration of bonding agents is, of course, a prerequisite often overlooked. The following two modes for different BA regeneration were envisaged: (1) The conventional, by changing the pH value; after separating it from the treated effluent, the loaded sorbent was mixed with a solution containing a strong acid (or alkal in the case of oxyanions) to shift the fixation equilibrium, to recover the metal in the acidic solution, and to produce a regenerated agent, where the protons have replaced the metal cations and could be recycled. (2) Electrodialysis with bipolar membranes for uncharged water-soluble bonding agents and modified electrodialysis for powdered agents (see Fig. 4). The loaded sorbent was fed into an electrodialysis reactor where, due to the electric field, the metals were separated from the material. The metal cations migrated in the electric field and crossed a cation-exchange membrane to enter into an other compartment, where they reacted with hydroxyl ions generated by a second bipolar membrane or by a cathode. The regenerated materials were recovered on one side, and a hydroxide sludge was recovered on the other side (18).

Elsewhere (19), another multistage process was proposed for removing aqueous cadmium consisting of, among others, elution at high concentrations of the sorbed metal ion from the biomass (the BA used here), recycling sorbent and eluant, wherever possible, and recovering cadmium electrochemically by a rotating cathode cell, in the form of metal powder as the end product. The flow diagram is shown with three cycles/routes for the combined process (investigated under an EU-funded research programme, too); the second-middle cycle represented flotation separation of the metal-loaded biomass. Biosorption, the uptake of heavy metals by dead biomass, has gained credibility during recent years, as it offers a technically feasible and economical approach. Several biological materials were investigated for heavy metals removal, including bacteria, yeasts, algae, and fungi.

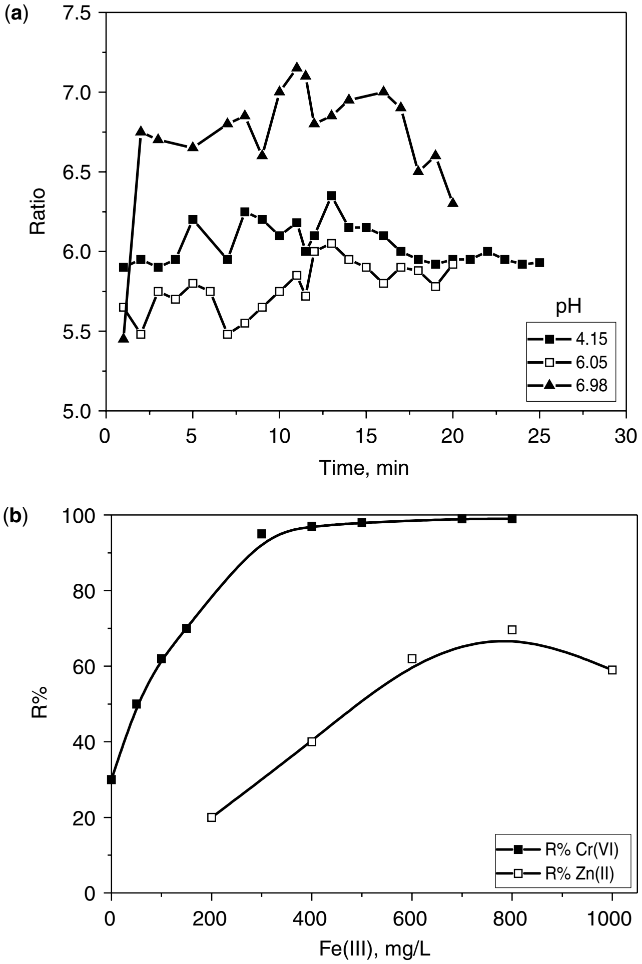

Figure 3. (**a**) Flocculation of synthetic goethite (0.5 g/L) fines by polyelectrolyte in the presence of As (III) (10 mg/L). Reprinted with permission from Reference 15; copyright (1999) Kluwer. (**b**) Removal of chromates and zinc as a function of Fe(III) concentration by in situ coprecipitation. Reprinted with permission from Reference 11; copyright (2004) Scientific Journals.

Concluding, the "*polluter pays*" principle ensures nowadays that companies have to pay the costs of environmental damage, or at least in part. Therefore, from their point of view, an economical and effective solution is required by developing techniques for improved treatment. On the other hand, many of the metal ions (cations or oxyanions) that are target compounds in effluents could be further concentrated for recycling; incineration of toxic sludge should be avoided, as this entails transferring pollution from one state to another. The strategy is to reuse water and metals, so "end-of-the-pipe" solutions will no longer be necessary. Attempts have been made to develop a more specific water treatment technique to provide industrial process water as close as possible to the source, applying quality assurance and efficiency control techniques for operational management. An innovative and cost-effective approach minimizes environmental impact from wastewater and prevents potential damage to health.

Acknowledgment

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BIBLIOGRAPHY

1. Colella, C. (1999). Environmental applications of natural zeolitic materials based on their ion exchange properties. In: *Natural Microporous Materials in Environmental Technology*. P. Misaelides, F. Macašek, T.J. Pinnavaia, and C. Colella (Eds.). Kluwer Academic, Dordrecht, The Netherlands, pp. 207–224.
2. Rees, L.V.C. (1997). Ion exchange in zeolites: Detergency and catalytic systems. In: *Progress in Ion Exchange—Advances and Applications*. A. Dyer, M.J. Hudson, and P.A. Williams (Eds.). RSC, pp. 393–402.
3. Ma, Q.Y., Traina, S.J., Logan, T.J., and Ryan, J.A. (1994). Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environ. Sci. Technol.* **28**: 1219–1228.
4. Mandjiny, S., Zouboulis, A.I., and Matis, K.A. (1995). Removal of cadmium from dilute solutions by hydroxyapatite. Part I. Sorption studies. *Sep. Sci. Tech.* **30**: 2963–2978.
5. Lo, S., Jeng, H., and Lai, C. (1997). Characteristics and adsorption properties of iron-coated sand. *Water Sci. Technol.* **35**(7): 63–70.
6. Bakoyannakis, D.N. et al. (2003). Akaganeite and goethite-type nanocrystals: Synthesis and characterization. *Microporous Mesoporous Mater.* **59**: 35–42.
7. Asouhidou, D.D., Lazaridis, N.K., and Matis, K.A. (2004). Sorbent materials for metal ions removal from aqueous solutions: A review. *Int. Conf. Protection Restoration Environ.* VII, NTUA & Stevens Inst. Tech., Myconos, Greece.

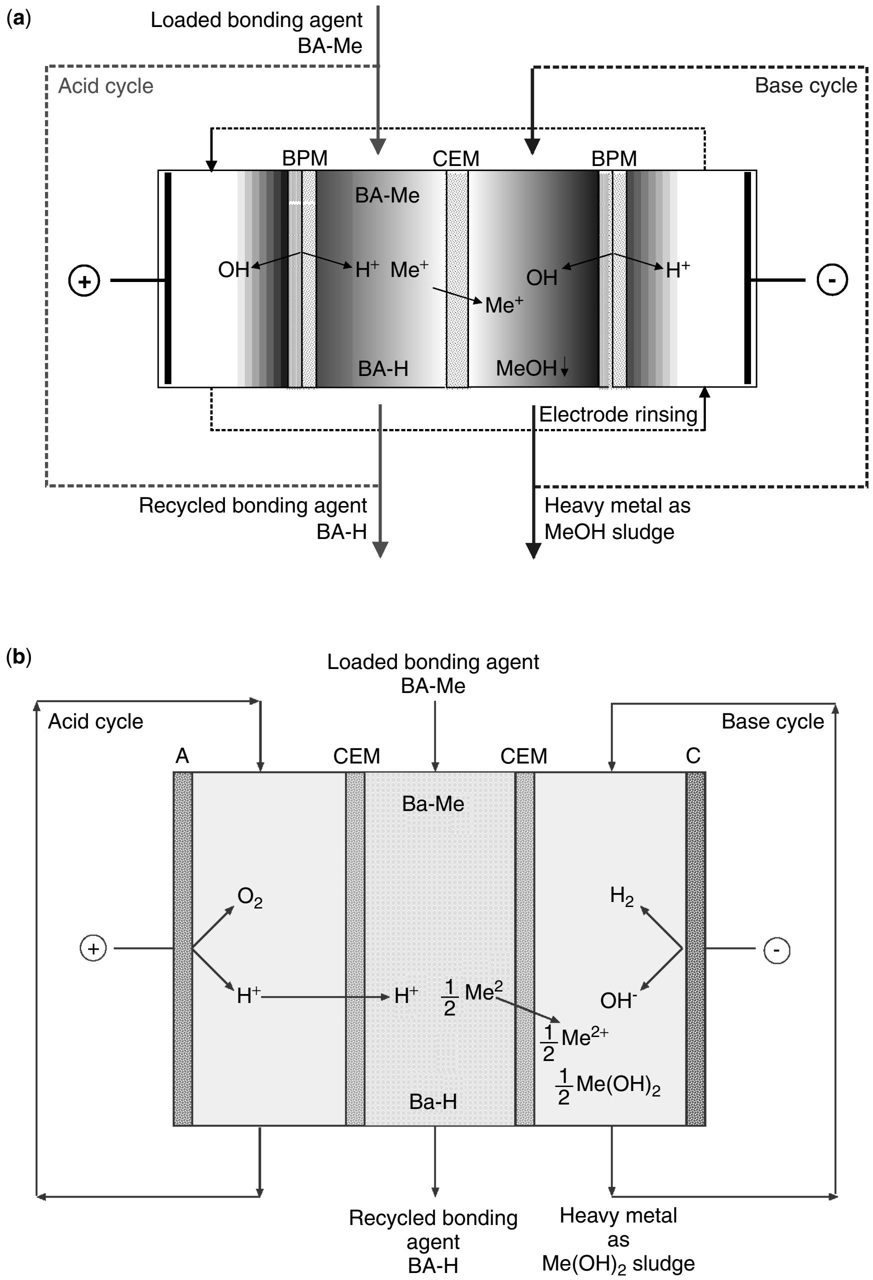

Figure 4. (**a**) Regeneration of water-soluble bonding agent by electrodialysis with bipolar membranes. (**b**) Regeneration of powdered bonding agent by modified electrodialysis. Reprinted with gratitude from Reference 10.

8. Evanko, C. and Dzombak, D. (1997). *Remediation of Metals-Contaminated Soils and Groundwater*. Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA.
9. Mavrov, V., Erwe, T., Blöcher, C., and Chmiel, H. (2003). Study of integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater. *Desalination* **157**: 97–104.
10. EU FP 5 Project METASEP. (2004). Public Report. Brussels.
11. Deliyanni, E.A., Lazaridis, N.K., Peleka, E.N., and Matis, K.A. (2004). Metals removal from aqueous solution by iron-based bonding agents. *Environ. Sci. Pollut. Res.* **11**: 18–21.
12. Deliyanni, E.A., Bakoyannakis, D.N., Zouboulis, A.I., and Matis, K.A. (2004). Development and study of iron-based nanoadsorbents. *36th Int. Oct. Conf. Min. Metall.* Serbia-Montenegro.
13. Hayes, K.F., Papelis, Ch., and Leckie, J.O. (1988). Modelling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces. *J. Coll. Interface Sci.* **125**: 717–726.
14. Lehmann, M., Zouboulis, A.I., and Matis, K.A. (2001). Modelling the sorption of metals from aqueous solutions on goethite fixed-beds. *Environ. Pollut.* **113**: 121–128.
15. Matis, K.A., Zamboulis, D., Zouboulis, A.I., and Lazaridis, N.K. (1999). Goethite mineral as a sorbent for heavy metals. In: *Natural Microporous Materials in Environmental Technology*. P. Misaelides, F. Macašek, T.J. Pinnavaia, and C. Colella (Eds.). Kluwer Academic, The Netherlands, pp. 425–433.
16. Matis, K.A. et al. (2004). Application of flotation for the separation of metal-loaded zeolites. *Chemosphere* **55**: 65–72.
17. Zouboulis, A.I., Matis, K.A., Lazaridis, N.K., and Golyshin, P.N. (2003). The use of biosurfactants in flotation: Application for the removal of metal ions. *Miner. Eng.* **16**: 1231–1236.

18. Schlichter, B., Mavrov, V., Erwe, T., and Chmiel, H. (2004). Regeneration of bonding agents loaded with heavy metals by electrodialysis with bipolar membranes. *J. Membrane Sci.* **232**: 99–105.
19. Butter, T.J. et al. (1998). The removal and recovery of cadmium from dilute aqueous solutions by biosorption and electrolysis at laboratory scale. *Water Res.* **32**: 400–406.

APPLICATION OF MICROFILTRATION TO INDUSTRIAL WASTEWATERS

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The examination of membrane processes started mostly as a search for effective product separation that is crucial to economical operation in process industries. Certain types of materials are inherently difficult to separate, and their processing has become of increased importance in recent years, especially due to the growth of the biotechnological industry (1) This new technology using synthetic membranes for process separations has developed rapidly. Industrial membrane processes are classified according to the size range of materials, which they are to separate, and the driving force used in separation. The most common pressure-driven process is microfiltration (often denoted as MF) (2). This technique separate a size range of 10–0.1 μm; typical examples of materials separated are small particles, large colloids, and microbial cells.

Conventional processes for treating wastewater, precipitation, precipitation/reduction, ion exchange/sorption bed filtration, etc., often have disadvantages such as high use of treatment chemicals; large quantities of sludge produced that has to be treated and disposed of; inadequate selectivity; slow kinetics of the metals and their oxyanions and therefore, large water treatment units and high investment costs are required; low capacity of ion exchangers and sorbents; the residual metal concentration in the treated water streams can be high and water reuse or discharge is problematic; fouling and scaling problems, very low membrane permeability, and low water yield (up to 75%) are problems often encountered in conventional membrane processes; treatment processes are periodic and not continuous, followed by a regeneration step in which regeneration chemicals and rinsing water are employed, ultimately generating a new quantity of wastewater; treatment of wastewater streams with large volume flow and high concentrations is mostly not cost-effective. So, combinations of treatment processes are usually applied in practice.

Such a combination could, for instance, have as the first step the use of a suitable bonding agent followed by another separation technique downstream as a membrane process (3); see also the article on Bonding of toxic metal ions in this *Encyclopedia of Water*. Metal ion recovery by membrane technologies from aqueous waste streams was reviewed by several vendors in the field (4). At a lower particle size range than that for microfiltration, as aforementioned, other membrane processes are applied. Some examples of these applications involve, among others, ultrafiltration (UF) of fruit juices using tubular configuration polymeric and ceramic membranes (5) and reverse osmosis in treating sugar beet press water (6). Different polymeric membranes from commercial companies were tested for wine clarification (7), and the ceramic membranes were compared with polymeric ones for removing of natural organic matter from drinking water sources (8).

Ceramics are good materials for producing membrane filtration tubes (9). The advantages of ceramic membranes compared to polymer membranes include resistance to high temperatures up to 280 °C (in specially developed modules and systems up to approximately 700 °C); good corrosion resistance: resistance to organic solvents and a wide pH range; suitability for cleaning and steam sterilization; high mechanical strength: the possibility to back pulse, resulting in efficient removal of the dirt layer and the possibility of treating fluids with high viscosity; chemical inertness: a wide range of application possible in the chemical industry; long operational life; and high membrane flux from a composite structure. The disadvantages of ceramic membranes compared to polymeric membranes are brittleness and so they must be handled with care; the surface area/volume ratio is low so systems have larger dimensions; and the investment in ceramic membranes is high.

Microfiltration constitutes a physical barrier to solid particles (as bonding agents), but has limitations because of increased fouling at high concentrations. Conventionally, cross-flow processes are applied, where high shear rates on the membrane surface are created to prevent fouling of membranes. The corresponding high energy consumption led to the development of so-called low-energy systems (10), which are characterized by immersed membranes operated by vacuum or hydrostatic pressure. Fouling is often controlled by air blowing from below the membranes, creating shear forces near the membrane surface. The energy consumption of these systems is considerably lower than that of cross-flow systems, yet still significant (11). Furthermore, flux is also low, especially at higher concentrations of suspended solids in the reactor. Immersed membranes have been used for a variety of applications, mainly biological wastewater treatment and drinking water production (12).

New MF/UF membrane modules were developed (13) with emphasis on crossflow or submerged operation, optimized hydrodynamics (in contrast to commercial hollow fiber or spiral-wound modules) to work at higher bonding agent (BA) concentration in water, high fluxes in real process water, low fouling tendency, easy cleaning suited for backwashing, and low production costs. Both

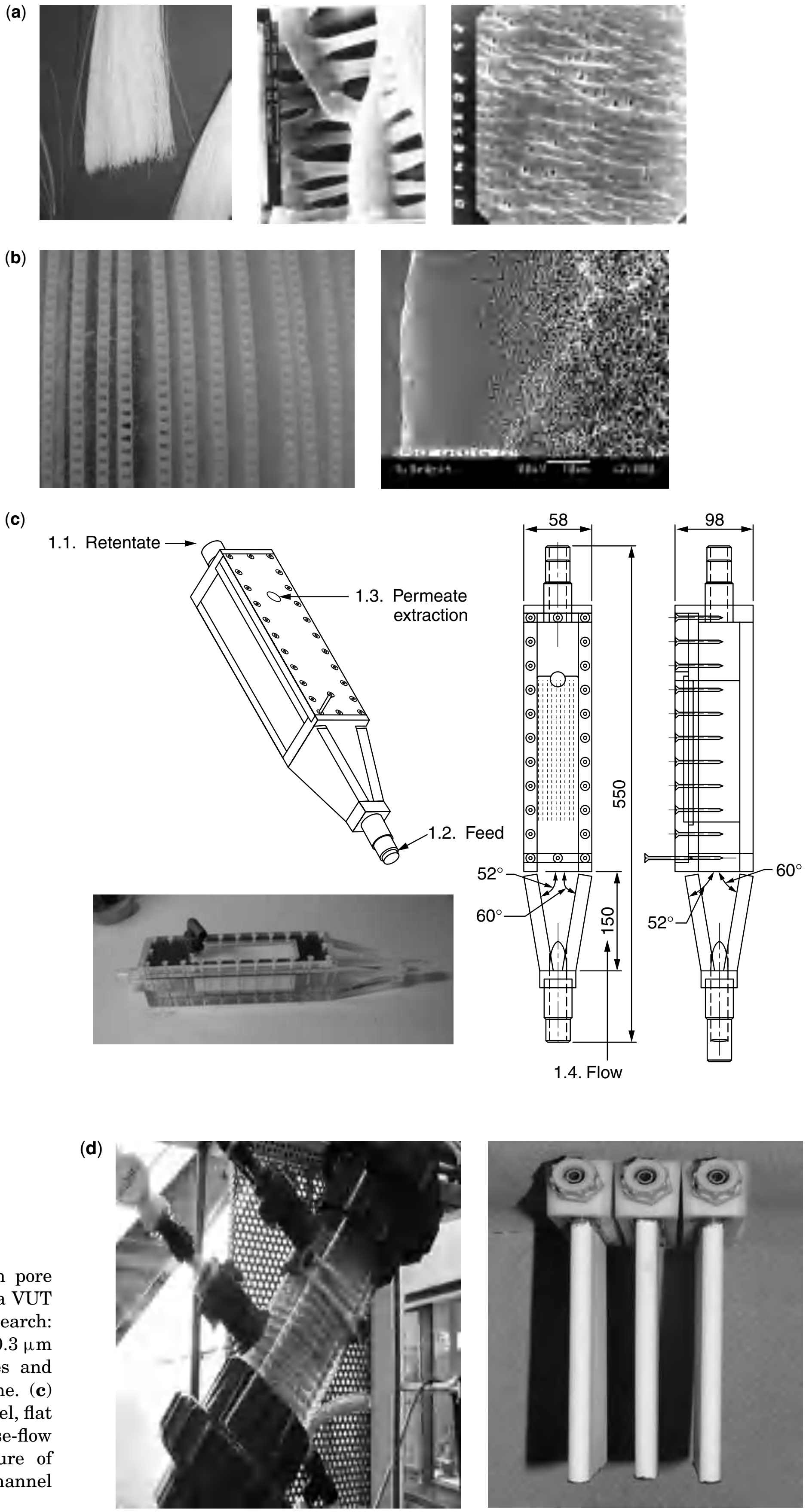

Figure 1. (**a**) PP membranes of 0.1 μm pore size produced by Eidos (and delivered via VUT Brno). (**b**) Membranes developed by S. Search: multichannel, flat sheet membranes (0.3 μm pore size), used for submerged modules and capillary outside skinned MF membrane. (**c**) Cross-flow module with PES, multichannel, flat sheet membranes. (**d**) Lab-scale transverse-flow membrane module by TNO, and picture of submerged module with ceramic multichannel flat sheet membranes.

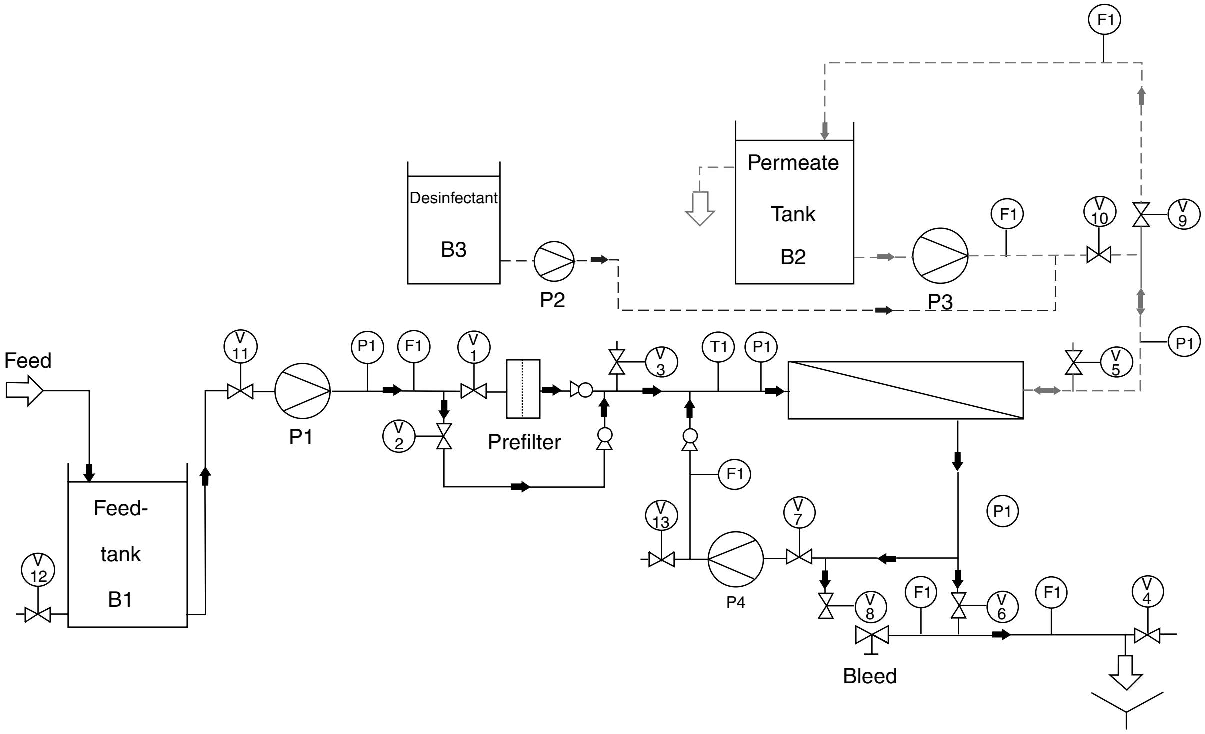

Figure 2. Process scheme of a bench-scale MF plant.

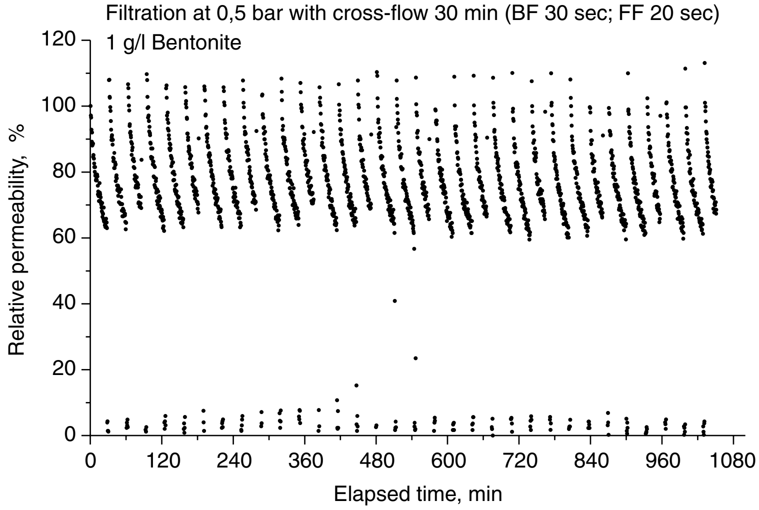

Figure 3. Filtration of bentonite suspension with PP membrane module in back-flush mode.

polypropylene (PP) as well as polyethersulphone (PES) based membranes were developed (see Fig. 1). PP fibers have a symmetrical wall, low flux and are inexpensive. PES capillaries have an asymmetrical wall, and higher flux, but are more expensive. Because of this trade-off, both membranes are of much interest in research. These PP fibers were used in common longitudinal membrane modules, as shown in Fig. 1a–d with bench-scale modules. Figure 1c shows a cross-flow module with PES multichannel, flat sheet membranes.

The PES capillary membranes were used for the transversal flow membrane module (TFM). Previous studies showed that within TFM modules, membranes tend to break because of the high stress at the potting-membrane interface. Much improved capillary membranes were developed. They possess three times the tensile strength at break (13). This was the result of adding a component to the extrusion mixture that resulted in a tighter sponge in the support layer. Figure 1d, left, shows the TFM module consisting of 10 active layers of 8 membranes next to each other in a grid.

The process scheme of the bench-scale plant used is presented in Fig. 2, based on feed-and-bleed processing; automatic back-flush was incorporated. Experiments with bentonite and the PP membrane modules in longitudinal outside mode showed that relative permeability decreased,

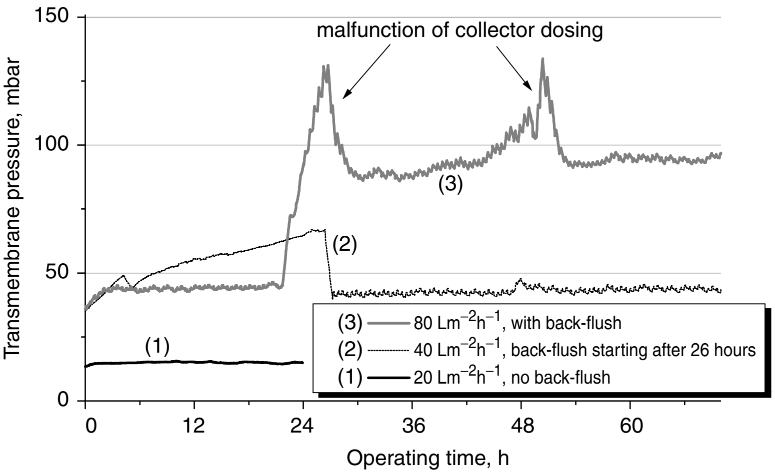

Figure 4. Transmembrane pressure as a function of time for the hybrid process at various operating modes, under the following conditions: c(zeolites) = 8 g/L, c(CTABr) = 20 mg/g, $u_g = 0.33$ cm/s, back-flushing (if applied) every 30 min for 10 s.

when the transmembrane pressure was increased. Somewhat surprising, but very promising was that the back-flush mode has been very effective. At least during 22 hours, permeability was constant (Fig. 3). When selecting membranes for efficiency and rejection of substances, permeability and pore size or molecular weight cutoff were examined as important criteria (14).

Today, there is a tendency for combined and more compact processes as, for example, membrane bioreactors (15). Membrane fouling was also said to be the main limitation to the faster development of the latter. A newly developed type that has the further advantage of energy saving is the submerged membrane bioreactor.

A large number of techniques have been used to limit membrane fouling, such as cross-flow liquid velocity, the use of baffles, back-flushing, transmembrane pressure (TMP) pulsing, and air sparging (16). Depending on the membrane process, the function of air can be different: a gas back-flush detaches and carries away deposited particles, the formation of a particle or concentration polarization may be prevented or limited, and even a compound may be transferred by gas to a liquid phase.

Air bubbling, under appropriate conditions, could also be used as the transport for flotation, which is another efficient separation method applied in water treatment (17). The aim of this innovative idea was integrating both processes in the same tank, taking advantage of dispersed-air flotation combined with microfiltration by submerged membranes. For this, ceramic flat-sheet membrane modules with multichannel geometry were tested; the pore size was 0.3 μm, pure water flux 3000 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$, the material of permeate collector polystyrene, and sealing material epoxy. The membrane distance was 20 mm, geometry 100 × 100 and area 0.054 m^2 (Fig. 1d, right). The hybrid cell was tested on-site at the Assarel-Medet open pit copper mine effluent, near Panagyurishte, Bulgaria (18). The flotation separation techniques employed and investigated were based on three different mechanisms: (1) ion flotation using xanthates, (2) precipitate flotation generating copper hydroxide, and (3) sorptive flotation using zeolites as sorbent material—see also the article on Flotation in this *Encyclopedia*.

A parallel economic study showed that the capital investment for the hybrid unit would be of the order of 0.92 M€. The operating cost of the plant is about 1.42 M€ per year. Comparison with separate systems (MF following flotation) showed that the hybrid system has a lower capital cost and lower operating costs. The former also requires larger membranes.

The advantageous influence of flotation may be apparent from Fig. 4. Membranes were operated at constant flux in all experiments. For an initial zeolite concentration of 8 g/L the membranes could be operated at 20 L/m^2h without back-flushing. Resulting transmembrane pressure was as low as 15 mbar. However, to achieve stable membrane performance at higher fluxes, back-flushing was necessary. A cycle of 10 s back-flushing every 30 min was sufficient, resulting in TMP of 45 and 90 mbar (the mean of two cycles between backwashing) for imposed fluxes of 40 and 80 L/m^2h, respectively. The relatively long time between back-flushing resulted in a permeate loss of less than 5% due to backwashing (19).

In Fig. 4, it can also be seen that the increase in transmembrane pressure when operating the membranes at 40 L/m^2h without back-flushing was fully reversible. Switching the operating mode of a membrane, that had been operated in continuous permeate withdrawal for 24 hours, to back-flushing resulted after less than 1 hour in the same transmembrane pressure as a membrane, which had been operated with back-flushing from the beginning. This proves that the loss in membrane performance was attributed to an easily removable cake layer, which was also visually observed. The resistance-in-series model (20) may be used in this case, which describes filtration resistance as the fraction of TMP to flux; the resistance of the cake layer can be evaluated according to

$$J = \frac{\mathrm{TMP}}{\eta(R_\mathrm{M} + R_\mathrm{C})} 3.6 \times 10^8, \tag{1}$$

where J is permeate flux, R_M is membrane resistance, R_C is the resistance of the cake layer or, in general, fouling resistance; and η the viscosity of water to be filtered. Cake resistance is of the same magnitude as membrane resistance and thus, quite low, which can be attributed to a highly permeable cake layer that zeolites form. These results could be also considered in terms of the concept of "critical flux" (the flux up to which the relation between flux and TMP is linear), which is currently often applied to microfiltration processes (21). Although this concept does not imply back-flushes, from a process point of view, it can also be concluded that the membranes in our process were operated in the subcritical flux region. In all investigations, the air supply was determined by that required for flotation. No additional aeration of the membranes was carried out. This has to be considered when relating membrane performance to conventional immersed membrane systems because the superficial air velocity used in the hybrid cell was about 10 times lower than that usually applied in these systems.

Concluding, one of the main objectives of environmental technology today is to design and implement processes to clean effluents from industrial production; recycling valuable materials and microfiltration has certainly a definite role having presented very promising results. Product recovery and waste recycling have been addressed by providing novel integrated processes for reusing water and the possibility of metal recycling, aiming to meet regulatory requirements with environmental benefits, not merely by reducing risks.

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BIBLIOGRAPHY

1. Coulson, J.M., Richardson, J.F., Backhurst, J.R., and Harker, J.H. (1991). *Chemical Engineering*. 4th Edn. Vol. 2. Pergamon, Oxford, UK.
2. Porter, M.C. (1986). Microfiltration. In: *Synthetic Membranes: Science, Engineering and Applications*. P.M. Bungay, H.K. Lonsdale, and M.N. de Pinho (Eds.). D. Reidel, Dordrecht, pp. 225–247.
3. Mavrov, V., Erwe, T., Blöcher, C., and Chmiel, H. (2003). Study of new integrated processes combining adsorption, membrane separation and flotation for heavy metals removal from wastewater. *Desalination* **157**: 97–104.
4. Radecki, P.P., Crittenden, J.C., Shonnard, D.R., and Bulloch, J.L. (Eds.). (1999). *Emerging Separation and Separative Reaction Technologies for Process Waste Reduction—Adsorption and Membrane Systems*. AIChE, Center for Waste Reduction Technologies, New York, pp. 199–219.
5. Capannelli, G., et al. (1994). The use of membrane processes in the clarification of orange and lemon juices. *J. Food Eng.* **21**: 473–483.
6. Hinkova, A., Bubnik, Z., Kadlec, P., and Pridal, J. (2002). Potentials of separation membranes in the sugar industry. *Sep. Purific. Tech.* **26**: 101–110.
7. Urkiaga, A., Fuentes, de las L., Acilu, M., and Uriarte, J. (2002). Membrane comparison for wine clarification by microfiltration. *Desalination* **148**: 115–120.
8. Lee, S. and Cho, J. (2004) Comparison of ceramic and polymeric membranes for natural organic matter (NOM) removal. *Desalination* **160**: 223–232.
9. Scott, K. (1997). *Handbook of Industrial Membranes*. Elsevier, Oxford, UK, p. 413.
10. Côté, P.L., Smith, B.M., Deutschmann, A.A., Rodrigues, C.F.F., and Pedersen, S.C. (1994). Frameless array of hollow fibre membranes and method of maintaining clean fiber surfaces while filtering a substrate to withdraw a permeate. World Patent WO 94/11094, Zenon Environmental Inc.
11. Guibert, D., Ben Aim, R., Rabie, H., and Côté, P.L. (2002). Aeration performance of immersed hollow-fibre membranes in a bentonite suspension. *Desalination* **148**: 395–400.
12. Côté, P.L., Mourato, D., Güngerich, C., Russell, J., and Houghton, E. (1998). Immersed membrane filtration for the production of drinking water: Case studies. *Desalination* **117**: 181–188.
13. EU FP 5 Project METASEP. (2004). Public Report, Brussels.
14. Schlichter, B., Mavrov, V., and Chmiel, H. (2000). Comparative characterization of different commercial UF membranes for drinking water production. *J. Water Supply: Res. Tech.-AQUA* **49**: 321–328.
15. Blöcher, C. et al. (2002). Recycling of spent process water in the food industry by an integrated process of biological treatment and membrane separation. *Desalination* **144**: 143–150.
16. Matis, K.A. et al. (2004). Air sparging during the solid/liquid separation by microfiltration: Application of flotation. *Sep. Puri. Tech.*. **40**: 1–7.
17. Lazaridis, N.K., Blöcher, C., Dorda, J., and Matis, K.A. (2004). A hybrid MF process based on flotation. *J. Membrane Sci.* **228**: 83–88.
18. Lazaridis, N.K., Peleka, E.N., Karapantsios, Th.D., and Matis, K.A. (2004). Copper recovery from effluents by various separation techniques. *Hydrometallurgy* **74**: 149–156.
19. Blöcher, C. et al. (2003). Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater. *Water Res.* **37**: 4018–4026.
20. Cheryan, M. (1998). *Ultrafiltration and Microfiltration Handbook*. Technomic, Lancaster, PA.
21. Cho, B.D. and Fane, A.G. (2002). Fouling transients in nominally subcritical flux operation of a membrane bioreactor. *J. Membrane Sci.* **209**: 391–403.

WATER TREATMENT IN SPENT NUCLEAR FUEL STORAGE

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Many facilities are changing their storage to dry mode, but in 1996, there were 100,000 tons of Zircaloy-clad spent nuclear fuel (SNF) in wet storage (1). Much of this fuel is stored in extended mode, beyond the period of time originally planned. Thus, this extended storage can create problems.

A typical spent nuclear fuel pool storage system is shown in Fig. 1. The main functions of water storage pools are to contain the fuel and any radionuclides that leak and to remove heat generated by radionuclide decay. Water is withdrawn from pools via overflow sumps and pumped through a filter to remove solids including microorganisms. The water is treated by ion exchange

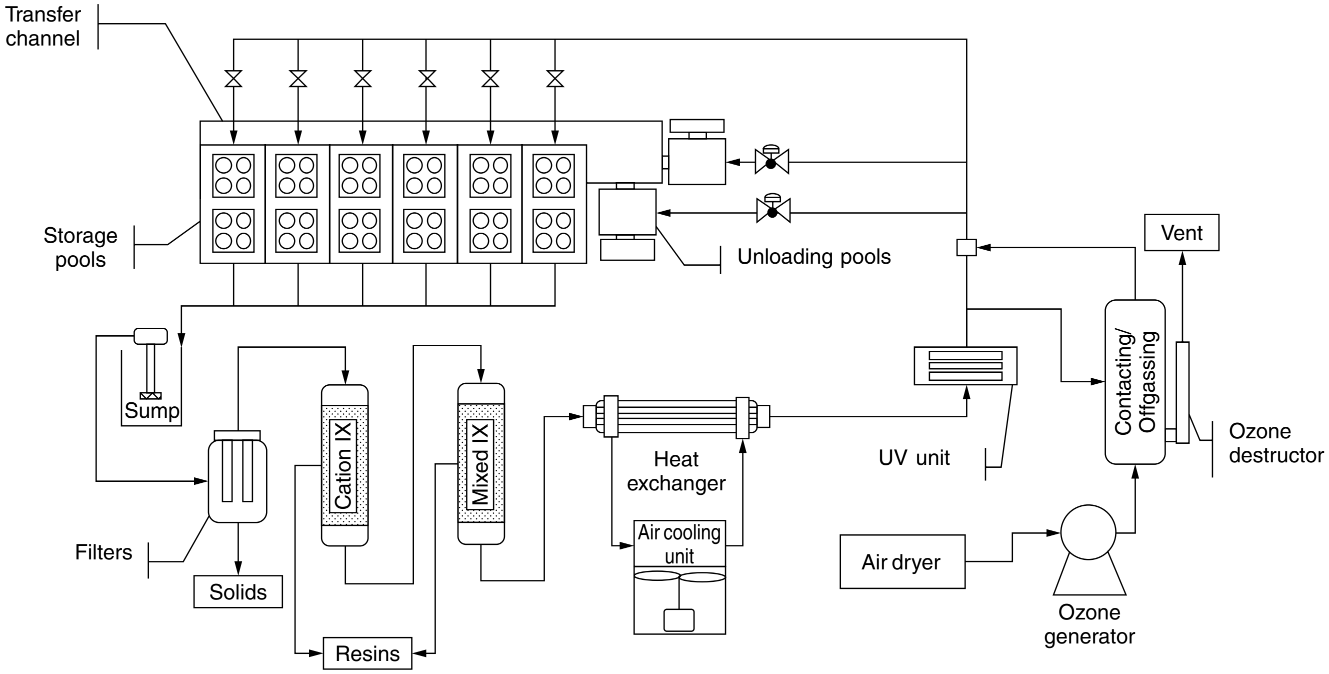


Figure 1. Typical spent fuel storage schematic.

to remove radionuclides and other dissolved substances. Heat exchangers remove the decay heat that the spent fuel transfers to the water. Some systems have ultraviolet (UV) light systems that kill microorganisms. An ozonator is also shown in Fig. 1, even though many systems do not have this. The supply makeup water normally has very low conductivity ($\kappa \leq 1$ μS/cm), so there is very little ion exchange capacity used up unless the fuel is in very bad shape and is leaking. There is also a need to provide basin chemistry/corrosion control to minimize corrosion of SNF, parts, and equipment. The following are typical limits imposed to minimize corrosion: $5.0 < \text{pH} < 8.0$, exclusion of heavy metals or their salts including Cu, Pb, Sn, Hg, Ni, and Co, keeping $\text{Cl}^- < 10$ ppm, and limiting conductivity <10 μmho/cm (μS/cm). There may be a potential for microbiologically induced corrosion (MIC) in storage pools, so it is important to control microorganisms. This article focuses on microbiological control that presents the biggest challenge facing pool storage systems. The corrosion of fuel element cladding must be minimized to ensure containment of radionuclides and worker protection. The general outline is a discussion of mechanisms, rationale for treatment, and treatment methods for storage pools.

MICROBIOLOGICAL MECHANISMS

Some of the variables that affect the growth of microorganisms include food/nutrient availability, temperature, pH, biocide concentrations, radiation, makeup water microorganism concentration, and predation. There are practical limitations to the types of activities that can be used to control microorganisms, for example, restricting the use of biocides or pH out of the range of water chemistry requirements.

The first substances on a surface during biofilm formation are trace organics (2). Almost immediately after the clean pipe surface comes into contact with water, an organic layer deposits on the water/solid interface (3). These organics form a conditioning layer that neutralizes excessive surface charge and surface free energy that may prevent a bacterial cell from approaching near enough to initiate attachment. In addition, the absorbed organic molecules often serve as a nutrient source for bacteria.

Some planktonic (free-floating) bacteria approach the pipe or equipment wall and become entrained within the boundary layer. Some of these cells strike and adsorb to the surface for some finite time and then desorb. This initial attachment is based on electrostatic attraction and physical forces. Some of the reversibly adsorbed cells begin forming structures that may permanently bond the cell to the surface. These cells become irreversibly adsorbed. Figure 2 provides a schematic of this stage of biofilm development.

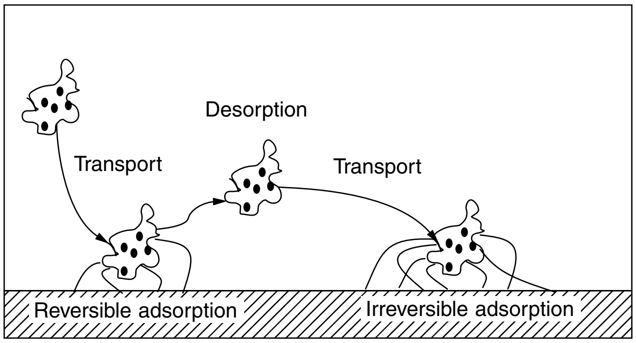


Figure 2. Biofilm development.

Biofilm bacteria excrete extracellular, polymeric substances that contain the biofilm and attach it to a wall. These polymer strands trap scarce nutrients and protect bacteria from biocides. Attachment is mediated by extracellular polymers that extend outward from the bacterial cell wall (3). The polymeric material, or glycocalyx, consists of charged and neutral polysaccharide groups that facilitate attachment and also act as an ion-exchange system for trapping and concentrating trace nutrients from the overlying water. As nutrients accumulate, the pioneer cells proceed to reproduce. The daughter cells then produce their own glycocalyx, greatly increasing the volume of ion-exchange surface. A viable colony of bacteria is thereby established (4).

A biofilm-covered surface is gelatinous and slippery because the glycocalyx matrix holds water (75–95%) (5). The glycocalyx net also absorbs other types of microbial cells through physical restraint and electrostatic interaction. These secondary colonizers metabolize wastes from the primary colonizers and produce their own waste that other cells then use in turn. Bacteria and other microorganisms develop cooperative colonies within the biofilm. An anaerobic biofilm may develop underneath the aerobic layer. The biofilm thickness will reach equilibrium as flowing water detaches cells extending out into turbulent flow.

Different species live in the films, helping each other to exploit food supplies and to resist biocides through synergistic interactions. Some species use toxic wastes produced by another species as food. By pooling their biochemical resources to build a colony, several species of bacteria, each with different enzymes, can break down food supplies that no single species could digest alone. The biofilms are permeated at all levels by a network of channels through which water, bacterial wastes, nutrients, enzymes, metabolites, and oxygen travel. Gradients of chemicals and ions between microzones provide the power to shunt substances around the biofilm (6).

A biofilm can spread at its own rate by ordinary cell division, and it also periodically releases new pioneer cells to colonize downstream sections of piping and equipment. As the film grows to a thickness that allows it to extend through the boundary layer into zones of greater velocity, some cells are sloughed off. These later pioneer cells more easily adsorb than their upstream predecessors because the parent film releases wastes into the stream that may serve as either the initial organic coating for uncolonized pipe sections downstream or as nutrient substances for other cell types (4).

The development of a mature biofilm may take several hours to several weeks, depending on the system (3). *Pseudomonas aeruginosa* is a common pioneering bacteria and is used frequently in biofilm research. In one experiment, researchers found that *Pseudomonas* cells adhere to stainless steel, even to electropolished surfaces, within 30 seconds of exposure (7). The association of bacteria with a surface and the development of a biofilm can be viewed as a survival mechanism. Bacteria benefit by acquiring nutrients and protection from biocides.

Potable water systems, especially high-purity water systems, are nutrient-limited environments, but even nutrient concentrations too low to measure are sufficient to permit microbial growth and reproduction. Bacteria and other organisms capable of growth in nutrient-limited environments are called oligotrophs. Bacteria have evolved the means to find and attach to surfaces to increase the chances of encountering nutrients.

In a study on the attachment of *Pseudomonas* to stainless steel surfaces (8), researchers put cells in a blender to remove the flagella. They found that the rate of cell attachment decreased at least 90% when flagella were removed.

Many organisms faced with the starvation conditions encountered in purified water systems respond by altering their cell wall structure to increase their affinity for surfaces. By altering the protein and lipid composition of the outer membrane, the charge and hydrophobicity can be changed. The cell wall becomes hydrophobic. Once in the boundary layer, they are attracted to a pipe surface (4).

Recent research has dispelled some earlier assumptions about bacteria and biofilms. In the past, microbiologists assumed that biofilms contained disorderly clumps of bacteria located in no particular structure or pattern. In most cases, the base of the biofilm is a bed of dense, opaque slime 5 to 10 μm thick. It is a sticky mix of polysaccharides, other polymeric substances, and water, all produced by the bacteria. Water currents that flow in channels between the colonies carry nutrients and waste (9).

Past researchers assumed that biofilm bacteria behaved much like solitary, free-floating microorganisms. Biofilm bacteria have exactly the same genetic makeup as their free-roving relatives, but their biochemistry is very different because they activate a different set of genes. The instant the bacteria dock to glass, they switch on certain genes involved in the synthesis of alginate (an unusually sticky form of slime), switching them off again once the bacteria are engulfed in alginate. It is now estimated that as many as 30 to 40% of the proteins in bacterial cell walls differ between sessile and planktonic bacteria. Some of the targets for biocides are not there any more, so the bacteria become difficult to kill.

Researchers are studying the chemicals (called sigma factors) which signal bacteria to change their biochemistry to life in a biofilm (9). If they can discover a reverse sigma factor which would change biofilm bacteria into planktonic free-floaters, it might be possible to dissolve biofilms by sending the equivalent of an evacuation signal (6).

The surface material has little or no effect on biofilm development. Stainless steel is just as susceptible as plastic pipe. Piping material to which microorganisms cannot adhere has yet to be discovered. Studies have shown that microbes adhere to stainless steel, Teflon, PVC, and PVDF (Kynar) nearly equally (4). Incorporating an antimicrobial additive into plastic to delay or reduce the attachment of biofilm is possible (10). However, the chemicals used are not normally safe for drinking water supplies. Some ion exchange resins have been silver-coated to prevent microbial growth. However, silver-tolerant bacterial populations can develop (11). There are no practical examples of toxic surface coatings for drinking water piping.

One major factor influencing biofilm development in purified-water systems is surface area. Industrial water systems, unlike most natural environments (lakes and rivers), offer a tremendous amount of surface area for attachment. RO membranes, ion exchange resins, storage tanks, cartridge filters, and piping systems all provide surfaces suitable for bacterial attachment and growth (3).

Although smoother surfaces delay the initial buildup of attached bacteria, smoothness does not significantly affect the total amount of biofilm that attaches to a surface. No surfaces have been found that are exempt from biofouling (12). Surface structure influences the rate of fouling, but only initially during the first few hours of exposure. In general, smooth surfaces foul at a slower initial rate than rough ones, but biofilm formation after a period of days is inevitable.

High water flow rates may alter biofilm growth but do not prevent the attachment of bacteria to pipe surfaces. Work by Mittelman (3), Patterson (13), and Meltzer (12) supports this conclusion. High flow does not prevent bacterial attachment or remove an existing biofilm for the following reasons:

- Low flow in the boundary layer. The velocity is zero at the wall of a pipe or other surface. Near the wall, a boundary layer exists that is controlled by viscous effects, whereas outside the boundary layer, the flow is not determined by viscous effects. Within this boundary layer, for both laminar and turbulent flow, particles and microorganisms can transport and attach to surfaces. Regardless of the water velocity, the velocity profiles are such that it flows most slowly in the layers adjacent to pipe surfaces. The laminar sublayer thickness was calculated (14) for various flow velocities and for five pipe sizes. The shear forces within the laminar sublayer are much less than the forces produced in biofilm attachment.
- Strong adhesion by exopolymers. In water systems where high-velocity flow is continuous, the bacteria that accumulate in a biofilm tend to be filamentous varieties (such as *Pseudomonas*) especially suited for attachment by filaments.
- Although high flow velocity does not prevent the attachment of bacteria to pipe surfaces, it does have the following effects on the biofilm structure:
  - Denser biofilm. At higher flow rates, a denser, somewhat more tenacious biofilm is formed (3).
  - Limited biofilm thickness. The maximum thickness of a biofilm can be considered the thickness of the laminar sublayer (see Table 1).
  - Limited nutrients. Like other living creatures, bacteria require certain nutrients for growth and reproduction. Limiting these nutrients limits, bacterial growth, but nutrient levels in high-purity systems are unequivocally sufficient to permit microbial growth and reproduction to a troublesome extent (15). Table 1 lists some sources of nutrients in purified water systems.

Table 1. Nutrients for Bacterial Growth Found in Pure Water Systems[a]

Nutrient	Sources
Organic carbon	Humic and fulvic acids (source water), pipe plasticizers and solvents, fiberglass-reinforced plastics (FRPs), pump and gauge lubricants, microbial by-products, personnel, airborne dust
Nitrogen	Humic and fulvic acids (source water), nitrates and nitrites (source water), microbial by-products, airborne dust
Phosphorus	Phosphates (source water), microbial by-products, airborne dust
Sulfur	Sulfates (source waters), sulfuric acid (RO pretreatment), membrane surfactants, airborne dust
Trace metals and salts	Source waters, process piping, fiberglass-reinforced plastics (FRPs), stainless steel system components, RO pretreatment, chemicals, personnel, airborne dust

[a] Reference 3.

Bacteria can get some of their nutrients from the pipe and fittings in a water system (11). Most plastics are not biodegradable, but pipe cements and plasticizers that leach from epoxy resins, PVC pipe, and polyamide pipe can be organic carbon sources for bacteria. Cellulose-based RO membranes can also be a nutrient source. That is why RO feedwater needs chlorination. Bacteria can also obtain trace metal nutrients from stainless steel and other metal components.

Currently available technology cannot reduce nutrient levels completely; so total control of bacteria is not achievable by simply controlling nutrients. Similarly, very small quantities of oxygen will adequately support bacterial growth, even if the bacteria do not revert to anaerobic respiration, which most bacteria can do. Therefore, a thriving bacterial population can exist, even in high-purity water systems (14). Nutrient-limiting environments can actually promote the attachment of bacteria to surfaces because that is where the trace organics accumulate and extracellular polymers in a biofilm capture trace nutrients. Although bacteria cannot be completely starved out, nutrient-poor reverse osmosis water will support less biofilm than regular tap water supplies.

Water samples collect only planktonic or free-floating bacteria. Free-floating bacteria in animal drinking water are either sloughed off the biofilm or pass through from the incoming water supply. If a plate count test is low, one should not assume that bacteria are not present in the watering system. More than 99% of the bacteria in water systems are in biofilms attached to pipe and equipment surfaces. A mature biofilm may not slough off many cells into the drinking water if the integrity has not been disrupted (e.g., by recent flushing or sanitization). However, it is still there.

TREATMENT RATIONALE

Some of the main reasons to control microorganisms include: water clarity/turbidity, heat transfer surfaces and other equipment problems, and microbiologically induced corrosion.

Water Clarity/Turbidity

Very clear water is required to see the bottom of a pool (≈10 m). Therefore, both algal and sedimentary, particles must be removed so that required clarity can be maintained. Turbidity refers to how clear the water is. The greater the amount of total suspended solids (TSS) in the water, the murkier it appears, and the higher the measured turbidity. Algal turbidity varies seasonally and with depth in a complex manner in response to physical, chemical, and biological changes. Figure 3 shows the effect of algae concentration on turbidity. A comparison with sediments is shown in Fig. 4. Turbidity is reported in nephelometric units (NTUs) referring to the type of instrument (turbidimeter or nephelometer) used for estimating light scattering from suspended particulate material. The nephelometer, also called a turbidimeter, has a photocell set at 90° to the direction of the light beam to estimate scattered rather than absorbed light. This measurement generally provides a very good correlation with the concentration of particles in the water that affect clarity.

Another inexpensive device is called a turbidity tube. It involves looking down a tube at a black and white disk (Secchi disk) and recording the depth of water that makes the disk disappear. Secchi disk depth, then, is a measure of water clarity. There have not been many efforts to correlate distance clarity and turbidity. However, a rough correlation is provided in Fig. 5. Turbidity units (NTU and JTU) are interchangeable units. They differ only in that their name reflects the device used to measure turbidity. One JTU is equivalent to 1 ppm of silica.

Heat Transfer/Equipment Problems

The waterside heat transfer systems of a treatment loop heat exchanger are susceptible to a biofilm that can reduce the overall heat transfer coefficient and hence efficiency. Microorganisms can cause biofilms to coat piping, valves, pumps, and other equipment. Further, biofilms can occur on ion exchange resins, filters, in-basin structures, and spent nuclear fuel. Minimizing microorganisms and biofilms to help prevent this is highly desirable. In general, water from natural sources leads to poor cooling performance unless adequate steps are taken (16). The extent of the problem, however, depends on the quality of the raw makeup water. Deposits on heat exchanger surfaces are complex, and are likely to include particulate matter, crystalline salts, corrosion products, and biofilms. It is necessary to counteract this problem of deposition onto surfaces to maintain heat exchanger effectiveness.

When using natural waters, the presence of microorganisms is probably the predominant cause of poor heat transfer efficiency. The conditions on the waterside of a cooler are usually conducive to the growth of microorganisms, notably bacteria, because of suitable temperature conditions and the availability of nutrients. The colonization of a heat transfer surface and the subsequent growth of a biofilm may, under favorable conditions, lead to a deposit 1 mm thick or more, unless preventive action is taken. This layer represents resistance to heat transfer: it acts as an insulating layer. The biofilm may also act as a trap for particulate matter and corrosion products. In

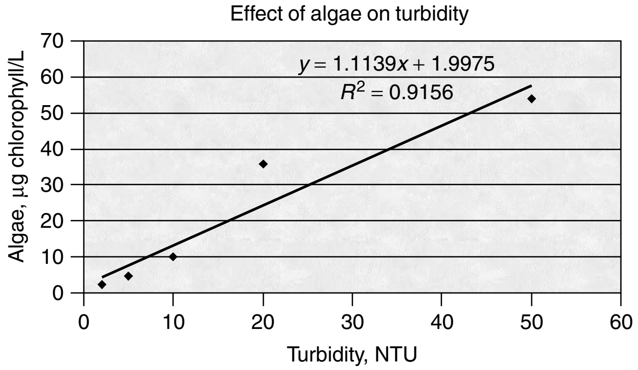


Figure 3. Turbidity vs. algae.

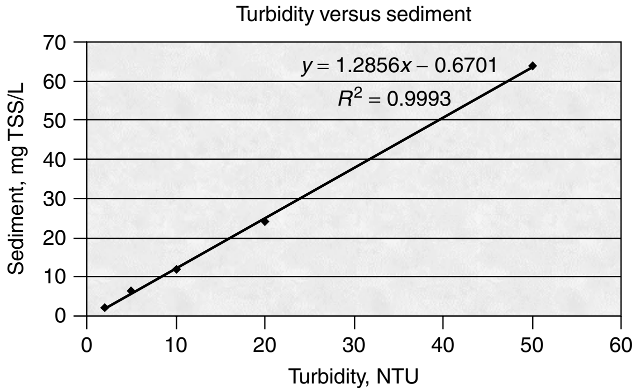


Figure 4. Turbidity vs. sediment.

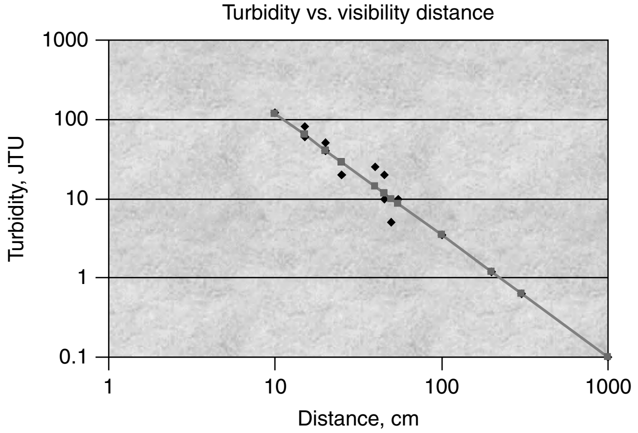


Figure 5. Turbidity vs. distance.

addition, the biofilm may encourage corrosion of the underlying metal due to biological activity, thereby adding to operating and maintenance costs.

The shape and structural arrangement of a biofilm growing in a flowing fluid influences the mass transfer characteristics of the biofilm system as well as the drag force exerted on individual biofilm structures (17). If the biofilm is highly compliant, the shape varies through the growth cycle of the biofilm and also due to variations in fluid shear stress (18). Changes in biofilm shape affect its porosity and density, therefore affecting the transfer of solutes into and through the biofilm. Fluctuations in biofilm shape also affect the hydrodynamic drag that in turn influences the detachment rate and pressure losses in a flowing system. In addition, it is thought that biofilm viscoelasticity may explain the large pressure drops observed in biofilm-fouled pipes (19). However, very few studies have been conducted on the material properties of intact biofilms, in part, due to the technical difficulty of such testing. The small dimensions and pliability of biofilms makes sample handling extremely difficult, and removal of the biofilm from the substratum radically changes the integrity of the sample.

Boundary layers have a large role in biofilm formation, so some discussion concerning them is instructive for the purposes of this section. In fluid mechanics, Prandtl (20) called the region where the viscous forces cannot be ignored the boundary layer. Prandtl arbitrarily suggested that it be considered the region where the x component of the velocity is less that 99% of the free-stream velocity. This is an arbitrary division that does not correspond to any physically measurable boundary but corresponds to an arbitrary mathematical definition. However, it is a very useful concept, clarified numerous unexplained phenomena, and provides a much better intellectual basis for discussing complicated flows (21).

An analogous concept exists for heat and mass transfer. The momentum boundary layer represents the flow regions dominated by viscous forces, and the thermal boundary layer represents a region dominated by conduction. Analogously, the mass boundary layer represents a region dominated by diffusion. The dimensionless numbers corresponding to them are the Reynolds (*Re*), Prandtl (*Pr*), and the Schmidt (*Sc*) numbers, respectively. Figure 6 shows laminar boundary layers and profiles for momentum, heat, and mass. In general, these will not be the same. The flat plate, boundary layer thickness for momentum, heat, and mass are given elsewhere as are the complicated profiles near the wall in turbulent flow (22).

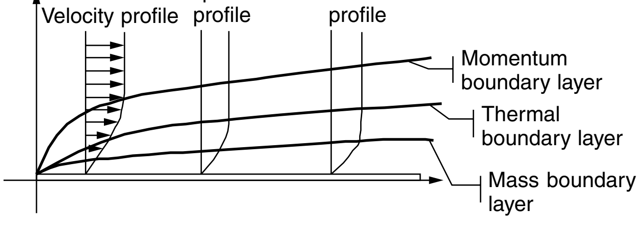


Figure 6. Laminar boundary layers.

The following provides an alternate, more practical correlation for determining the laminar, flat plate momentum boundary thickness (21):

$$\delta_{\mathrm{m}} \approx 5\sqrt{\frac{\nu\, x}{\nu_{\infty}}}. \tag{1}$$

Turbulent boundary layers differ in that there are several zones, including a laminar sublayer, a buffer zone, and a turbulent core. As the distance along a flat plate increases, a transition region develops followed by turbulence, as shown in Fig. 7. Estimating the turbulent boundary layer thickness can be done from (21)

$$\delta_{\mathrm{m}} = 0.37x\left[\frac{\nu}{\nu_{\infty}x}\right]^{1/5}. \tag{2}$$

The laminar sublayer is quite thin but represents the largest resistance to transport in the flow. However, the resistance is much less for turbulent than for laminar flow because the laminar sublayer is so thin and gradients are much steeper.

Microbiologically Induced Corrosion

Microbial cells on a metal surface can cause microbiologically influenced corrosion (MIC) or biocorrosion. The forms of corrosion caused by bacteria are not unique. Biocorrosion results in pitting, crevice corrosion, selective dealloying, stress corrosion cracking, and underdeposit corrosion. The basic corrosion equations for the corrosion cell shown in Fig. 8 are

$$\mathrm{M} \longrightarrow \mathrm{M}^{2+} + 2e^{-} \tag{3}$$

$$\mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} + 2e^{-} \longrightarrow 2\mathrm{OH}^{-} \tag{4}$$

Nonuniform (patchy) colonies of biofilm result in the formation of differential aeration cells where areas under respiring colonies are depleted of oxygen relative to surrounding noncolonized areas. Having different oxygen concentrations at two locations on a metal creates a difference in electrical potential and consequently corrosion currents. Under aerobic conditions, the areas under the respiring colonies become anodic, and the surrounding areas become cathodic.

Oxygen depletion at the surface of stainless steel can destroy the protective passive film. Stainless steels rely

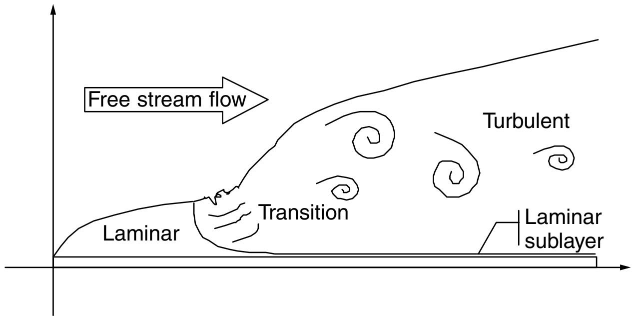


Figure 7. Turbulent boundary layer.

on a stable oxide film to provide corrosion resistance. Corrosion occurs when the oxide film is damaged or oxygen is kept from the metal surface by microorganisms in a biofilm. Oxygen depletion at the surface also provides a condition for anaerobic organisms such as sulfate-reducing bacteria (SRB) to grow. This group of bacteria is one of the most frequent causes for biocorrosion. They reduce sulfate to hydrogen sulfide that reacts with metals to produce metal sulfides as corrosion products. Aerobic bacteria near the outer surface of the biofilm consume oxygen and create a suitable habitat for the sulfate-reducing bacteria at the metal surface. SRBs can grow in water trapped in stagnant areas, such as dead legs of piping. Symptoms of SRB-influenced corrosion are hydrogen sulfide odor, blackening of waters, and black deposits. The black deposit is primarily iron sulfide (5). One method of limiting SRB activity is to reduce the concentration of their essential nutrients: phosphorus, nitrogen, and sulfate. Thus, purified (RO or DI) waters would have fewer problems with SRBs. Also, Any practices that minimize biofilm thickness (flushing, sanitizing, eliminating dead-end crevices) minimize the anaerobic areas in a biofilm that SRB need (5).

Bacteria can produce aggressive metabolites, such as organic or inorganic acids. For example, *Thiobacillus thiooxidans* produces sulfuric acid and *Clostridium aceticum* produces acetic acid. Acids produced by bacteria accelerate corrosion by dissolving oxides (the passive film) from the metal surface and accelerating the cathodic reaction rate. Many microorganisms produce hydrogen gas as a product of carbohydrate fermentation. Hydrogen gas can diffuse into metals and cause hydrogen embrittlement.

Iron-oxidizing bacteria, such as *Gallionella, Sphaerotilus, Leptothrix,* and *Crenothrix,* are aerobic and filamentous bacteria that oxidize iron from a soluble ferrous (Fe^{+2}) form to an insoluble ferric (Fe^{+3}) form. The dissolved ferrous iron could be from either the incoming water supply or the metal surface. The ferric iron these bacteria produce can attract chloride ions and produce ferric chloride deposits that can attack austenitic stainless steel. The deposits of iron bacteria on austenitic stainless steel are typically brown or red-brown mounds.

TREATMENT METHODS

Once the microorganisms have attached, they can withstand normal disinfection processes. Biofilm bacteria display high resistance to biocides (23). Research demonstrates that biofilm associated bacteria may be 150–3000 times more resistant to free chlorine and 2–100 times more resistant to monochloramine than free-floating bacteria. Research (24) suggests that *Pseudomonas* has a clever way of eluding its attackers. It secretes a sticky slime that builds up on the pipe interior. A germicide flushed through the water distribution system kills free-floating microbes, but it is less effective against bacteria embedded in the slimy biofilm.

When bacteria are in a film, they are very resistant to biocides. They often produce more exopolymers after biocide treatment to protect themselves. To destroy the cell responsible for forming a biofilm, the disinfectant must first react with the surrounding polysaccharide network. The cells themselves are not actually more resistant; rather they have surrounded themselves with a protective

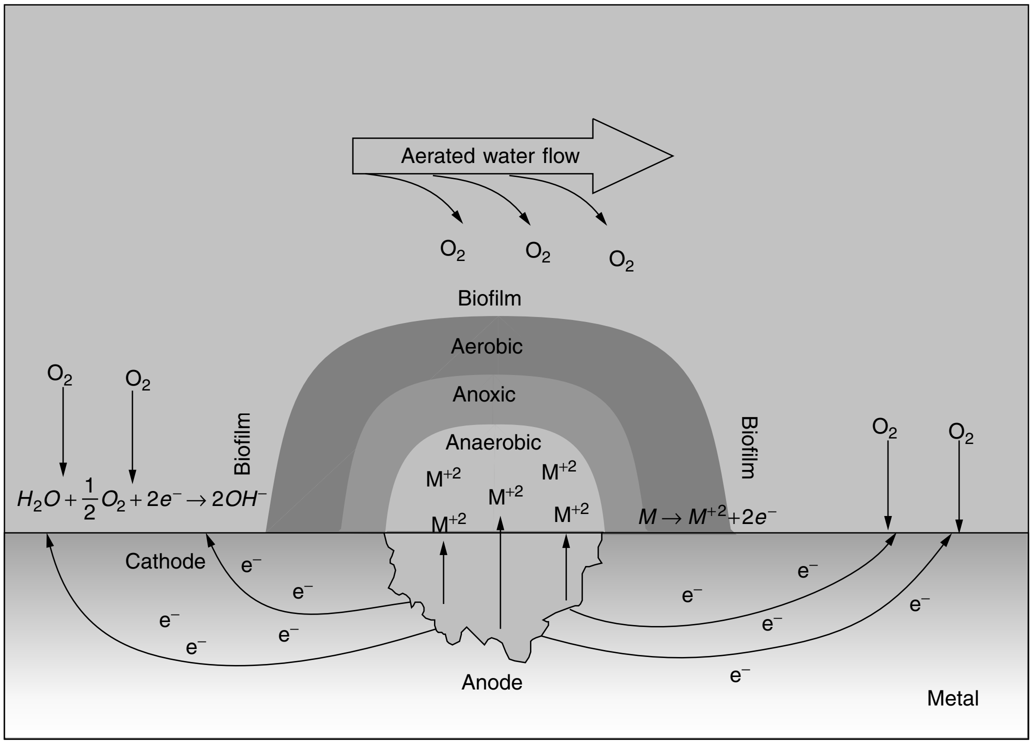


Figure 8. Biofilm corrosion mechanism.

film. The disinfectant's oxidizing power is used up before it can reach the cell.

When cells are attached to a pipe wall, delivery of the disinfectant is limited by the rate of diffusion of the compound across the boundary layer and through the film. It takes a higher concentration in a longer contact time for the disinfectant to reach the bacteria cells in a biofilm compared to free-floating organisms. Trace organics concentrate on surfaces. Extracellular polymers further concentrate trace nutrients from bulk water. Secondary colonizers use waste products from their neighbors. By pooling their biochemical resources, several species of bacteria, each that has different enzymes, can break down food supplies that no single species could digest alone.

Traditional disinfectant testing has been done using single-species free-floating laboratory cultures. The CT constant (concentration × time) for a disinfectant required to kill a particular bacteria should not be extrapolated to bacteria in biofilms. This explains how bacterial counts can be measured, even when water contains low levels of chlorine. Typical chlorine levels in tap water are from 0.5–2.0 ppm. This amount of chlorine kills free-floating bacteria but may not be enough to kill biofilm bacteria. Chunks of sloughed off biofilm can contain viable bacteria which show up in plate counts. This is a particular problem with *Pseudomonas* that is a great slime producer, and so is more chlorine resistant.

The development of biocide resistance is not understood, but recent studies have used a variety of model systems to determine how and why biofilms are so resistant to antimicrobial agents (25). As the importance of biofilms in water treatment has increased, much energy has been directed toward the study of the effects of antimicrobial agents on these surface-attached communities. Biofilm resistance mechanisms include physical or chemical diffusion barriers to antimicrobial penetration into the biofilm, slow growth of the biofilm owing to nutrient limitation, activation of the general stress response, and the emergence of a biofilm-specific phenotype.

Biofilms can be removed and/or destroyed by chemical and physical treatments. Chemical biocides can be divided into two major groups: oxidizing and nonoxidizing. Any chemical that may result in residuals, attack ion exchange resins, or cause corrosion must not be used to control microorganisms. Physical treatments include mechanical scrubbing and hot water. An article by Mittelman (26) has the most comprehensive information on treatment of biofouling in purified water systems. Table 2 provides typical dosage levels and contact times for various biocides.

The effectiveness of oxidizing biocides in purified water systems based on an equal milligram-per-liter dosage decreases in the following order:

$$\text{Ozone } (O_3) > \text{chlorine dioxide } (ClO_2) > \text{chlorine } (Cl_2) > \text{iodine } (I_2) > \text{hydrogen peroxide } (H_2O_2).$$

Chlorine is probably the most effective and least expensive of all oxidizing and nonoxidizing biocides (26). The level of activity of chlorine against attached biofilms is particularly high; planktonic and biofilm bacteria are killed, and chlorine also reacts with and destroys the polysaccharide web and its attachments to the surface. By destroying extracellular polymers, chlorine breaks up the physical integrity of a biofilm. Characklis (27) recommends improving a chlorine treatment program by taking specific additional measures.

Table 2. Typical Biocide Dosage Levels[a]

Biocide	Dosage Level, mg/L	Contact Time, h
Chlorine	50–100	1–2
Ozone	10–50[b]	<1
Chlorine dioxide	50–100	1–2
Hydrogen peroxide	10% (v/v)	2–3
Iodine	100–200	1–2
Quaternary ammonium compounds	300–1,000	2–3
Formaldehyde	1–2% (v/v)	2–3
Anionic and nonionic surfactants	300–500	3–4

[a] Reference 26.

[b] Ozone dosage is 10–50 mg/L, but the residual levels in water were 1–2 mg/L.

In addition to their biocidal activity, quaternary ammonium compounds are effective surfactants/detergents, which may be an important factor in their use for biofilm inactivation and removal from surfaces. Rinseability can be a problem because removal from a purified water system often requires exhaustive rinsing. Formaldehyde has been applied to pharmaceutical-grade systems. It is relatively noncorrosive to stainless steel. Its effectiveness against biofilms is questionable, and it is a toxic carcinogen. Anionic and nonionic surface-active agents (surfactant or detergent compounds) have limited biocidal activity against the bacteria in purified water systems. Applications may be found for these detergents in conjunction with other biocides to improve biofilms and other particulate removal.

Pharmaceutical water-for-injection systems use recirculating hot water loops (hotter than 80 °C) to kill bacteria. When these systems are used continuously, planktonic bacteria are killed, and biofilm development is reduced (26). Biofilms are even found in hot water (80 °C). Periodic hot water sanitization can also be used to destroy bacteria in a biofilm, but this requires a temperature of 95 °C for a period in excess of 100 minutes (28).

Heavy biofilms cannot be removed from storage tank walls by chemicals alone; mechanical scrubbing or scraping, high-pressure spraying, or a combination is also required. Mechanical removal of biofilm from distribution systems is impractical (26).

Unlike antibiotics used to fight bacteria associated with human, animal, and plant diseases, bacteria do not develop the same type of resistance to industrial biocides. The difference between antibiotics and industrial biocides is that an antibiotic may have a small number of target sites on or in a bacterial cell, but all oxidizing biocides have a multitude of potential target sites. It is thought that chlorine, for example, has more than a hundred potential target sites on or in microorganisms. It is virtually impossible for microorganisms to develop general resistance to such compounds (26). However, bacteria in a biofilm can resist biocides because they are shielded in slime.

Bacteria associated with biofilms are much more difficult to kill and remove from surfaces than planktonic organisms. Numerous investigators and plant operators have observed a rapid resumption of biofouling immediately following chlorine treatment (27). Incomplete removal of the biofilm allows it to return quickly to its equilibrium state, causing a rebound in total plate counts following sanitization. Initially, the bulk water bacteria count in one study dropped to zero after sanitization, but this was followed by a gradual increase in numbers to levels at or below pretreatment levels. In this example, regrowth started after 2 days and was back up to equilibrium levels after 20 days. Biofilms can also recover based on various mechanisms (27).

As an oxidizer, ozone is approximately twice as powerful as chlorine at the same concentrations. Like chlorine dioxide, ozone must be generated on-site because of its high reactivity and relative instability. Systems must be designed of appropriate ozone-resistant materials. Ozone is usually dosed continuously at 1–2 mg/L. Success in employing higher dosages noncontinuously has been limited, possibly because of the limited solubility of ozone in purified water; it is difficult to produce high concentrations of ozone in solution (26). Although chlorine is not as powerful as ozone when you compare 1–2 mg/L of each, chlorine can be used in higher sanitizing concentrations with equal disinfecting strength.

Ozone is soluble in water only up to the partial pressure above it; therefore, the concentration of ozone in the generator gas stream becomes very important. According to Henry's law, the efficiency of absorbing a specific gas into an aqueous phase is based on the partial pressure of that particular gas in the total gas flow. Therefore, the higher the partial pressure of ozone in the generator gas stream, the more complete is the concentration of ozone in the water. Table 3 shows the theoretical residuals of ozone that can be achieved in water, based on an ozone gas partial pressure of 1.0 atmosphere and Henry's law constants given in Perry (29). As would be expected, ozone solubility decreases as water temperature increases. Also as a consequence of Henry's law, the solubility of ozone increases as the partial pressure of ozone in the gas stream increases. In practical applications, ozone does not have sufficient contact time to achieve equilibrium conditions, resulting in solubility levels lower than those shown in Table 3. Figure 9 shows a multiple chamber diffusion contact system. The ozonated water stream is led along a pipe located at the bottom of each contact tank. The pipe is perforated by small holes to allow fine bubbles to escape and diffuse into solution.

The latest ozone engineering principle involves using a self-contained ozone contacting/off-gassing system. This system means that the large contact tanks found in older system designs are no longer required. This results in significant capital savings on a new pool or retrofit (typically 50 to 75%). This system replaces the traditional contact tank design with a compact self-contained contacting system that is 98% efficient. Instead of a 20,000–30,000 gallon contact tank for a 100,000-gallon pool, the new system uses a powered contacting/mixing/off-gas unit.

Table 3. Maximum Ozone Solubility at $p_{O_3} = 1.0$ Atmosphere

T, °F	H, Atmosphere/x	Solubility, mg/L (ppm)
32	1940	1374.57
41	2180	1223.24
50	2480	1075.27
59	2880	925.93
68	3760	709.22
77	4570	583.52
86	5980	445.93

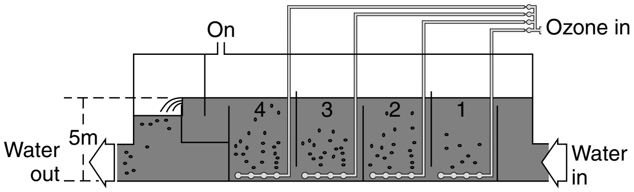


Figure 9. Diffusion contact chambers.

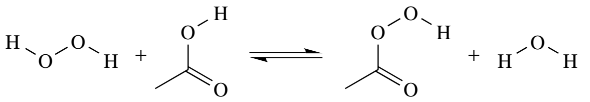
Ozone is an oxidative and reactive gas that is harmful to humans above certain concentrations. Ozone gas is heavier than air; therefore, any undissolved ozone must be removed from the system and disposed of correctly. Several methods are available for ozone destruction, the simplest is by ozone adsorption and reaction with granulated activated carbon (GAC). Activated carbon adsorption is extensively used for small applications where air is the ozonator feed gas. This is an adsorption process whereby the reaction consumes the carbon medium. The material used is elemental carbon which has been steam activated to provide a large internal surface area. Carbon is a strong reducing agent; therefore, upon contact with ozone gas, the carbon is oxidized to carbon monoxide and carbon dioxide, resulting in destruction of the ozone molecule. This reaction degrades or powderizes the GAC; therefore, it has a finite life. To this end, the ozone consumes the carbon by slow-rate combustion. Due to the consumption of carbon, the medium must be replaced regularly. When the carbon is saturated with water and washed with sprays, the reaction becomes partially catalytic and requires a larger volume of GAC. For ozone installations where oxygen is used as the feed gas, carbon adsorption destructors must not be used, due to the dangers of combustion. The other method is heat treatment that degrades the ozone rapidly to oxygen.

Hydrogen peroxide is frequently used as a biocide in microelectronic-grade purified water systems because it produces no by-products and rapidly degrades to water and oxygen. A 10% by volume solution in purified water is effective in killing planktonic bacteria, but more studies are needed on the effectiveness against attached biofilms (26). The use of hydrogen peroxide, though not expected to be as effective as ozone, would be very simple to implement.

Peracetic acid, a derivative of hydrogen peroxide, displays a very wide bandwidth of attack against microbes. Research has shown that peracetic acid will be used to an ever-increasing degree in the field of human medicine due to its bacterial, fungicidal, sporicidal, and antiviral action. Because of the wide spectrum of attack, peracetic acid is very suitable as a wide bandwidth disinfectant for ion exchange resins (results of work done by Degussa Technical Applications Department in conjunction with Chemiewerk Homburg). Using a 0.2% peracetic acid solution (in water, with a reaction time of 1 hour), a slime concentration of 104–105/ mL, including mold, was reduced to almost zero. The short rinsing time after using peracetic acid is important (typically about 45 minutes or 10–15BV). In addition to the excellent disinfection action, peracetic acid (according to experiments) has a minimal effect on the ion exchange properties of cation or anion resins.

Peracetic acid (peroxyacetic acid), $C_2H_4O_3$, the peroxide of acetic acid, is a disinfectant that has the desirable properties of hydrogen peroxide: broad-spectrum activity against microorganisms, lack of harmful decomposition products, and infinite water solubility.

Peracetic acid forms in an equilibrium reaction where hydrogen peroxide and acetic acid react:



(5)

Peracetic acid also has greater lipid solubility and is free from deactivation by catalase and peroxidase enzymes. However, it is corrosive, and degradation products may have to be rinsed from the surface of disinfected materials. Peracetic acid is a more powerful antimicrobial agent than hydrogen peroxide and most other disinfectants (30–32). It has advantages for disinfection and sterilization not found in any other agent. Against spores of *Bacillus thermoacidurans,* it was reportedly the most active of 23 germicides (33); against a range of bacteria it is lethal at 6–250 ppm, toward yeasts at 25–83 ppm, fungi at 50–500 ppm, bacterial spores at 100–500 ppm, and viruses at 15–2,000 ppm (34). The values obtained are determined by the medium employed and the time necessary for inactivation.

Table 4 gives a comparison of peracetic acid and two other disinfectants against food-poisoning bacteria (35). Peracetic acid retains its activity better than many disinfectants at refrigeration temperatures and is more effective at lower pH values (31). Aqueous solutions are comprised of the acid in combination with hydrogen peroxide, acetic acid, sulfuric acid, water, and a stabilizing agent. All of these ingredients are necessary to keep it stable in storage; the concentration of the hydrogen peroxide in some formulations may considerably exceed that of the peracetic acid. Peracetic acid vapor, like that of hydrogen peroxide, is active against bacterial spores and has been found most effective at 80% relative humidity, it has little activity at 20% relative humidity.

Table 4. Comparison of Disinfectants Against Food-Poisoning Bacteria[a,b]

Organism	Peracetic Acid	Active Chlorine	Benzalkonium Chloride
	At 20 °C		
Listeria monocytogenes	45	100	200
Staphylococcus aureus ATCC 6538	90	860	500
Enterococcus faecium DSM 2918	45	300	250
	At 5 °C		
Listeria monocytogenes	90	860	500
Staphylococcus aureus ATCC 6538	90	1,100	750
Enterococcus faecium DSM 2918	90	450	500

[a] Lethality in 5 min.

[b] Concentrations of disinfectants given in ppm.

Peracetic acid has been accepted worldwide in the food processing and beverage industries as an ideal for clean-in-place systems (36); it does not require rinsing where the breakdown product, acetic acid, is not objectionable in high dilution. Peracetic acid is more toxic than hydrogen peroxide and is a weak carcinogen but can be used with safety when diluted. Like all peroxides, it is a powerful oxidizer and should be handled with proper safety precautions. It is more corrosive to metals and plastics than hydrogen peroxide (36).

UV energy is found in the electromagnetic spectrum between visible light and X rays and can best be described as invisible radiation. The energy employed for UV water treatment is further categorized into two primary levels measured as wavelengths—254 nm and 185 nm, where nm = 1/1000 of a micron. For disinfection and ozone destruction, the 254-nm wavelength is used. All living organisms contain DNA (deoxyribonucleic acid). DNA provides the mechanism for all functions needed to sustain life.

UV light disinfection systems emit UV light that penetrates the outer cell membrane of microorganisms, passes through the cell body, reaches the DNA, and alters the genetic material. The microorganism is thereby destroyed nonchemically and cannot reproduce.

Ultraviolet processing involves using radiation from the ultraviolet region of the electromagnetic spectrum for disinfection (37). Typically, the wavelength for UV processing ranges from 100 to 400 nm, as shown in Fig. 10. This range may be further subdivided into UVA (315 to 400 nm) normally responsible for changes in human skin that lead to tanning; UVB (280 to 315 nm) that can cause skin burning and eventually lead to skin cancer; UVC (200 to 280 nm), called the germicidal range, because it effectively inactivates bacteria and viruses, and the vacuum UV range (100 to 200 nm) that can be absorbed by almost all substances and thus can be transmitted only in a vacuum.

The germicidal properties of UV irradiation are mainly due to DNA mutations induced through absorption of UV light by DNA molecules. This mechanism of inactivation

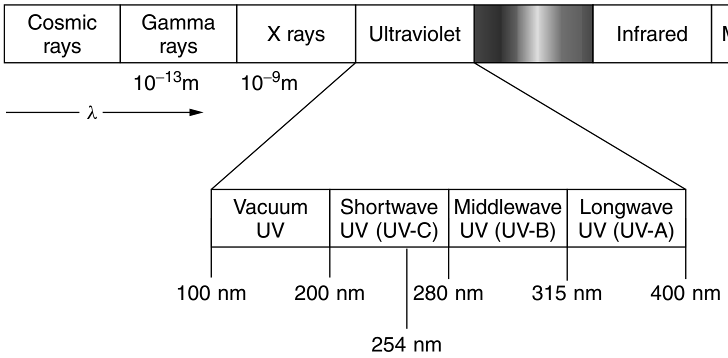


Figure 10. UV light spectrum.

results in a sigmoidal curve of microbial population reduction. To achieve microbial inactivation, the UV radiant exposure must be at least 400 J/m^2 in all parts of the product. Critical factors include the transmissivity of the product; the geometric configuration of the reactor; the power, wavelength and physical arrangement of the UV source(s); the product flow profile; and the radiation path length. UV may be used in combination with other alternative processing technologies, including powerful oxidizing agents such as ozone and hydrogen peroxide. Applications include disinfection of water supplies and food contact surfaces. Recently, interest has increased in using UV to reduce microbial counts in juices.

The shape of the curve for microbial inactivation by UV light is sigmoidal. Figure 11 is an idealized depiction of a sigmoidal curve. The initial plateau is due to an injury phase of the microorganism in response to UV exposure. After the initial plateau, the maximum amount of injury has been surpassed; thus, minimal additional UV exposure would be lethal for microorganisms, and survivor numbers rapidly decline. The end of the curve has a tailing phase due to UV resistance of the microorganisms and to experimental components, such as suspended solids, that may block the UV irradiation.

Much of the prior literature has focused on UV disinfection of water supplies. The literature is insufficient to develop comprehensive microbial inactivation reaction kinetics data or models. There are, however, studies relative to the UV radiant exposure required to obtain a four-log reduction of various microorganisms. These data suggest that the log reduction is related to the UV radiant exposure. The curve has a linear section with a shoulder and tailing effects (38). All organisms tested were reduced by four-log cycles when UV radiant exposure was less than 400 J/m^{237}. In some bacterial cells, photoreactivation, a repair mechanism that is enhanced by visible light in the blue spectral range, may occur. Photoreactivated cells show greater resistance to UV radiation than nonreactivated cells.

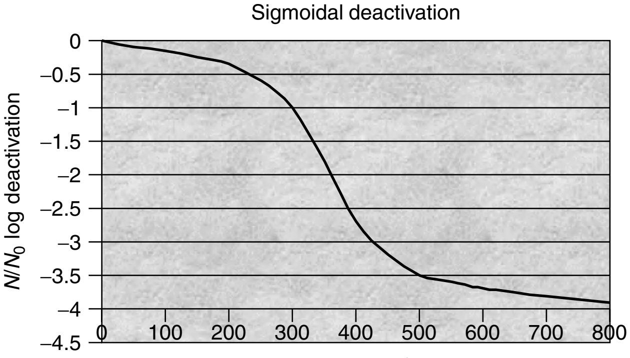


Figure 11. Idealized microorganism deactivation.

The germicidal properties of ultraviolet irradiation are due to DNA absorption of the UV light, causing cross-linking between neighboring pyrimidine nucleoside bases (thymine and cytosine) in the same DNA strand (39). Due to the mutated base, formation of hydrogen bonds to purine bases on the opposite strand is impaired. DNA transcription and replication is thereby blocked, compromising cellular functions and eventually leading to cell death. The amount of cross-linking is proportional to the amount of UV exposure. The level of mutations that can be reversed depends on the UV repair system in the target microorganism. Once the threshold of cross-linking is exceeded, the number of cross-links is beyond repair, and cell death occurs (39). This phenomenon is reflected in the shape of the inactivation curve described before. The cross-linking threshold corresponds to the point of rapid decline after the initial plateau phase on the sigmoidal survival plot of UV exposure.

To disinfect water, it is essential that all parts (each volume element) of the product receive UV radiant exposure of at least 400 J/m^2 (at 254 nm) to reduce human pathogens and viruses by at least four-log cycles (40). Thus, the homogeneity of the flow pattern and the radiation field may have critical effects on disinfection. An additional critical factor is the transmissivity of the material being disinfected. If the material is highly transparent to UV light, disinfection may be more effective; turbid materials attenuate and scatter UV radiation, resulting in less microbial inactivation. The thickness of the radiation path through a material is also important because attenuation increases with the length of passage; thus, the geometric configuration of process systems is critical. Another critical factor to consider is the UV wavelength used because it affects microbial inactivation.

The growth of organisms increases as temperature increases. The effect of temperature on the reaction rate of a biological process is usually expressed in the following form (41):

$$r_T = r_{20}\theta^{(T-20)} \tag{6}$$

This is similar to the Arrhenius equation used in chemistry; an approximate doubling of reaction rate for each 10 °C temperature rise. The range is limited because there is little biological activity in ice or boiling water. Figure 12 illustrates this and shows that a decrease from 80 to 60 °F has a significant impact on the growth rate. The growth rate can be reduced, but the temperature changes that are practical in pools do not kill the organisms.

Increasing temperature also increases the kill rate (decreases kill time). The effect of temperature on the kill rate of microorganisms is well represented by a form of the Van't Hoff–Arrhenius relationship (41). In terms of the kill time (t in the equation) required for a given percentage kill, the relationship is

$$\ln\frac{t_1}{t_2} = \frac{E(T_2 - T_1)}{RT_1T_2} \tag{7}$$

Using $T_2 = 20\,^\circ\mathrm{C}$ and chlorine at pH = 7.0, the effects of temperature on kill rate are illustrated in Fig. 13. Figure 13 shows that kill time can be significantly reduced by modest increases in temperature.

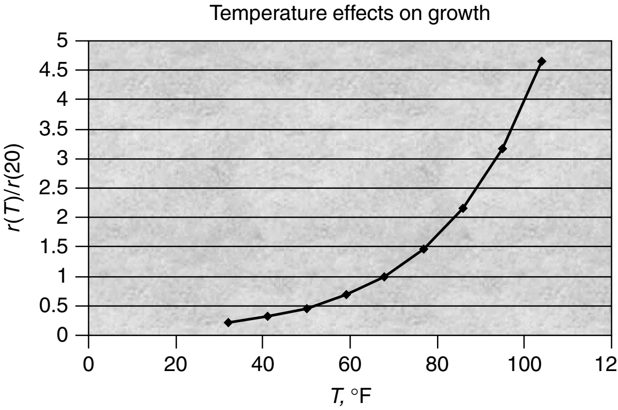


Figure 12. Temperature effects on biological growth.

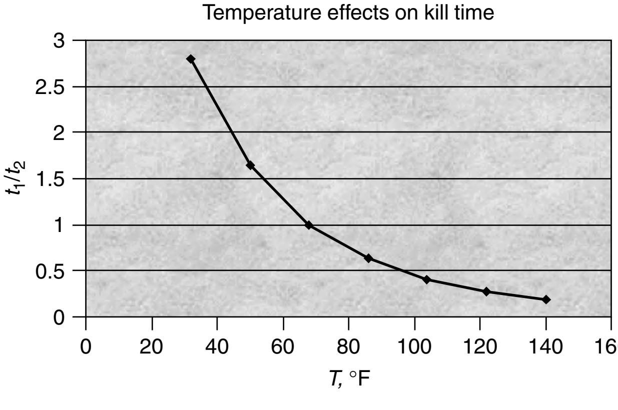


Figure 13. Temperature effects on kill time.

The reduction of light may reduce the growth rate of some microorganisms. Microbes may be classified according to their energy and carbon requirements (42). Growth from light is expected for some organisms as a result of photosynthesis. For example, algae use carbon dioxide in photosynthetic activity to produce new cells, oxygen, and water.

The criteria for chemical addition and other microbiological control for a typical nuclear fuel storage pool include

- minimal corrosion
- no damage occurs to other parts and/or systems
- no residual remains that can adsorb onto ion exchange resins
- personnel safety.

This severely limits the treatment chemicals that can be used, for example, chlorine cannot be used. Although there may be beneficial affects from controlling and/or manipulating light and temperature, the focus is on treatment to remove microorganisms and keep them minimized. Also, as previously discussed, the chemicals focus on those that will not leave residuals or cause corrosion. Therefore, the focus is on ozone, peracetic acid, and hydrogen peroxide. The International Atomic Energy Agency has studied this in some detail (1). They provided a list of potential methods for removing microorganisms from spent fuel pools that should be considered in a final study or evaluation. Ion exchange columns must be bypassed when ozone is at a high concentration in the water because ozone attacks and degrades the resins (43). It is believed that ozone is effective in long residence times and for sustained residuals. This expectation is partly based on experience from vendors using ozone in biofilm-fouled swimming pools (44).

The use of chemical agents must be demonstrated for personnel safety. The maximum possible dissolved ozone in the pools that transfers to the atmosphere would be related to Henry's law. At 86 °F, $H = 5980$ atmospheres/mole fraction, and the residual is 1 mg/L. The mole fraction (x) is then,

$$x = \frac{1\ \text{mg}}{L} \times \frac{L}{1,000\ \text{g}} \times \frac{18\ \text{g}}{\text{mole}} \times \frac{\text{mole}}{48\ \text{g}} \times \frac{\text{g}}{10^3\ \text{mg}} = 4\times10^{-7}$$

The partial pressure (maximum) in equilibrium with the pool surface is based on Henry's law constant (H) in Table 3:

$$\begin{aligned} p_i &= Hx = 5980 \times 4 \times 10^{-7} \\ &= 2 \times 10^{-3}\ \text{atmospheres (2,000 ppm)} \end{aligned}$$

The STEL/Ceiling/TWA is 0.1 ppm, so this is significantly higher. A material balance is used to determine the effective vapor phase concentration. Figure 14, material balance shows the ozone transferring from the water surface into the ventilation air. The material balance is thus:

$$Q_{\text{ozone}} = (Q_{\text{vent}} + Q_{\text{ozone}})\, y_{\text{ozone}} \tag{8}$$

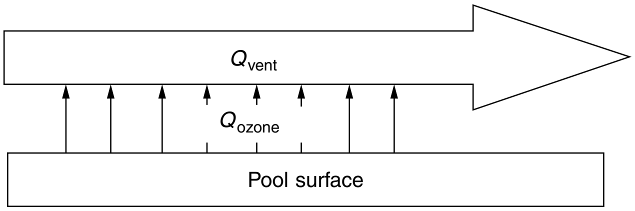


Figure 14. Material balance [SCA1][nlh2]diagram.

A dissolved gas has two resistances, gas-phase and liquid-phase. The mass transfer (F) flux is

$$F = K_{\text{L}}(C_{\text{B}} - C^{*}) = K_{\text{G}}(p^{*} - p_{\text{B}}) \tag{9}$$

The flux is also equal to the individual driving forces as

$$F = k_{\text{G}}(p_{\text{I}} - p_{\text{B}}) = k_{\text{L}}(C_{\text{B}} - C_{\text{I}}) \tag{10}$$

By combining these and using Henry's law, the following are determined for the overall mass transfer coefficients, and either one can be used:

$$K_{\text{L}} = \frac{1}{\dfrac{1}{Hk_{\text{G}}} + \dfrac{1}{k_{\text{L}}}} \tag{11}$$

$$K_{\text{G}} = \frac{1}{\dfrac{1}{k_{\text{G}}} + \dfrac{H}{k_{\text{L}}}} \tag{12}$$

According to Thibodeaux (45), the gas-phase and liquid-phase coefficients for water and CO_2 are 3000 cm/h and 20 cm/h, respectively. The ozone value can be directly used as 20 because the molecular weight falls in the range for direct substitution. However, the value of the gas-phase coefficient is determined from the ratio of the cube roots of molecular weights (46):

$$k_{\text{G}-\text{O}_3} = k_{\text{G}-\text{H}_2\text{O}}\left(\frac{18}{48}\right)^{1/3} = 2163$$

The overall coefficient is then

$$K_{\text{L}} = \frac{1}{\dfrac{1}{5,980 \times 2,163} + \dfrac{1}{20}} = 20$$

Thus it is seen that the transfer is totally controlled by the liquid phase. The material balance then becomes

$$\frac{p_{\text{B}}}{P_{\text{T}}}\frac{M_{\text{O}_3}}{M_{\text{air}}} = \frac{K_{\text{L}}A\left(C_{\text{B}} - \left(\frac{p_{\text{B}}}{H}\right)\right)}{K_{\text{L}}A\left(C_{\text{B}} - \left(\frac{p_{\text{B}}}{H}\right)\right) + Q_{\text{vent}}} \tag{13}$$

For small p_{B}, this can be simply solved as

$$p_{\text{B}} = \frac{K_{\text{L}}AC_{\text{B}}}{K_{\text{L}}AC_{\text{B}} + Q_{\text{vent}}}\frac{M_{\text{air}}}{M_{\text{O}_3}}P_{\text{T}} \tag{14}$$

The estimated partial pressure of ozone was based on the values in Table 3. The NIOSH time weighted average (TWA) is 0.1 ppm. The estimated concentration is 1.27 ppm that exceeds the limit. Therefore, the liquid concentration would need to be controlled at less than 0.1 mg/L to ensure personnel protection. However, an ozone system that intermittently supplies high-concentration ozone was effective in preventing biofilm formation using a 1-mg/L ozone dose for 10 minutes (47). Asea Brown Boveri (ABB) carried out tests with ozone as a biocide on the water of a small industrial cooling tower in Switzerland (48). The test results showed that ozone is an excellent biocide. In 1988, an ozonation plant was installed at the side stream cooling water system of a heating power station in Germany (49). The operation showed that ozone works well at 0.1 mg/L for 2–3 hours contacting time per day. Ozone destroys and reacts with pollutants in the air. If this is considered, the ozone concentration in air in pool areas will be much lower than the worse case calculation (Table 5).

The concentration above the pools using the 10-minute treatment is then

$$C_{10\,\text{min}} = 1.27 \times \frac{10\,\text{min}}{24\ \text{h} \times 60\ \text{min/h}} = 0.00882$$

This result is well below the TWA of 0.1 ppm.

NOMENCLATURE

A	Area
C	Concentration
C_{I}	Concentration at interface
C_{B}	Concentration in bulk solution
C^{*}	Fictitious concentration in bulk gas
CT	Concentration × time
E	Activation energy, J/g mole
F	Mass transfer flux
H	Henry's law constant
k_{G}	Local gas mass transfer coefficient
k_{L}	Local liquid mass transfer coefficient
K_{G}	Overall mass transfer coefficient, based on gas
K_{L}	Overall mass transfer coefficient, based on liquid
M	Molecular weight
p	Partial pressure, atmospheres
p_{I}	Partial pressure at interface, atmospheres

Table 5. Calculation of Ozone Above Pools

Parameter	Value
M_{O_3}, g/mole	48.00
M_{air}, g/mole	29.00
P_{T}, atm	0.87
Q_{vent}, scfm	28,100
Q_{vent}, g/h	6.2E+07
C_{B}, mg/L	1.00
K_{L}, cm/h	20.00
K_{L}, m/h	0.20
A, m^2	648.14
$F \times A$, g/h	129.63
Calculated p, atm	1.10E−06
Calculated O_3, ppm	1.27

p_B	Partial pressure in bulk, atmospheres
p^*	Fictitious pressure in bulk liquid
P_T	Total pressure, atmospheres
Q	Gas mass flow rate
R	Gas constant
Re	Reynolds number
r_T	Reaction rate at $T\,^\circ$C
r_{20}	Reaction rate at 20 °C
T	Temperature
t	Time
v	Velocity
x	Mole fraction
y	Vapor mass fraction
δ	Boundary layer thickness
κ	Conductivity
ν	Kinematic viscosity
θ	Temperature-activity coefficient

BIBLIOGRAPHY

1. International Atomic Energy Agency. (1988). *Durability of Spent Nuclear Fuels and Facility Components in Wet Storage*. IAEA-TECDOC-1012, Vienna, Austria.
2. Edstrom. (2002). Available: http://www.edstrom.com/Resources.cfm?doc_id=23.
3. Mittelman, M.W. (1985). Biological fouling of purified-water systems: Part 1, Bacterial growth and replication. *Microcontamination* **3**(10): 51–55, 70.
4. Mayette, D.C. (1992). The existence and significance of biofilms in water. *Water Rev.* Water Quality Research Council, Lisle, IL, pp. 1–3.
5. Geesey, G.G., Lewandowski, Z., and Flemming, H.-C. (Eds.). (1994). *Biofouling and Biocorrosion in Industrial Water Systems*. Lewis, Ann Arbor, MI.
6. Coghlan, A. (1996). Slime city. *New Sci.* **15**(2045): 32–36.
7. VanHaecke, E. et al. (1990). Kinetics of *Pseudomonas aeruginosa* adhesion to 304 and 316-L stainless steel: Role of cell surface hydrophobicity. *Appl. Environ. Microbiol.* **56**(3): 788–795.
8. Stanley, P.M. (1983). Factors affecting the irreversible attachment of *Pseudomonas aeruginosa* to stainless steel. *Can. J. Microbiol.* **29**(11): 1493–1499.
9. Costerton, J.W. et al. (1995). Microbial biofilms. *Annu. Rev. Microbiol.* **49**: 711–745.
10. Hamilton, N.F. (1988). Antimicrobial controls effects of bioslime. *Modern Plast.* 166–168.
11. Flemming, H.C. and Geesey, G.G. (Eds.). (1991). *Biofouling and Biocorrosion in Industrial Water Systems*. Springer-Verlag, New York.
12. Meltzer, T.H. (1993). *High-Purity Water Preparation for the Semiconductor, Pharmaceutical, and Power Industries*. Tall Oaks, Littleton, CO.
13. Patterson, M.K., Husted, G.R., Rutkowski, A., and Mayette, D.C. (1991). Isolation, identification, and microscopic properties of biofilms in high-purity water distribution systems. *Ultrapure Water* **8**(4): 18–24.
14. Pittner, G.A. and Bertler, G. (1988). Point-of-use contamination control of high purity water through continuous ozonation. *Ultrapure Water* **5**(4): 16–22.
15. Husted, G.R., Rutkowski, A.A., and Couture, A. (1994). Response of oligotrophic biofilm bacteria in high-purity water systems to stepwise nutrient supplementation. *Ultrapure Water* **11**(6): 43–50.
16. Bott, T.R. (1998). Techniques for reducing the amount of biocide necessary to counteract the effects of biofilm growth in cooling water systems. *Appl. Thermal Eng.* **18**(11): 1059–1066.
17. Stoodley, P., Lewandowski, Z., Boyle, J.D., and Lappin-Scott, H.M. (1999). Structural deformation of bacterial biofilms caused by short-term fluctuations in fluid shear: An *in situ* investigation of biofilm rheology. *Biotechnol. Bioeng.* **65**(1): 5.
18. Boyle, J.D., Dodds, I., Stoodley, P., and Lappin-Scott, H.M. (1997). Stress management in biofilms. In: *Biofilms: Community Interactions and Control*. J.W.T. Wimpenny, P.S. Handley, P. Gilbert, H.M. Lappin-Scott, and M. Jones (Eds.). BioLine, Cardiff, UK, pp. 15–22.
19. Picologlou, B.F., Zelver, N., and Characklis, W.G. (1980). Biofilm growth and hydraulic performance. *J. Hydraul. Div. Am. Soc. Civ. Eng.* **106**(HY5): 733–746.
20. Prandtl, L. (1904). *Ueber Fluessigkeitbewegung mit Kleiner Reibung (Concerning Fluid Movements with Small Friction)*, *Verhandl. III Int. Math.*-Kong., Heidelberg; also reprinted in *Vier Abhandlungen zur Hydrodynamik*. Goettingen, 1927.
21. De Nevers, N. (1970). *Fluid Mechanics*. Addison-Wesley, Reading, MA.
22. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (1960). *Transport Phenomena*. John Wiley & Sons, New York.
23. LeChevallier, M.W., Cawthon, C.D., and Lee, R.G. (1988). Inactivation of biofilm bacteria. *Appl. Environ. Microbiol.* **54**(10): 2492–2499.
24. Anderson, R.L. et al. (1990). Effect of disinfectants on *Pseudomonas* colonized on the interior surface of PVC pipes. *AJPH*. 17–21.
25. Mah, T.C. and O'Toole, G.A. (2001). Mechanisms of biofilm resistance to antimicrobial agents. *Trends Microbiol.* **9**(1): 34–39.
26. Mittelman, M.W. (1986). Biological fouling of purified-water systems: Part 3, Treatment. *Microcontamination* **4**(1): 30–40, 70.
27. Characklis, W.G. and Marshall, K.C. (Eds.). (1990). *Biofilms*. John Wiley & Sons, New York.
28. Collentro, W.C. (1995). Microbial control in purified water systems—case histories. *Ultrapure Water* **12**(3): 30–38.
29. Perry, R.H. and Green, D.W. (1979). *Perry's Chemical Engineers' Handbook*, 6th Edn. McGraw-Hill, New York.
30. Eggensberger, H. (1979). *Zentralbl. Bakteriol. Mikrobiol. Hyg. [B]* **168**: 517–524.
31. Baldry, M.G.C. (1983). *J. Appl. Bacteriol.* **54**: 417–423.
32. Krzywicka, H. et al. (1975). *Resistance of Microorganisms to Disinfectants*. W.B. Kedzia (Ed.). Polish Acad. of Sciences, Warsaw.
33. Hutchins et al. (1949).
34. Block, S.S. (1991). *Disinfection, Sterilization, and Preservation*, 4th Edn. Lea and Febiger, Philadelphia, PA, pp. 167–181.
35. Orth, R. and Mrozeck, H. (1989). *Fleischwirtsch* **69**: 1575–1576.
36. Dychdala, G.R. (1988). *Proc. 4th Conf. Prog. Chem. Disinfection*. Binghamton, NY, pp. 315–342.
37. FDA. (2000). Available: http://vm.cfsan.fda.gov/∼comm/ift-uv.html.

38. Hoyer, O. (1998). Testing performance and monitoring of UV systems for drinking water disinfection. *Water Supply* **16**(1/2): 419–442.
39. Miller, R., Jeffrey, W., Mitchell, D., and Elasri, M. (1999). Bacterial responses to ultraviolet light. *Am. Soc. Microbiol.* **65**(8): 535–541.
40. Bernhardt, H. (1994). Desinfektion Aufbereiteter Oberflachenwasser mit UV-Strahlen. *Wasser-Abwasser*. **135**(12): 677–689.
41. Tchobanoglous, G. and Burton, F.L. (1991). *Wastewater Engineering; Treatment, Disposal, and Reuse*, 3rd Edn. Metcalf & Eddy, McGraw-Hill, New York.
42. Frobisher, M., Hinsdill, R.D., Crabtree, K.T., and Goodheart, C.R. (1994). *Fundamentals of Microbiology*. Saunders, Philadelphia, PA.
43. Purolite. (2002). Personal conversation, Sam Ashworth with Francis Boodoo, The Purolite Company, Bala Cynwyd, PA.
44. Finney, A. (2002). Personal communication, Sam Ashworth with Allan Finney (email), Envron Inc., Regina, Sk., Canada.
45. Thibodeaux, L.J. (1979). *Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil*. Wiley-Interscience, New York.
46. Crowl, D.A. and Louvar, J.F. (1990). *Chemical Process Safety Fundamentals with Applications*. Prentice-Hall, Englewood Cliffs, NJ.
47. Nakayama, S. et al. (1985). Anti-biofouling ozone system for cooling water circuits. II. An application of seawater. *Ozone: Sci. Eng.* **7**(1): 31–46.
48. Wellauer, R. (1990). Cooling water treatment with ozone. *Ozone: Sci. Eng.* **12**(3): 243–253.
49. Liechti, P.A. et al. (1992). One year full-scale study of ozone cooling water treatment at a German electric power station. *Ozone: Sci. Eng.* **14**(6): 531–544.

INDUSTRIAL MINE USE: MINE WASTE

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INTRODUCTION

Intensive industrial development and particularly the production of effluents from mining operations has led to worldwide concern for environmental and health impacts following decades of contaminated effluent discharge into natural waterways (1). Developing economies often depend heavily on extractive or primary industry, and many third-world governments face the difficult task of reconciling economic development with environmental and social protection. Concern arising from the discharge of polluted effluent from the mining industry was recorded as early as 1556 (2), and the legacy of unsustainable development is clearly chronicled in sediments worldwide (3–6). as the discharge of mining and industrial effluents has led to a substantial increase in riverine, estuarine, and marine sediment metal concentrations (7–9).

Several types of acid and toxic effluents are produced by mining and metallurgical processes during operations and following site decommission (Table 1). These effluents include tailings excess decant (rainwater or process water running off tailings impoundments), process acid streams, and mine drainage waters. Drainage from tailings impoundments is often circumneutral in pH and contains low concentrations (<20 mg/L) of total dissolved metals (10). Process acid stream effluents originate from the use or generation of acids during metallurgical processes and can contain very high levels of dissolved solids and toxic metals. Mine drainage waters are commonly of three main types: (1) saline formation waters; (2) acidic, heavy-metal- and sulfate-containing waters formed during biologically mediated and abiotic oxidation of sulfides (so-called acid mine drainage or AMD); and (3) alkaline, hydrogen-sulfide-containing, heavy-metal-poor waters resulting from buffering reactions (usually carbonate) and sulfate reduction within AMD (11,12). AMD surfaces as discharge from adits and abandoned workings of sulfidic mines or as drainage from sulfide-rich overburden material or spoil heaps (13).

ACID MINE DRAINAGE GENERATION

Acidity generation due to sulfide oxidation occurs by two processes: proton acidity and metal acidity. The former occurs during the oxidation of sulfides, and the latter is from the hydrolysis of metal species in solution (15). Each is discussed here in more detail.

Iron pyrite, the most common mineral leading to AMD, reacts with oxygen and water according to the following reaction (16):

$$2FeS_2 + 7O_2 + 2H_2O \leftrightarrow 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+ \qquad (1)$$

This reaction often occurs in underground workings or deep within spoil heaps and overburden, resulting in the removal of oxygen and the discharge of an anaerobic effluent. Accordingly, oxygen is a limiting substrate within the deeper workings or lower levels of the spoil heap where anaerobic conditions prevail throughout the year. Younger (17) differentiates the production of AMD from flooded workings into “juvenile” and “vestigial” acidity: the former is the dissolution of weathering salts formed on sulfides when the water table within the workings rises following cessation of dewatering activities; the latter is the continuing oxidation of sulfides in the seasonally flooded zone of the workings as the water table rises and drops within the annual hydrologic cycle.

Table 1. Typical Mine Drainage Composition[a]

	Coal Mines	Cu–Pb–Zn Mixed Sulfide Mines	EPA Statutory Limits
pH	2.6–6.3	2.0–7.9 mg/L	6–9
Al	1–58		
Cu		0.005–76	0.05
Fe	1–473	8.5–3200	3.5
Mn	1–130	0.4	2
Pb		0.02	0.2
Zn		0.04–1600	0.2–0.5

[a] Reference 14.

On contact with the atmosphere, which often commences only at the site of effluent discharge from flooded workings or spoil heaps, the oxidation of ferrous to ferric iron and the precipitation of ferric oxyhydroxides generates further acidity:

$$Fe^{2+} + O_2 + 4H^+ \leftrightarrow Fe^{3+} + 2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \quad (3)$$

As noted, Equations 1 and 2 are dependent on an aerobic environment. However, once ferric iron has been formed, Fe^{3+} acts as the oxidizing agent and the oxidation of pyrite can proceed in an anaerobic environment:

$$FeS_2 + 14Fe^{3+} + 8H_2O \leftrightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \quad (4)$$

The reaction kinetics in Equations 1 and 3 are significantly higher than those of Equation 2, and accordingly the oxidation of ferrous iron is the rate-limiting step in this series (11). However, numerous iron oxidizing bacteria can markedly increase the oxidation of ferrous to ferric iron. Of these, *Thiobacillus ferrooxidans* and *Leptospirilium ferrooxidans* are likely to be the most important organisms, increasing the rate of reaction by six orders of magnitude (10^6) (11). These organisms function optimally below pH 3, thus requiring a degree of pyrite oxidation and ferric hydrolysis to lower the solution pH to optimal levels (18). Johnson and Hallberg (19) and Hallberg and Johnson (20) show that a host of other organisms known as moderate acidophils, which include sulfur-oxidizing bacteria and archaea, heterotrophic microorganisms, and some lower eukaryotic life-forms, function optimally at pH 3–5.5 and may be involved in the initial sulfide oxidation and proton acidity generation.

Other members of the pyrite family, such as arsenopyrite (FeAsS) and chalcopyrite ($CuFeS_2$), also generate proton acidity upon oxidation, releasing As or Cu into solution in addition to Fe. Monosulfide minerals, such as chalcocite (Cu_2S), sphalerite (ZnS), and galena (PbS), are also often encountered in sulfidic deposits. Although the oxidation of these minerals does not generate proton acidity (see Equation 5), subsequent hydrolysis of the metal ions generates metal acidity as in Equation 3:

$$ZnS + 2O_2 \leftrightarrow Zn^{2+} + SO_4{}^{2-} \quad (5)$$

TYPES OF MINE EFFLUENT REMEDIATION FACILITIES

Mine effluent discharge is almost always a point source, so mine-water problems may be addressed by isolating the contaminant source and either treating the discharge *in situ* (i.e., within the working or the spoil heap by suppressing the reactions releasing contaminants) or by active or passive water treatment following discharge. Innovative *in situ* treatment techniques such as galvanic suppression, application of bactericides, and introduction of neutralizing or reducing agents are receiving increasing attention and represent real potential. However, such techniques have not yet achieved widespread application and require further applied and fundamental research on both field and laboratory scales.

Active or conventional treatment processes for effluent remediation usually involve expensive technology and infrastructure and high process costs. Kuyucak (10) lists some of the common active, physicochemical processes:

1. active neutralization systems
2. ion exchange materials, such as resins and zeolites (21)
3. membrane processes, such as reverse osmosis, ultrafiltration/microfiltration
4. solvent extraction
5. electrochemical treatment (22)
6. bioremediation through controlled sulfate reduction (23,24)

Passive treatment technology, which as the name implies has significantly lower capital and maintenance costs, commonly includes (13)

1. aerobic, surface-flow wetlands (reed beds)
2. subsurface flow systems, such as reducing and alkalinity producing systems—RAPS (25,26)
3. combination wetlands, such as compost wetlands (27)
4. anoxic and oxic limestone drains (28,29)
5. biosorbents (30–32)

Active neutralization facilities are still most widely used to treat mine waters but vary greatly in the degree of sophistication, depending on the geography and local specifications of the site, the nature of the effluent, and various other environmental, technical, and financial constraints. As such, the facilities can range from the simple addition of neutralizing agents to the effluent stream, to complex chemical plants consisting of reactors, clarifiers, and sludge dewatering technology. Lime as CaO or $Ca(OH)_2$ is the most common neutralizing agent used for treating low pH effluent, owing to the widespread availability, low cost, and high reactivity of the material. However, lime neutralization results in poor quality effluent and the need to dispose of large volumes of sludge; accordingly, certain situations require using other neutralizing reagents, such as $Mg(OH)_2$, Na_2S, NH_3, Na(OH) and $CaCO_3$ (10).

The current state-of-the-art active lime neutralization process is called the high density sludge process (HDS), where more than one reactor is used to perform the neutralization, and a mixture of sludge, recycled from the clarifier, and lime is used as the neutralizing agent in the first reactor (Fig. 1). Polymers are added to improve flocculation, and a clarifier is used to enhance solid/liquid separation, decreasing the volume and increasing the stability of the disposal sludge.

PROCESS IN MINE EFFLUENT REMEDIATION

The activity of hydrogen ions in solution (the pH of the solution) is the key determinant in the composition of mine waters and of their toxicity (16). Metal mineral solubility

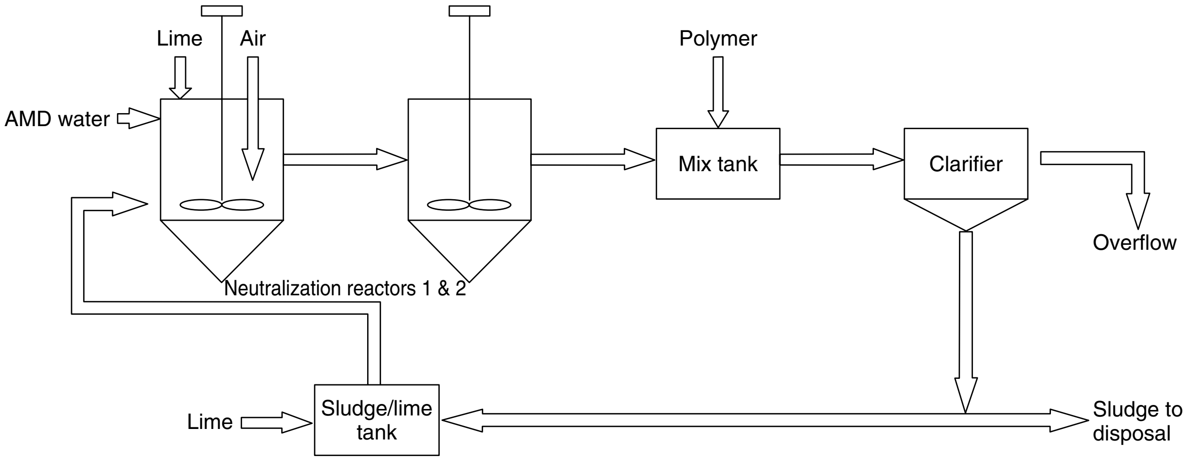

Figure 1. The high density sludge process (10).

increases markedly at low pH, and the precipitation of the dissolved metal cation as an insoluble species is low. Moreover, adsorption, which is often a primary process of metal removal from anthopogenically polluted systems (7,9), is also often strongly pH dependent (33). Adsorption approaches zero as the pH decreases below the adsorption edge of the metal, which for common metals such as Cu, Co, Ni, Pb, and Zn is around pH 4–5 (34). Anions, for example SO_4, demonstrate the converse; a pH decrease leads to greater anion adsorption (34,35). The free aquo ion is the most bioavailable, so the pH of the solution also affects its toxicity, directly through pH-mediated effects on organisms and indirectly as a result of its effect on the concentration of anions (e.g., oxyanions of Cr and As) and toxic metals such as Cu, Pb, and Zn (36–38). As such, correcting the pH is the most important and first consideration in mine effluent remediation (13).

Assuming that effluent pH has been regulated within an acceptable range (pH 5–9), Hammer (39) and Dunbabin and Bowmer (40) list the most common chemical and biological processes by which mine effluent quality is improved:

1. oxidation and hydrolysis
2. reduction reactions
3. adsorption of pollutant complexes to organic and inorganic surfaces
4. uptake of pollutants by plants
5. physical filtering of suspended solids by plants and substrate
6. Neutralization and precipitation by the formation of ammonium ($NH_4{}^+$) and carbon dioxide (CO_2)

Oxidation and Hydrolysis

The change in valence state following oxidation of certain metals can dramatically influence their solubility: oxidation of Fe^{2+} and Mn^{2+}, both highly soluble in the reduced state, to Fe^{3+} and Mn^{4+} results in rapid metal precipitation as oxide and (oxy)hydroxides.

The complexation of metal cations with hydroxide ions results in the formation of insoluble metal hydroxide (Equation 6), oxide, and oxyhydroxide precipitates (33,41). Hydrolysis and oxidative hydrolysis are the most common processes of metal precipitate formation in aerobic surface waters (13,42). However, hydroxide precipitation decreases the pH of the water due to the production of hydrogen ions: the metal acidity discussed above (Equation 6). As such, oxidation of effluent with high metal concentrations [e.g., Wheal Jane, see (43)] can rapidly lower the pH of the water and hence affect the mobility and solubility of other metals (15,44).

$$M^{2+(or)3+} + H_2O \leftrightarrow M(OH)_{2(or)3} \downarrow + 2(or)3H^+ \qquad (6)$$

Reduction Reactions

Reduction processes are used in active bioreactors and in RAPS, and numerous researchers identify bacterially mediated sulfate reduction as the most effective way to decrease sulfate and heavy metal concentrations in contaminated mine drainage (23,45,46). The reduction of sulfate and the production of hydrogen sulfide lead to an increase in alkalinity and the precipitation of insoluble metal sulfides (Equations 7 and 8):

$$SO_4 + C_xH_yO_z \leftrightarrow H_2S + wHCO_3 \qquad (7)$$

$$M^{2+} + H_2S \leftrightarrow MS \downarrow + 2H^+ \qquad (8)$$

Adsorption by Organic and Inorganic Surfaces

Adsorption and surface complexation commonly occurs on sediments, suspended or colloidal matter, and plant surfaces (47). Within contaminated drainage, transport of pollutants is often facilitated by adsorption on a variety of suspended and colloidal solid surfaces. Colloidal aggregate formation and settling and the settling of suspended solids are common processes whereby such contaminants are incorporated into sediments.

Adsorption is highly pH-dependent (33,41), for example, SO_4 adsorption onto $Fe(OH)_3$ approaches 100% below pH 3, whereas metal cations dominate the adsorption surface above pH 4.5 (34). The most important and widely studied adsorption surfaces in mine effluent impacted systems are (oxy)hydroxide precipitates of iron and manganese (35,48–51). The order of metal affinity for MnO_2 binding sites is $Co > Ni \geq Zn > Cu$ (52), and that for FeOOH sites is $Pb > Zn \geq Co \geq Ni > Cu$ (34).

Metals are also complexed with a range of organic material such as algae, bacterial cells, detritus, and organic coatings on mineral surfaces (40,47,53,54). The organic adsorption affinity of metals decreases in the order $Cu = Fe \gg Zn \gg Mn$ (55,56). Adsorption and surface complexation are rapid processes producing pollutant attenuation from the water column but are transitory due to marked pH dependency (33,41). Ions immobilized as surface complexes are rapidly released during changes in effluent pH conditions.

The Effect of Aquatic Vegetation

The uptake and accumulation of metals in plant biomass has been extensively studied under laboratory conditions (57–59). Dunbabin and Bowmer (40) investigated the partitioning of metals within emergent hydrophytes and found that the majority of metals were stored in the roots and rhizomes. Floating wetland plants have been shown to hyperaccumulate Cu and Fe up to 78 times their concentration in wastewater (57). However, direct uptake and accumulation of metals within plant biomass usually constitutes a minor component of the overall removal processes (14,60–62).

In addition to metal uptake, wetland plants attenuate metal contaminants through a number of further mechanisms:

- Plants release oxygen through their roots, creating a zone of aerobic conditions in the substrate (14,40). The oxidizing conditions within the substrate increase metal oxidation with insoluble precipitate formation [commonly Fe (oxy)hydroxide plaques]. These precipitates provide a further surface for trace metal adsorption (63).
- Bacterial biofilms forming on root surfaces are strong adsorbents of trace metals (63).
- The turnover of aquatic vegetation is the dominant source of simple carbohydrates, which are the main substrate for sulfate-reducing bacteria and other fermentative organisms important in the production of sulfides, ammonium, carbon dioxide, and alkalinity (14,40,64,65).
- The humic substances of organic decay play an important role in aquatic contaminant chemistry through the adsorption of metals and subsequent transport as colloidal complexes or incorporation into the sediment as settled solids.

The Role of Microbial Processes

Microbial activity is integral to many of the processes described above. The importance of the microbiology of mine effluent remediation has recently been recognized, as evidenced by numerous studies in this discipline (66–69). Nordstrom (70) provides a good review of the state of knowledge and the gaps in the present understanding of the microbiology of acid mine waters. The processes that use or depend on, microbial action have been described above. Hence, listed here are the most common examples of microbial involvement in processes of mine effluent remediation:

- oxidation of Mn (71,72)
- oxidation and hydrolysis of Fe (73,74)
- oxidation of sulfides (11)
- sulfate reduction
- products of organic decay (CO_2, NH_4^+, and organic acids)
- surfaces for adsorption

BIBLIOGRAPHY

1. Vernet, J.-P. (1991). *Heavy Metals in the Environment*. Elsevier, Amsterdam.
2. Agricola, G. (1556). *De Re Metallica*. H.C. Hoover and L.H. Hoover (Eds.). (1950). Dover, New York.
3. Chen, M.H. and Hung, T.W. (1993). Copper, cadmium and lead in sediment from Kaohsiung River and its harbour area, Taiwan. *Mar. Pollut. Bull.* **30**(12): 879–884.
4. Everaarts, J.M. (1989). Heavy metals (Cu, Zn, Cd, Pb) in sediment of the Java Sea, estuarine and coastal areas of East Java and some deep sea areas. *Neth. J. Sea Res.* **23**: 403–413.
5. Sabri, A.W., Rasheed, K.A., and Kassim, T.I. (1993). Heavy metals in the water, suspended solids and sediments of the River Tigris Impoundment at Samarra. *Water Res.* **27**(6): 1099–1103.
6. Sin, S.N., Chua, H., Lo, W., and Ng, L.M. (2001). Assessment of heavy metal cations in sediments of the Shing Mun River, Hong Kong. *Environ. Int.* **26**: 296–301.
7. Förstner, U. (1983). Assessment of metal pollution in rivers and estuaries. In: *Applied Environmental Geochemistry*. I. Thornton (Ed.). Academic Press, London, pp. 395–423.
8. Förstner, U. and Wittmann, G.T.W. (1979). *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
9. Tessier, A. and Campbell, P. (1988). Partitioning of trace metals in sediments. In: *Metal Speciation: Theory, Analysis and Application*. H.E. Allen (Ed.). Lewis, Ann Arbor, MI, pp. 183–199.
10. Kuyucak, N. (1998). Mining, the environment and the treatment of mine effluents. *Int. J. Environ. Pollut.* **10** (2): 315–325.
11. Singer, P.C. and Stumm, W. (1970). Acid mine drainage: The rate limiting step. *Science* **167**: 1121–1123.
12. Banks, D., Younger, P.L., Arnesen, R.T., Iversen, E.R., and Banks, S.B. (1997). Mine-water chemistry: The good, the bad and the ugly. *Environ. Geol.* **32**(3): 157–174.
13. Younger, P.L., Banwart, S.A., and Hedin, R.S. (2002). *Mine Water: Hydrology, Pollution, Remediation*. Kluwer Academic, Dordrecht, the Netherlands.
14. Gazea, B., Adams, K., and Kantapoulos, A. (1996). A review of passive treatment systems for the treatment of acid mine drainage. *Miner. Eng.* **9**(1): 23–42.
15. Younger, P.L. (1998). Coalfield abandonment: Geochemical processes and hydrochemical products. In: *Energy and the Environment: Geochemistry of Fossil, Nuclear and Renewable Resources*. K. Nicholson (Ed.). Society for Environmental Geochemistry and Health, McGregor Science, Aberdeen, Scotland, pp. 1–29.

16. Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry*. John Wiley & Sons, New York.
17. Younger, P.L. (1997). The longevity of minewater pollution: A basis for decision-making. *Sci. Total Environ.* **194**: 457–466.
18. Bigham, J.M. (1996). Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. *Appl. Geochem.* **11**(6): 845–849.
19. Johnson, D.B. and Hallberg, K.B. (2003). The microbiology of acidic mine waters. *Res. Microbiol.* **154**(7): 466–473.
20. Hallberg, K.B. and Johnson, D.B. (2003). Novel acidophiles isolated from moderately acidic mine drainage waters. *Hydrometallurgy* **71** (1–2): 139–148.
21. Riveros, P.A. (2004). The extraction of Fe(III) using cation-exchange carboxylic resins. *Hydrometallurgy* **72**(3–4): 279–290.
22. Chartrand, M.M.G. and Bunce, N.J. (2003). Electrochemical remediation of acid mine drainage. *J. Appl. Electrochem.* **33**(3–4): 259–264.
23. Buisman, C.J. and Schultz, C.E. (2000). From microbiology to industrial application of sulphate reducing bacteria. *WISA-Minewater Drainage Technol. Conf.* Rhodes University, Grahamstown, January 23–28, 2000.
24. Kaksonen, A.H., Riekkola-Vanhanen, M.L., and Puhakka, J.A. (2003). Optimization of metal sulphide precipitation in fluidized-bed treatment of acidic wastewater. *Water Res.* **37**(2): 255–266.
25. Sikora, F.J., Behrends, L.L., Brodie, G.A., and Taylor, H.N. (2000). Design criteria and required chemistry for removing manganese in acid mine drainage using subsurface flow wetlands. *Water Environ. Res.* **72**(5): 536–544.
26. Stephenson, B., Harris, T.M., and Rosche, W.A. (2001). Treatment of mine drainage with subsurface flow wetlands. *Abs. Papers Am. Chem. Soc.* **221**: 506.
27. Wieder, R.K. (1993). Ion input/output budgets for 5 wetlands constructed for acid coal-mine drainage treatment. *Water Air Soil Pollut.* **71**(3–4): 231–270.
28. Cravotta, C.A. and Trahan, M.K. (1999). Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Appl. Geochem.* **14**(5): 581–606.
29. Cravotta, C.A. (2004). Size and performance of anoxic limestone drains to neutralize acidic mine drainage. *J. Environ. Qual.* **33**(3): 1164–1164.
30. Xie, J.Z., Chang, H.L., and Kilbane, J.J. (1996). Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents. *Bioresource Technol.* **57**(2): 127–136.
31. Kratochvil, D. and Volesky, B. (1998). Biosorption of Cu from ferruginous wastewater by algal biomass. *Water Res.* **32**(9): 2760–2768.
32. Utgikar, V., Chen, B.Y., Tabak, H.H., Bishop, D.F., and Govind, R. (2000). Treatment of acid mine drainage: I. Equilibrium biosorption of zinc and copper on nonviable activated sludge. *Int. Biodeterioration Biodegradation* **46**(1): 19–28.
33. Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Prentice-Hall, Englewood Cliffs, NJ.
34. Dzombak, D.A. and Morel, F.M. (1990). *Surface Complexation Modelling: Hydrous Ferric Oxide*. John Wiley & Sons, New York.
35. Rose, S. and Elliott, W.C. (2000). The effects of pH upon the release of sulphate from ferric precipitates formed in acid mine drainage. *Appl. Geochem.* **15**(1): 27–34.
36. Campbell, P.G.C. and Stokes, P.M. (1985). Acidification and toxicity of metals to aquatic biota. *Can. J. Fish. Aquatic Sci.* **42**(12): 2034–2049.
37. Gerhardt, A. (1993). Review of the impact of heavy metals on stream invertebrates with special emphasis on acid conditions. *Water Air Soil Pollut.* **66**: 289–314.
38. Mason, C.F. (1996). *Biology of Freshwater Pollution*. Addison Wesley Longman, Edinburgh.
39. Hammer, D.A. (1990). *Constructed Wetlands for Wastewater Treatment*. Lewis, Ann Arbor, MI.
40. Dunbabin, J.S. and Bowmer, K.H. (1990). Potential use of constructed wetlands for treatment of industrial wastewater containing metals. *Sci. Total Environ.* **111**: 151–168.
41. Pankow, J.F. (1991). *Aquatic Chemistry Concepts*. Lewis, Ann Arbor, MI.
42. Eger, P. (1994). Wetland treatment for trace metal removal from mine drainage: The importance of aerobic and anaerobic processes. *Water Sci. Technol.* **29**(4): 249–256.
43. Hamilton, Q.U.I., Lamb, H.M., Hallett, C., and Proctor, J.A. (1999). Passive treatment systems for the remediation of acid mine drainage at Wheal Jane, Cornwall. *J. Chartered Inst. Water Environ. Manage.* **13**(2): 93–103.
44. Younger, P.L. (2000). Mine water pollution in the long-abandoned Cleveland Ironstone field, north-east England. *7th Natl. Hydrol. Symp.* British Hydrological Society, Newcastle Upon Tyne, September 6–8, 2002.
45. Cloete, E. (2000). Biological sulphate reduction in artificial acid mine drainage using different carbon sources. *WISA-Minewater Drainage Technol. Conf.* Rhodes University, Grahamstown, January 23–28, 2000.
46. Hedin, R.S., Hammack, R., and Hyman, D. (1990). Potential importance of sulphate reduction processes in wetlands constructed to treat mine drainage. In: *Constructed Wetlands for Wastewater Treatment*. D.A. Hammer (Ed.). Lewis, Ann Arbor, MI, pp. 508–514.
47. Drever, J.I. (1997). *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, NJ.
48. Kay, J.T., Conklin, M.H., Fuller, C.C., and O'Day, P.A. (2001). Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe Mining District, Arizona. *Environ. Sci. Technol.* **35**(24): 4719–4725.
49. Kim, J.-Y. and Chon, H.-T. (2001). Pollution of a watercourse impacted by acid mine drainage in Imgok Creek of the Gangreung coal field, Korea. *Appl. Geochem.* **16**: 1387–1396.
50. Schemel, L.E., Kimball, B.A., and Bencala, K.E. (2000). Colloid formation and metal transport through two mixing zones affected by acid mine drainage near Silverton, Colorado. *Appl. Geochem.* **15**: 1003–1018.
51. Yu, J.-Y. and Heo, B. (2001). Dilution and removal of dissolved metals from acid mine drainage along Imgok Creek, Korea. *Appl. Geochem.* **16**: 1041–1053. .
52. Suarez, D.L. and Langmuir, D. (1976). Heavy metal relationships in Pennsylvania soil. *Geochim. Cosmochim. Acta* **40**: 589–598.
53. Noller, B.N., Woods, P.H., and Ross, B.J. (1994). Case studies of wetland filtration of mine waste water in constructed and naturally occurring systems in Northern Australia. *Water Sci. Technol.* **29**(4): 257–265.
54. Stevens, S.E., Dionis, K., and Stark, L.R. (1990). Manganese and iron encrustation on green algae living in acid mine drainage. In: *Constructed Wetlands for Wastewater Treatment*. D.A. Hammer (Ed.). Lewis, Ann Arbor, MI, pp. 765–773.

55. Cohen, R.H. (2000). Conjunction of geochemical modelling and pilot scale experiments for testing bioreactor removal of arsenic and chromium. *WISA-Minewater Drainage Technol. Conf.* Rhodes University, Grahamstown, January 23–28, 2000.
56. Tipping, E. and Hurley, M.A. (1992). A unifying model of cation binding by humic substances. *Geochim. Cosmochim. Acta* **56**: 3627–3641.
57. Jain, S.K., Vasudevan, P., and Jha, N.K. (1989). Removal of some heavy metals from polluted water by aquatic plants: Studies on duckweed and water velvet. *Biological Wastes* **28**: 115–126.
58. Zayed, A., Gowthaman, S., and Terry, N. (1998). Phytoaccumulation of trace metals by wetland plants: Duckweed. *J. Environ. Qual.* **27**: 715–721.
59. Zhu, Y.L., Zayed, A.M., Qian, J.-H., de Sousa, M., and Terry, N. (1999). Phytoaccumulation of trace metals by wetland plants: Water hyacinth. *J. Environ. Qual.* **28**: 339–344.
60. Cohen, R.H. and Staub, M.W. (1992). *Technical Manual for the Design and Operation of a Passive Mine Drainage Treatment System*. Report to the U.S. Bureau of Land Reclamation. Colorado School of Mines, Golden, CO.
61. Hedin, R.S., Nairn, R.W., and Kleinmann, R.L.P. (1994). *Passive Treatment of Polluted Coal Mine Drainage, Bureau of Mines Information Circular 9389*. United States Department of the Interior, Washington, DC.
62. Shutes, R.B., Ellis, J.B., Revitt, D.M., and Zhang, T.T. (1993). The use of *Typha latifolia* for heavy metal pollution control in urban wetlands. In: *Constructed Wetlands for Water Quality Improvement*. G.A. Moshiri (Ed.). Lewis, Ann Arbor, MI.
63. Hansel, C.M. and Fendorf, S. (2001). Characterisation of Fe plaque and associated metals on the roots of mine-waste impacted aquatic plants. *Environ. Sci. Technol.* **35**(19): 3863–3868.
64. Batchelor, A. (2000). Some perspectives on the use of wetlands for the amelioration of mine drainage. *WISA-Minewater Drainage Technol. Conf.* Rhodes University, Grahamstown, January 23–28, 2000.
65. Pulles, W. (2000). Development of passive mine water treatment technology. *WISA-Minewater Drainage Technol. Conf.* Rhodes University, Grahamstown, January 23–28, 2000.
66. Costley, S.C. and Wallis, F.M. (2001). Bioremediation of heavy metals in a synthetic wastewater using a rotating biological contactor. *Water Res.* **35**(15): 3715–3723.
67. Glombitza, F. (2001). Treatment of acid lignite mine flooding water by means of microbial sulphate reduction. *Waste Manage.* **21**(2): 197–203.
68. Pagnanelli, F., Toro, L., and Veglio, F. (2002). Olive mill solid residues as heavy metal sorbent material: A preliminary study. *Waste Manage.* **22**(8): 901–907.
69. Podda, F., Zuddas, P., Minacci, A., Pepi, M., and Baldi, F. (2000). Heavy metal coprecipitation with hydrozincite $[Zn\text{-}_5(CO_3)_2(OH)_6]$ from mine waters caused by photosynthetic micro-organisms. *Appl. Environ. Microbiol.* **66**(11): 5092–5098.
70. Nordstrom, D.K. (2000). Advances in the hydrogeochemistry and microbiology of acid mine waters. *Int. Geol. Rev.* **42**(6): 499–515.
71. Chapnick, S.D., Moore, W.S., and Nealson, K.H. (1982). Microbially mediated manganese oxidation in a fresh-water lake. *Limnol. Oceanogr.* **27**(6): 1004–1014.
72. Thornton, F.C. (1995). Manganese removal from water using limestone filled tanks. *Ecological Eng.* **4**: 11–18.
73. Burke, S.P. and Banwart, S.A. (2002). A geochemical model for removal of iron (II) (aq) from mine water discharges. *Appl. Geochem.* **17**(4): 431–443.
74. Zhang, C.L. et al. (1997). Physiochemical, mineralogical, and isotopic characterization of magnetite-rich iron oxides formed by thermophilic iron-reducing bacteria. *Geochim. Cosmochim. Acta* **61**(21): 4621–4632.

SUGARCANE INDUSTRY WASTEWATERS TREATMENT

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Sugar (sucrose) is a sweet, crystalline, white or colorless substance, derived from the juice of several plants. World sugar production amounts approximately to 120 million tonnes, of which two-thirds come from sugarcane and one third from sugarbeet. Sugarcane is a perennial grass that grows between the tropics (30° latitude north and 30° latitude south) in more than 100 countries. It is the most efficient earth grass plant for storing solar energy as biomass and reaches field yields up to 150 ton/ha. A variety of products are obtained from this versatile plant (Fig. 1). Many studies on sugarcane are published in journals and books. Sugarcane processing to produce sugar represents one of the oldest "industries" in modern times. In America, the first sugarcane processing plants were located in the New Spain territories as well as in the Caribbean islands since the sixteenth century. In Mexico, for example, the first sugarcane mill was established in Veracruz on the Gulf of Mexico in 1525 (1,2).

The power for sugarcane mills originally came from water sources (rivers) and from cane bagasse burning. Considering that up to the first half of the twentieth century, industry was a synonym for smoke, wastewater, and wastes in general, the sugarcane industry was no exception. Therefore, considering modern sustainability concepts, the more than 2000 sugar processing plants still operate around the world with relatively poor technologies from an environmentally friendly point of view. Figure 2 shows a schematic diagram of a sugarcane factory, including the wastes generated.

Roughly, one metric tonne of sugarcane renders the following products:

350	kg wet bagasse	35%
100	kg sugar	10%
60	kg straw and leaves	6%
40	kg final syrup, molasses	4%
40	kg cachasses	4%
100	kg cane heads	10%
310	kg evaporated water	31%
1000	kg sugarcane	100%

After sugar, the by-product with more added value is the final syrup, known as molasses. Molasses is a

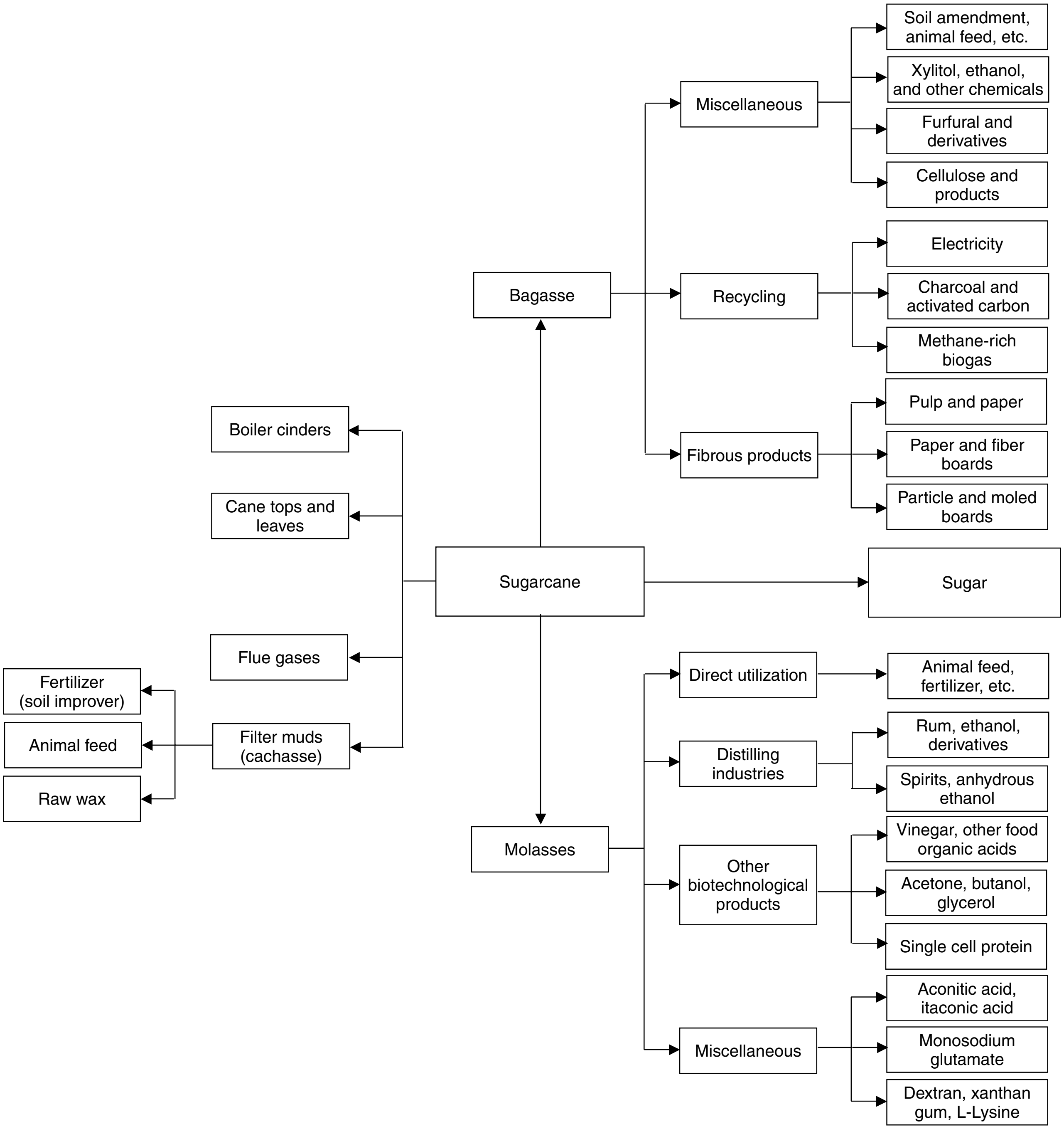

Figure 1. Versatile sugarcane use.

very inexpensive carbon source for many biotechnological products, including vaccines and antibiotics (Table 1). Of course, fermented and distilled beverages, such as rum, are more widely known biotechnological products.

In Figs. 3 and 4, diagrams for sugar and ethyl alcohol production are presented. In Fig. 3, the example is the production of raw sugar. The two other most popular sugar commercial products are the so-called plantation white sugar or mill white sugar (in Mexico, it is known as “standard” sugar) and refined sugar. Literature presents block diagrams for the production of these different types of sugar (1). Wastewaters are the most conspicuous wastes, and many processes have been devised to reduce their polluting impact and to gain some added value from treating them (5). Tables 2 and 3 show the average composition of some of these wastewaters, and Table 4 presents the regulatory limits that Mexico established in the 1990s for this agro-based industry.

It is clear from Table 3 that liquid effluents from a distillery in the sugarcane mill have a very important impact on the overall composition of its wastewaters. Also, to comply with the regulations for both sugar production and distilled products, namely ethanol (ethyl alcohol), a removal efficiency of more than 95 and

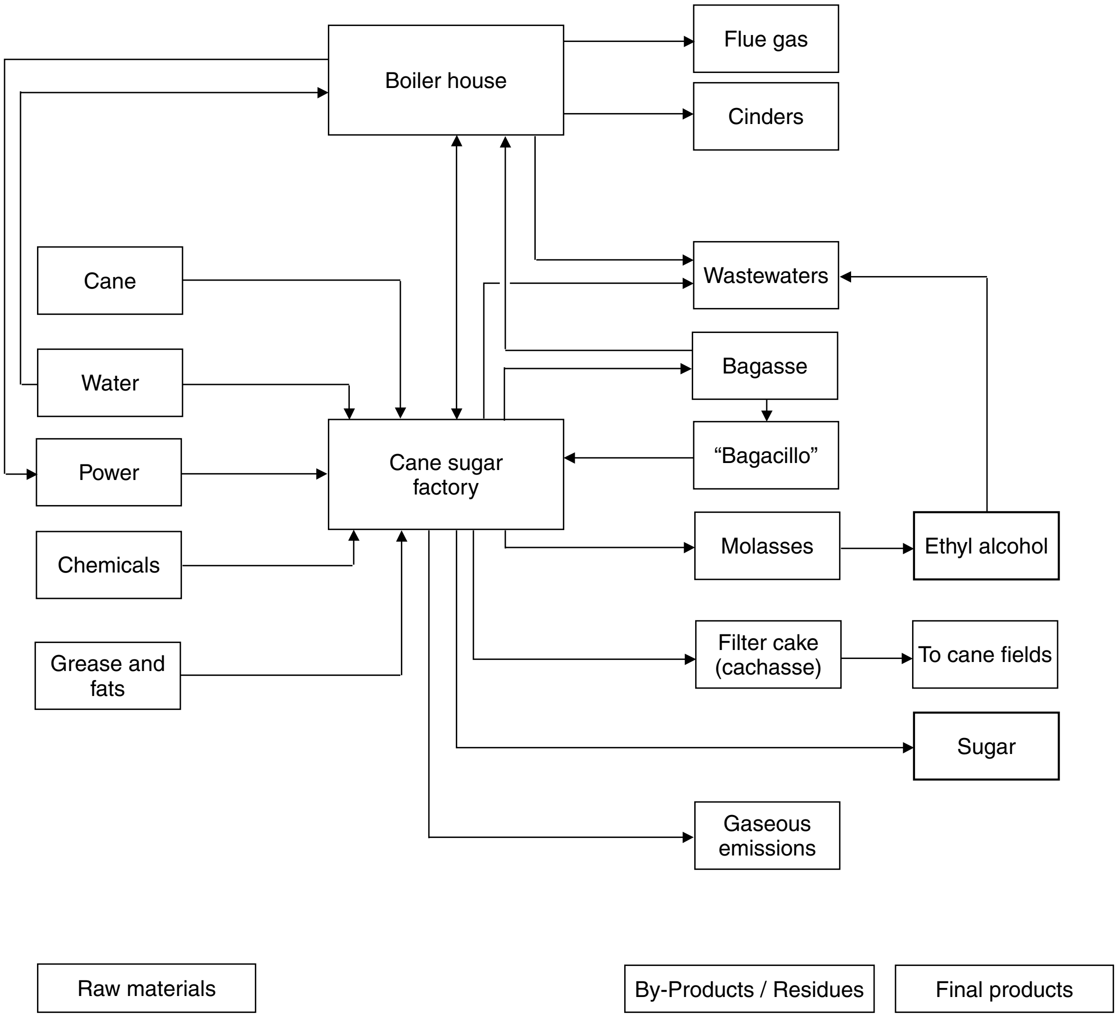

Figure 2. Raw materials, products, and by-products of the sugarcane industry.

99.8% must be reached for general wastewaters and vinasses, respectively. Most of these vinasses, to date, are discharged to receiving bodies (soil, surface water sources) without any treatment or with a partial depuration because of the notion that these wastewaters improve soil. However, this is true only when soils are very poor. For good agricultural soils, they have a negative effect (9–11).

To reduce costs, biological systems are preferred to physicochemical processes. For that reason, in general, anaerobic systems are chosen for treating those process streams that contain biodegradable compounds because methane-rich biogas can be a plus from the bioconversion. To improve the biotreatment and reuse the water in the process, aerobic polishing and sometimes a physicochemical treatment are added. From the aerobic treatment, the biomass produced can be used in feedlots, particularly for fish (12). Leftover treated water can be used for irrigating cane fields. In tropical countries, it is very common to "cultivate" river shrimp (*Cammarus montezumae*), known in Mexico as "*acociles*" (from the Nahuatl or Aztec language, atl = water, cuitzilli = bent, that bends in the water). Then, an interesting biological cycle is rendered. Aerobic biomass together with carotenoproteins from cephalothorax and exoskeleton from river shrimp (the unedible portion), are pelleted for fish feedlots, and the unedible residues from fish are ground and used for shrimp cultivation. Figure 3 shows a complete nature-like cycle process instead of the typical man-made linear polluting processes (Fig. 2).

Table 1. Molasses Composition[a]

Parameter	% weight	Parameter	% weight
Water	20	K_2O	3.5
Sucrose	32	CaO	1.5
Glucose	14	P_2O_5	0.2
Fructose	14	Carbonates, CO_3^{2-}	1.6
Nitrogen compounds and other	10	Sulfate ions	0.4
Organic products		Other inorganics	0.8
		Density, g m/L	1.42

[a] Reference 3.

When wastewaters contain mainly high concentrations of inorganic compound and they are highly soluble, as

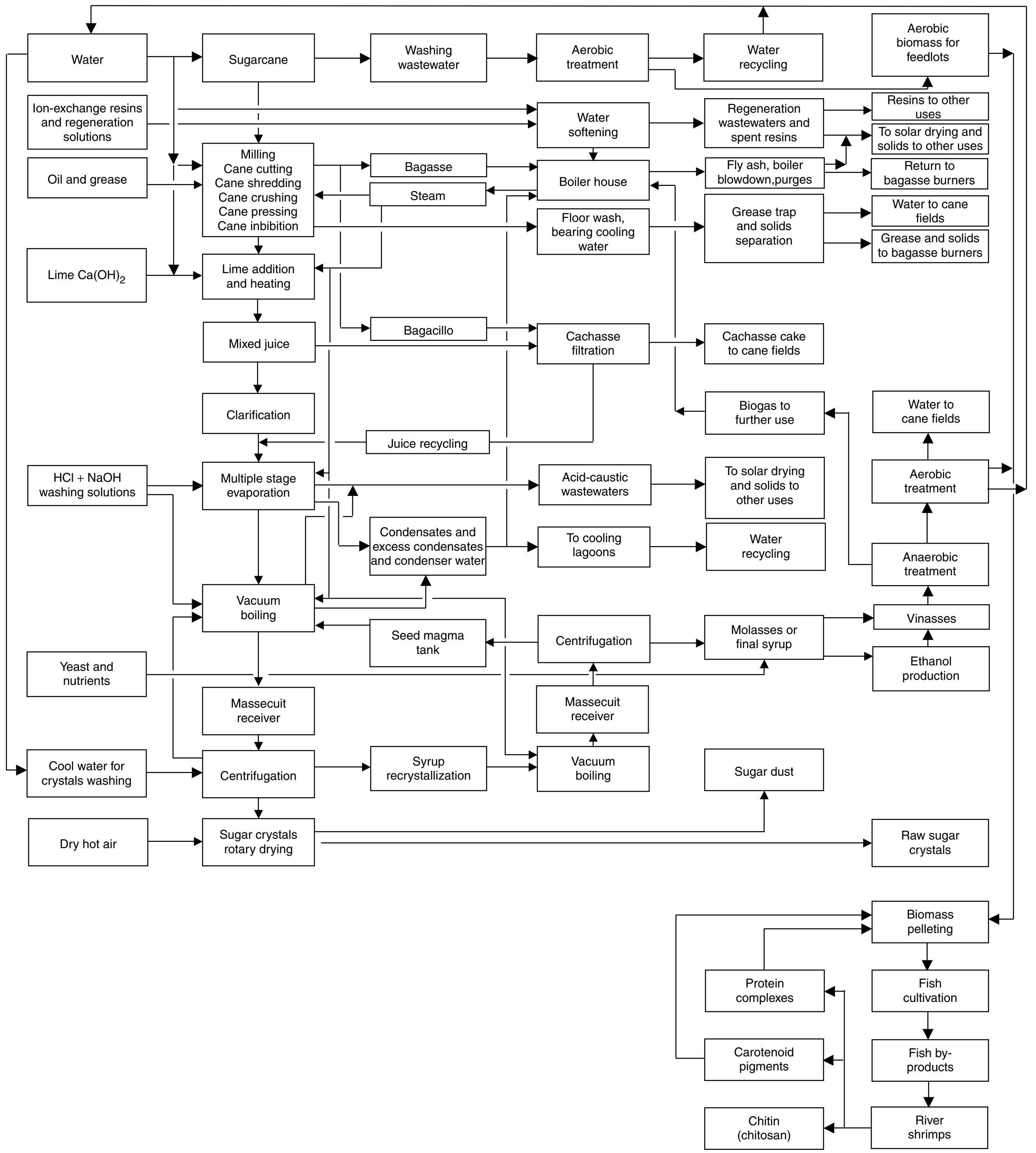

Figure 3. Example of water use, wastewater generation, and treatment proposals for raw sugar.

happens with boilers purges and acid-caustic solutions used to clean heat transfer surfaces in evaporators and vacuum boiler pans, the most suitable process is to eliminate water by evaporation (preferably solar evaporation, taking advantage of climatic conditions in tropical areas). The resulting impure salts, collected as dry solids, may be recycled by the companies that sell the caustic and acid products used as raw materials in the sugarcane mill, reducing the environmental impact of both enterprises (2).

Figures 5 and 6 present schemes of an aerobic plant for treating wastewaters generated in a plantation sugar production plant (14). This plant wastewater treatment system had a different approach. The wastewater

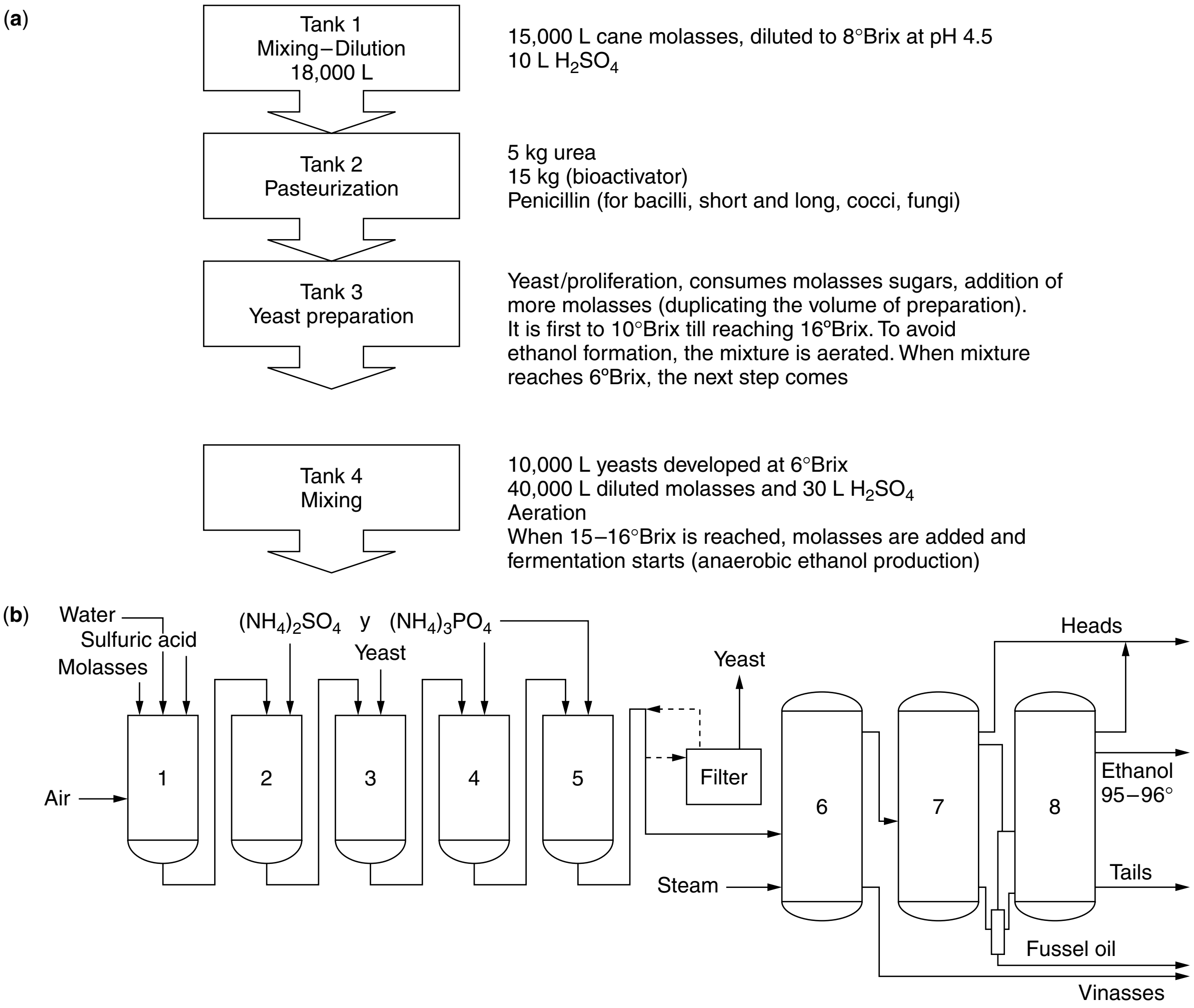

Figure 4. (**a**) Sequential steps for ethanol production in a typical Mexican sugarcane mill using the final syrup or molasses as a carbon source (4). (**b**) Ethanol production flow in a typical Mexican sugarcane mill using the final syrup or molasses as a carbon source (4).

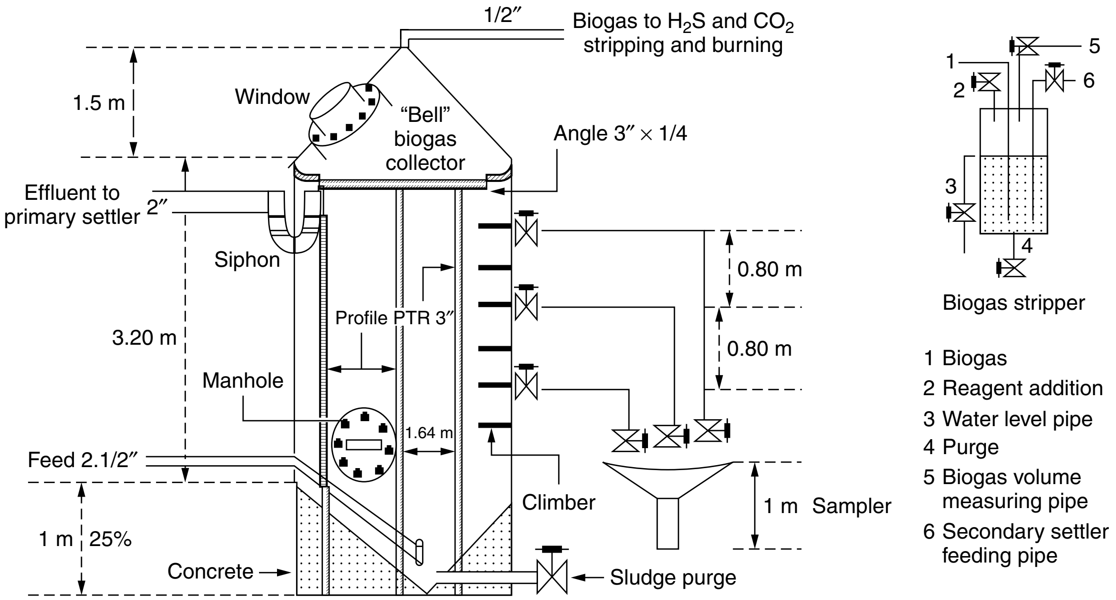

Figure 5. Upflow anaerobic sludge bed reactor (UASB) and biogas absorber tower (13).

Table 2. Liquid Effluent Characteristics of Some Cane Sugar Processing Plants in the World

Parameter	Puerto Rico[a]	Hawaii[a]	Philippines[a]	Louisiana[a]	India[a]	Mexico[b]
pH	5.3–8.8	n.r.[d]	5.3–7.9	n.r.	6.8–8.4	6–10
Biochemical oxygen demand (BOD_5), mg/L	112–225	115–699	130–1220	81–562	67–660	20–36,700[c]
Chemical oxygen demand (COD), mg/L	385–978	942–2340	50–1880	720–1430	890–2236	47–176,635[c]
Total suspended solids, mg/L	500–1400	3040–4500	n.r.	409	792–2043	20–46,190
Total nitrogen, mg/L	n.r.	n.r.	n.r.	n.r.	n.r.	0.2–1260
Total phosphorus, mg/L	n.r.	n.r.	n.r.	n.r.	n.r.	0.2–2000
Grease and oil, mg/L	n.r.	n.r.	n.r.	n.r.	n.r.	0–570

[a] Reference 6.
[b] Reference 7.
[c] When vinasses are considered.
[d] n.r.: not reported.

composition is similar to those of other countries that do not contain vinasses (Table 2), so once the suspended matter is eliminated in a primary settler, an aerobic reactor is adequate for removing most of the dissolved biodegradable pollutants. Here, the feasibility of using an anaerobic reactor to "digest" the aerobic biomass when it is not used for feedlots is shown (13). This reactor gives the added value of methane-rich biogas production, once the gas is stripped in a column using the treated water to dissolve H_2S leaving the methane-rich gas free of this corrosive compound and "enriching" the treated wastewater in sulfur compounds before sending it to cane fields as irrigation water.

Table 3. Average Vinasse Compositions[a]

Parameter		Parameter	
pH	4.8–4.9	Total volatile solids, g/L	76–83
Biochemical oxygen demand, mg/L	90,000	Total fixed solids, g/L	21–23
Chemical oxygen demand, mg/L	106,000	Dissolved volatile solids, g/L	69–76
Organic nitrogen, mg/L	446	Dissolved fixed solids, g/L	18–22
Total nitrogen, mg/L	730		
Ammonium ion, mg/L	310	Phosphorus, mg/L	150
Grease and oil, mg/L	2	Calcium, mg/L	2,960
Settleable solids, mL/L	27	Magnesium, mg/L	1,370
Total solids, g/L	97–106	Sodium, mg/L	310
Total suspended solids, g/L	8–10	Potassium, mg/L	2,550
Total dissolved solids, g/L	87–97	Sulfate ions, mg/L	10,500

[a] Reference 3.

BIBLIOGRAPHY

1. Chaux, D., Durán-de-Bazúa, C., and Cordovés, M. (1991). *Towards a Cleaner and More Profitable Sugar Industry*. UNIDO, Vienna, Austria.
2. Durán-de-Bazúa, C., Cordovés, M., and Zedillo, L.E. (1994). *Demonstration of Cleaner Production Techniques for the Sugar Cane Agroindustry*. *Final Draft, Consultancy Report 1994.* United Nations Industrial Development Office. Project US/INT/91/217/15-01-2. UNIDO/UNDP, Mexico City, Mexico.
3. Jiménez, R., Martínez, M., Espinoza, A., Noyola, A., and Durán-de-Bazúa, C. (1995). *La Caña de Azúcar, su Entorno Ambiental*. Parte II. Tratamiento de vinazas en una planta piloto en México en un reactor anaerobio de lecho de lodos. Informe técnico de proyecto VIN-01-95. GEPLACEA, CNIIAA, PIQAYQA-FQ-UNAM. Facultad de Química, UNAM, México D.F., México.
4. Castro-González, A., Bernal-González, M., and Durán-de-Bazúa, C. (2004). Tratamiento de vinazas de plantas

Table 4. Regulatory Limits Established in Mexico for Cane Sugar and Ethanol Production Plant Liquid Effluents[a]

	Cane Sugar		Distilling Industry	
Parameter	Daily Average Value	Instantaneous Value	Daily Average Value	Instantaneous Value
pH	6–9	6–9	6–9	6–9
BOD_5, mg/L	60	72	200	240
COD, mg/L	n.r.[b]	n.r.	260	360
Total suspended solids, mg/L	n.r.	n.r.	200	240
Settleable solids, mg/L	1.0	1.2	1.0	2.0
Total nitrogen, mg/L	n.r.	n.r.	10	12
Total phosphorus, mg/L	n.r.	n.r.	5	6
Grease and oils, mg/L	15	20	10	20
Phenols, mg/L	0.5	0.75	n.r.	n.r.

[a] Reference 8.
[b] n.r. not reported

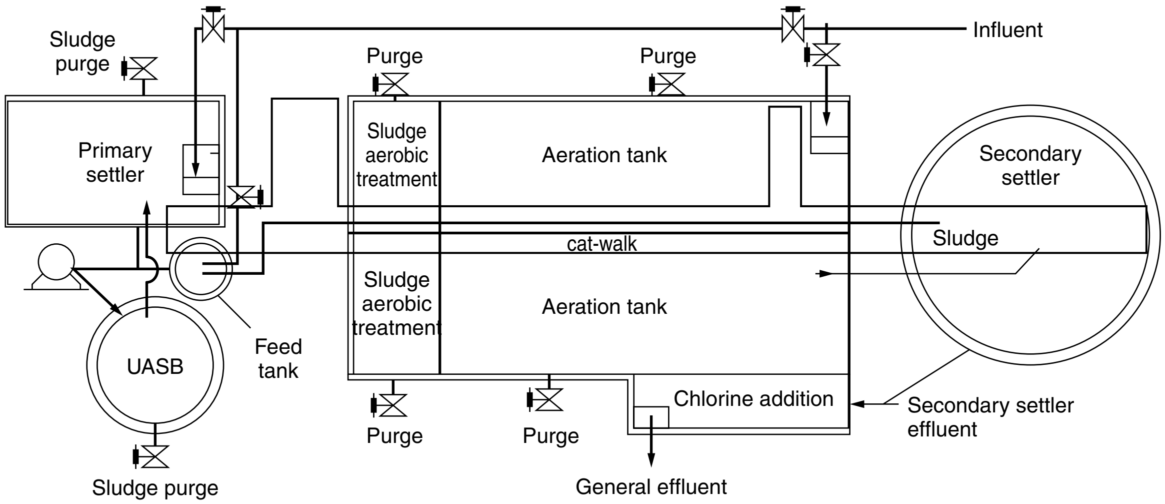

Figure 6. Complete sugarcane mill wastewater treatment plant, including a primary settling tank, an anaerobic feed tank, a UASB reactor, and a biogas absorption tank (biogas stripping) (14).

destiladoras de alcohol usando consorcios microbianos anaerobios. *Bebidas Mexicanas* **13**(3): 12–14, 16–20, 22–25.

5. Durán-de-Bazúa, C. (2004). *Tratamiento Biológico de Aguas Residuales Industriales*. PIQAyQA-Facultad de Química, UNAM, 5th Edn. (1994). México, D.F. Mexico. 6th Edn., in press.
6. Bao-Guo-Yu and Chen-Shi-Zhi. (1990). *Treatment and Utilization of Pollution Effluents of Cane Sugar Factories in China*. UNIDO. Workshop on pollution control and low waste technologies in agro-based industries. Shanghai, China.
7. Anonymous. (1976). *Uso del Agua y Manejo Del Agua Residual en la Industria*. Vol. 8. Azúcar. Secretaría de Recursos Hidráulicos. México, D.F. Mexico.
8. DOF. (1993, 1995). *Normas Oficiales Mexicanas en Materia de Protección Ambiental*. NOM-002-ECOL-1993, Proy. NOM-064- ECOL-1995. Diario Oficial de la Federación, Secretaría de Desarrollo Social (Sedesol), Mexico City, Mexico.
9. Bautista-Zúñiga, F., Reina-Trujillo, T. de J., Villers-Ruiz, L., and Durán-de-Bazúa, C. (2000). *Mejoramiento de Suelos Agrícolas Usando Aguas Residuales Agroindustriales*. Caso: Vinazas crudas y tratadas. Serie: Química Ambiental del Suelo. Vol. 1. PIQAyQA-FQ, UNAM. México D.F., México.
10. Bautista-Zúñiga, F., Durán-de-Bazúa, C., Reyna-Trujillo, T., and Villers-Ruiz, L. (2000). Agroindustrial organic residues: Handling options in cane sugar processing plants. Part I and Part II. *Sugar y Azúcar* **95**(9): 32–45; **95**(10): 23–37.
11. Villatoro-Reséndiz, J. (1998). *Estudio de la Transformación de la Materia Orgánica Biodegradable de la Vinaza Cruda y Tratada en Los Suelos Acrisol y Vertisol, Del Municipio Miguel Alemán en el Estado de Veracruz, México*. Tesis profesional (Biología). UNAM, Facultad de Ciencias, México D.F., México.
12. Durán-Domínguez, M.C., Pedroza-Islas, R., Rosas-Vázquez, C., Luna-Pabello, V.M., Sánchez-Zamora, A., Capilla-Rivera, A., Paredes-Gómez, L., Valderrama-Herrera, S.B., and Vázquez-Cedeño, I. (1991). Producción de alimentos para peces: Utilización de subproductos del tratamiento de aguas residuales. In: *Premio Nacional Serfín El Medio Ambiente*. J.J. De Olloqui (Ed.). Futura Eds., Méx., México, pp. 79–106.
13. Castro-González, A., Enríquez-Poy, M., and Durán-de-Bazúa, C. (2001). Design, construction, and starting-up of an anaerobic reactor for the stabilisation, handling, and disposal of excess biological sludge generated in a wastewater treatment plant. *Anaerobe (Biotechnology)* **7**: 143–149.
14. Castro-González, A., Durán-de-Bazúa, M.C., Enríquez-Poy, M., and Pliego-Bravo, Y. (1998). Consideraciones en un ingenio azucarero para minimizar las descargas líquidas y mejorar las condiciones de operación de su planta de tratamiento de aguas residuales. *Ingenio* (México) **3**(34): 2–7.

ESTIMATED USE OF WATER IN THE UNITED STATES IN 1990 INDUSTRIAL WATER USE

U.S. Geological Survey

Industrial water use includes water for such purposes as processing, washing, and cooling in facilities that manufacture products. Major water-using industries include, but are not limited to, steel, chemical and allied products, paper and allied products, and petroleum refining.

Many States have developed permit programs that require reporting of industrial withdrawals and return flows. Estimates for 1990 are improved over those of previous years because of the availability of more comprehensive inventories of industrial facilities and more complete water-use records. Information on deliveries from public suppliers to industrial users were estimated from a variety of methods if not available directly from public suppliers. Consumptive-use estimates generally were based on coefficients ranging from 3 to 80 percent (depending on the type of industry) of withdrawals and deliveries.

Industrial water use (freshwater withdrawals, public-supply deliveries, saline water withdrawals) during 1990 was an estimated 19,300 Mgal/d of self-supplied

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Table 1. Industrial Water Use By Water-Resources Regions [Figures May Not Add to Totals Because of Independent Rounding. All values in Million Gallons Per Day]

	Self-Supplied Withdrawals							
	By Source and Type							
	Ground water		Surface water		Total			
Region	Fresh	Saline	Fresh	Saline	Fresh	Saline	Total	Reclaimed Waste Water
New England	96	0.0	382	68	479	68	547	
Mid Atlantic	361	.2	1,370	1,470	1,730	1,470	3,200	6
South Atlantic-Gulf	896	0	1,920	94	2,810	94	2,910	
Great Lakes	235	3.7	3,950	0	4,190	3.7	4,190	
Ohio	532	0	1,840	0	2,370	0	2,370	
Tennessee	23	0	1,170	0	1,190	0	1,190	
Upper Mississippi	349	0	618	0	967	0	967	
Lower Mississippi	501	.6	2,120	67	2,620	67	2,690	
Souris-Red-Rainy	1.3	0	47	0	49	0	49	
Missouri Basin	114	0	57	0	171	0	171	
Arkansas-White-Red	67	0	301	0	368	0	368	
Texas-Gulf	141	1.1	600	1,460	741	1,460	2,200	2
Rio Grande	11	0	1.0	0	12	0	12	
Upper Colorado	2.9	0	2.5	0	5.4	0	5.4	
Lower Colorado	49	0	124	0	174	0	174	
Great Basin	77	2.3	29	0	106	2.3	108	
Pacific Northwest	336	0	691	36	1,030	36	1,060	
California	126	0	4.8	25	130	25	156	
Alaska	5.2	0	106	0	111	0	111	
Hawaii	20	.6	23	0	43	.6	44	
Caribbean	11	1.2	0	50	11	51	62	
Total	3,950	9.7	15,400	3,260	19,300	3,270	22,600	9

Table 2. Industrial Water Use By States [Figures May Not Add to Totals Because of Independent Rounding. All values in Million Gallons Per Day]

	Self-Supplied Withdrawals							
	By Source and Type							
	Ground water		Surface water		Total			
State	Fresh	Saline	Fresh	Saline	Fresh	Saline	Total	Reclaimed Waste Water
Alabama	31	0.0	753	0.0	784	0.0	784	0.0
Alaska	5.2	0	106	0	111	0	111	0
Arizona	39	0	124	0	163	0	163	2.3
Arkansas	99	0	78	0	177	0	177	0
California	125	0	3.4	25	129	25	154	.8
Colorado	33	0	85	0	118	0	118	0
Connecticut	19	0	61	68	80	68	148	0
Delaware	18	0	47	6.0	65	6.0	71	0
D.C.	.5	0	0	0	.5	0	.5	0
Florida	282	0	121	56	403	56	459	0
Georgia	346	0	311	33	657	33	689	.5
Hawaii	20	.6	23	0	43	.6	44	0
Idaho	170	0	26	0	196	0	196	0
Illinois	155	0	309	0	464	0	464	0
Indiana	129	0	2,350	0	2,480	0	2,480	0
Iowa	71	0	148	0	219	0	219	0
Kansas	50	0	3.8	0	53	0	53	.5
Kentucky	93	0	220	0	313	0	313	0
Louisiana	289	.6	2,070	67	2,360	67	2,430	0
Maine	9.8	0	244	0	254	0	254	0

Table 2. (*continued*)

	Self-Supplied Withdrawals							Reclaimed Waste Water
	By Source and Type				Total			
	Ground water		Surface water					
State	Fresh	Saline	Fresh	Saline	Fresh	Saline	Total	
Maryland	21	0	49	379	70	379	450	63
Massachusetts	65	0	22	0	87	0	87	0
Michigan	175	3.7	1,510	0	1,680	3.7	1,690	0
Minnesota	65	0	89	0	154	0	154	0
Mississippi	144	0	126	0	269	0	269	0
Missouri	53	0	32	0	85	0	85	0
Montana	30	0	27	0	57	0	57	0
Nebraska	39	0	2.4	0	41	0	41	0
Nevada	9.4	0	.8	0	10	0	10	0
New Hampshire	.3	0	37	0	37	0	37	0
New Jersey	53	.2	273	1,020	326	1,020	1,340	0
New Mexico	4.6	0	1.7	0	6.3	0	6.3	0
New York	85	0	189	0	274	0	274	0
North Carolina	63	0	328	5.5	390	5.5	396	0
North Dakota	2.	0	6.6	0	8.8	0	8.8	0
Ohio	123	0	230	0	354	0	354	0
Oklahoma	3.3	0	32	0	35	0	35	0
Oregon	31	0	254	0	284	0	284	1.6
Pennsylvania	180	0	1,690	0	1,870	0	1,870	0
Rhode Island	2.5	0	9.1	0	12	0	12	0
South Carolina	47	0	585	0	632	0	632	0
South Dakota	5.0	0	10	0	15	0	15	0
Tennessee	69	0	813	0	882	0	882	0
Texas	143	1.1	741	1,460	884	1,460	2,340	22
Utah	77	2.3	29	0	106	2.3	108	0
Vermont	1.0	0	43	0	44	0	44	0
Virginia	195	0	300	66	495	66	561	0
Washington	104	0	397	36	501	36	536	0
West Virginia	106	0	26	0	132	0	132	0
Wisconsin	58	0	409	0	468	0	468	0
Wyoming	6.0	0	9.9	0	16	0	16	0
Puerto Rico	11	0	0	0	11	0	11	0
Virgin Islands	.1	1.2	0	50	.1	51	51	0
Total	3,950	9.7	15,400	3,260	19,300	3,270	22,600	90

freshwater, 5,190 Mgal/d of public-supplied freshwater, and an additional 3,270 Mgal/d of saline water. (See Table 1: water-resources regions and Table 2: States.) Industrial freshwater use during 1990 was 13 percent less than during 1985 and represents 7 percent of total freshwater use for all offstream categories. Surface water was the source for about 82 percent of self-supplied industrial withdrawals; ground water, 18 percent; and reclaimed wastewater, only a fraction of 1 percent. Public-supplied deliveries to industries accounted for 13 percent of public-supply withdrawals.

The source and disposition of water for industrial purposes are shown in the pie charts below (or as a GIF file or PostScript file (94 Kb)). The consumptive use of freshwater for industrial purposes during 1990 was 3,330 Mgal/d, or 14 percent of freshwater withdrawals and deliveries; saline consumptive use was 913 Mgal/d, or about 28 percent of saline water withdrawals.

In 1990, the Great Lakes and Mid Atlantic water-resources regions had the largest withdrawals for industrial purposes as shown in figure 20 (GIF file), or (PostScript file (620 Kb)). Indiana, Louisiana, Texas, Pennsylvania, and Michigan reported the largest state withdrawals for industries as shown in figure 21 (GIF file) or (PostScript file (508 Kb)). Indiana, Louisiana, Pennsylvania, and Michigan reported the largest freshwater use (figure 22 (GIF file)), or (PostScript file (508 Kb)), and Maryland and Texas reported the largest quantities of reclaimed wastewater used by industries.

WASTE WATER TREATMENT

AERATION

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OVERVIEW

The aeration of wastewater and byproducts is a key process in the operation of most modern wastewater treatment plants (WWTP), which is reflected in the energy consumption of a WWTP's aeration system, which can be up to 70% of the WWTP's total energy consumption.

As most wastewater treatment plants and many sludge treatment plants include aerobic biological processes, the transfer of oxygen into the wastewater (or sludge) is a key operation.

As a result of the large quantities of CO_2 produced in the course of the aerobic degradation of organic matter, the pH in such a reactor can be significantly lower than that of its feed. These CO_2-related effects can be amplified when nitrification occurs or when the liquor's alkalinity is low. This drop in pH can lead to decreased performance of the plant as well as to impacts such as concrete and metal corrosion if not managed properly. The second key function of an aeration system is therefore to remove CO_2 from the reactor (1).

One of the important functions that an aeration system has to provide is mixing to prevent settling of the biomass in the reactors and optimize the contact of wastewater with the biomass.

TERMS AND DEFINITIONS

The following terms and definitions will be used herein:

1. α (alpha) factor is the ratio of the apparent volumetric mass transfer coefficient kL in wastewater to that in clean water. α is normally <1.
2. Oxygen transfer rate (OTR) is the mass of oxygen dissolved by a given aeration system in a given volume of water under given water temperature, barometric pressure, and operating conditions [initial dissolved oxygen (DO) concentration, gas flow rate, power input] per unit time.
3. Standard oxygen transfer rate (SOTR) is the OTR in clean water at 20°C, whose initial DO concentration is zero in all parts of the waterbody, and is at 101.3 kPa barometric pressure.
4. Oxygen transfer efficiency (OTE) is the fraction of oxygen in an injected gas stream that is transferred into water at given initial DO, gas flow rate, water temperature, and barometric pressure.
5. Standard oxygen transfer efficiency (SOTE) is the OTE in clean water at 20°C, whose initial DO concentration is zero in all parts of the waterbody, and is at 101.3 kPa barometric pressure. The oxygen transfer efficiency per meter submergence for a given aeration system under given ambient and operating conditions is relatively constant for installation depths in the technically most important range around 4 to 5 meters. It is, therefore, often quoted in percent per meter submergence to allow the user of this information to calculate the OTE or SOTE case-by-case for the respective aerator installation depths rather than providing a long list of values for different submergences.
6. Aeration efficiency (AE) is the OTR divided by the total power input for the aeration system, measured as either brake power or wire power.
7. Standard aeration efficiency (SAE) is the AE based on the SOTR.

Further explanations and definitions of further parameters and terms used to characterize aeration systems and their design are provided in Refs. 2 and 3.

AERATION SYSTEMS

Numerous aeration mechanisms are used in wastewater treatment plants; each has its particular advantages. The oxygen transfer from air (or pure oxygen where it is applied) into liquor can take place only through a common surface of the two media; so the common goal of all aeration mechanisms is to make as much active surface area available as possible. A classification of the technical systems used for aeration purposes can be based on the mechanical equipment that is used. Alternatively, the systems can be classified on the basis of where the oxygen transfer mainly takes place, which indicates how the design calculations are carried out. Aeration systems are therefore differentiated into

- — surface aeration and
- — submerged aeration.

SURFACE AERATION

Natural Aeration

The specific characteristic of natural aeration is that no energy is directly applied and/or no mechanical equipment is directly involved in the oxygen transfer. Examples are

- — the oxygen transfer through the water surface of a facultative wastewater treatment pond;
- — the aeration of wastewater in a trickling filter where natural draft is relied on to move the air through the filter when it is brought into contact with the wastewater; or
- — postaeration of secondary effluent in a cascading system before it is discharged into the receiving waters.

The first two types of systems are typically designed on the basis of specific loads of biochemical or chemical oxygen demand (BOD or COD) and/or nitrogen (e.g., in kg BOD/(ha · d)) without explicitly designing the aeration process per se. Depending on the system, the contribution of algae to the oxygen balance in a pond may also be considered in the design calculation. These systems are not discussed here.

The secondary effluent can be postaerated by natural aeration in a cascade, although other systems such as fine bubble diffused air aeration can also be applied. The key design parameter of a cascade postaeration system is its height and the shape of the cascade, for example, a weir or steps. The required height is calculated based on the oxygen deficit ratio, the ratio of the difference between the saturation concentration and the actual oxygen content to the difference of the saturation concentration and the target effluent concentration. As the saturation concentration decreases with increasing water temperature, these systems typically have to be designed for the highest temperature when the deficit ratio and hence the required cascade height is greatest.

Mechanical Surface Aeration

An aeration system is referred to as mechanical surface aeration system when air is entrained in the liquor at the surface by moving mechanical equipment. These systems are usually operated with uncompressed ambient air. Low- and high-speed aeration turbines, rotating brush aerators, and aspirating mixer aerators are probably the most commonly used types of mechanical surface aerators.

Aeration turbines and brush aerators work on the principle of lifting some liquid up and accelerating and dispersing it in the air above the liquid surface, which achieves oxygen transfer mainly through the large total surface area of the small liquor droplets in the air and, to a lesser extent, through the turbulent surface of the liquor in the tank and air entrainment when the accelerated liquid falls back down and hits the liquor surface.

Aspirating mixers are high-speed mixers with a hollow inclined or vertical shaft. They use the vacuum created by the rapid motion of the liquid at the mixer tip to suck ambient air through the hollow mixer shaft into the zone of rapid liquid movement at the mixer tip and in the mixer's jet stream. The high shear forces in this area result in mixing the two streams.

Application of Mechanical Aeration Systems

Mechanical surface aeration systems are typically preferred if one or more of the following criteria are met:

— Shallow reactor. Diffused air aeration systems are inefficient here; their efficiency is a function of depth, whereas the efficiency of mechanical aeration systems is almost unaffected by depth. Note that, although this criterion of shallowness is often met in lagoons and mechanical aerators are, therefore, often used in lagoons, it would be wrong to deduce a genuine requirement to aerate lagoons with mechanical aerators because diffused air aeration systems are available that are specifically designed for lagoons.

— Very deep reactor. Fine bubble diffused air aeration is not preferred in such installations because of their reduced CO_2-removal efficiency. Instead, systems that have a lower oxygen transfer efficiency such as coarse bubble diffused air aeration or mechanical aeration are preferred for deep tanks (see below).

— Reactor and process configuration lend itself for it. A typical example is oxidation ditches. These reactor/process layouts typically benefit from the combined aerating and mixing action of mechanical, rotating-brush surface aerators, whereas diffused air aeration systems would require additional horizontal mixers to provide sufficient velocity of mixed liquor circulation.

— Simplicity is imperative. The installation of mechanical aeration systems comprises less components and is significantly simpler than that of diffused air aeration systems that have associated benefits regarding maintenance, for example, that all equipment can be easily accessed from the surface.

— Medium unsuitable for fine bubble diffused air aeration. A typical example would be the aeration of sludge, where fine bubble diffused air aeration loses its efficiency advantage due to effects of the medium, most of all bubble coalescence. Systems that produce coarser bubbles, such as coarse bubble diffused air aeration or mechanical aeration, lose their respective disadvantage, and other benefits, such as simplicity, become the driver for equipment selection. Other examples would be wastewaters that have a high tendency to scale up or foul the diffusers or one that is aggressive to the rubber or other compounds used in the diffusers, all of which can render their use impracticable and be a driver toward mechanical aeration.

The biggest drawback of mechanical aeration compared with fine bubble diffused air aeration is its lower AE in medium deep tanks of around 4 m depth and deeper. In particular, in medium and large municipal installations, this difference in AE often outweighs the advantages of mechanical aeration in capital and maintenance costs and leads to lower life cycle costs for diffused air aeration. Typical AE for mechanical aeration systems is in the range of 1.3–2 kg O_2/kWh. Note that fine bubble diffused air aeration systems may end up in the 2 kg O_2/kWh range as well after a few years of operation, which can lead to process problems. Mechanical aeration systems, in contrast, will stay on their initial AE level, and the oxygen input is at a point source; thus a tapered DO profile can be achieved that can enhance nitrogen removal.

SUBMERGED AERATION SYSTEMS

Submerged aeration systems can be differentiated into

— mechanical submerged aeration systems and

— diffused air aeration systems.

Mechanical Submerged Aeration Systems

A mechanical submerged aeration system entrains ambient air or compressed air in the liquor by moving mechanical equipment at a point close to the tank floor. The concept is to increase the contact time between air and liquor, and hence the oxygen transfer, by letting the air bubbles travel through the liquor and to attempt to produce fine bubbles via agitation. Mechanical submerged aeration systems comprise floor-mounted aspirating or sparger (when operated with compressed air) mixers and ejector pumps.

Aspirating and sparging mixers are high-speed, submerged mixers that introduce air at or below the rotor where it is dispersed and mixed with the liquid, as shown in Fig. 1. In the aspirating mode, the working principle is as described before for aspirating mixers for surface aeration. However, in some cases, the oxygen demand requires a supply of compressed air (sparger mixer). Figure 2 shows an installation of a submerged aspirating mixer.

Ejector pumps use a venturi nozzle on the pump's discharge to entrain ambient air or compressed air into a jet of pumped liquid. They work with the vacuum created by the acceleration of the liquid in the nozzle, which sucks air into this highly turbulent zone where the two streams are mixed.

Diffused Air Aeration

Diffused air aeration is a system where air (or pure oxygen) is compressed and then diffused into small bubbles by a passive component.

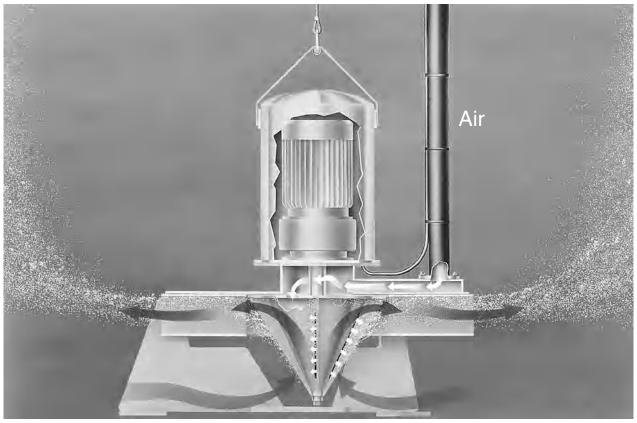

Figure 1. Working principle of a submerged aerating mixer.

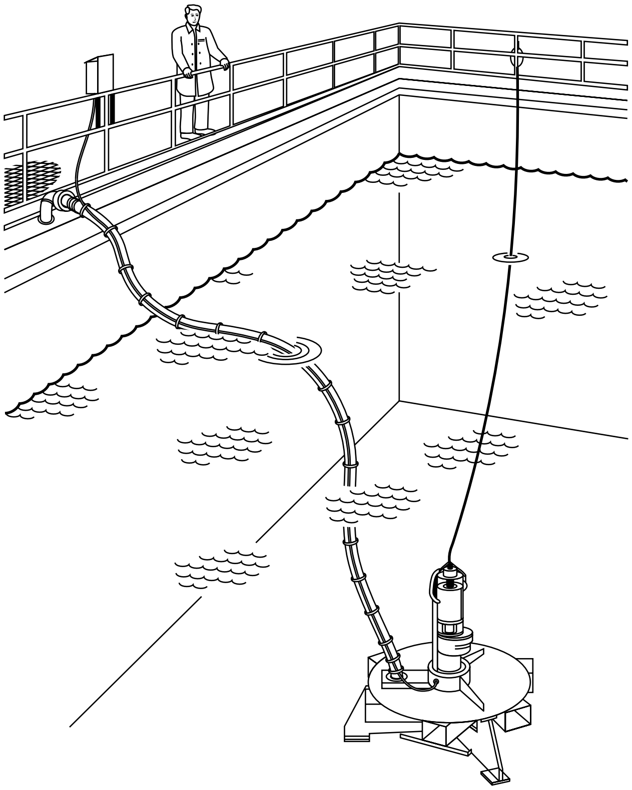

Figure 2. Installation of a submerged aspirating mixer.

Medium or coarse bubble diffusers are being used for applications requiring mixing, in deep tanks, or for the aeration of sludge. They have relatively large openings for the air to pass through. Rubber membranes and rigid porous materials are rarely used for these diffuser types, which include static mixer type arrangements, compressed air jets, perforated pipes, and orifices. Some examples of coarse bubble diffusers are shown in Fig. 3.

Fine bubble systems are used for wastewater aeration applications. Compressed air is passed through floor-mounted, finely slotted rubber membranes or rigid porous diffuser bodies to form small bubbles that rise through the mixed liquor to the surface. An example of a rubber

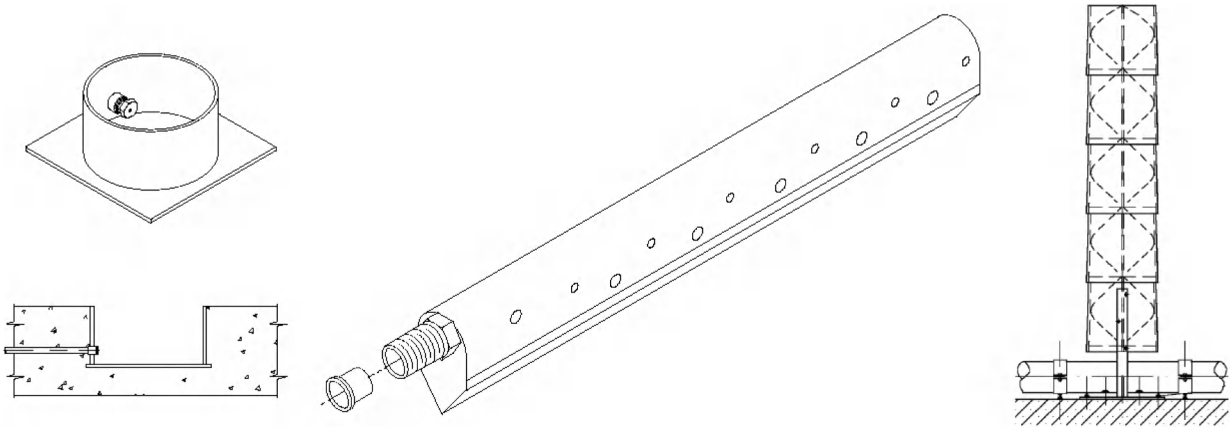

Figure 3. Coarse bubble diffuser types.

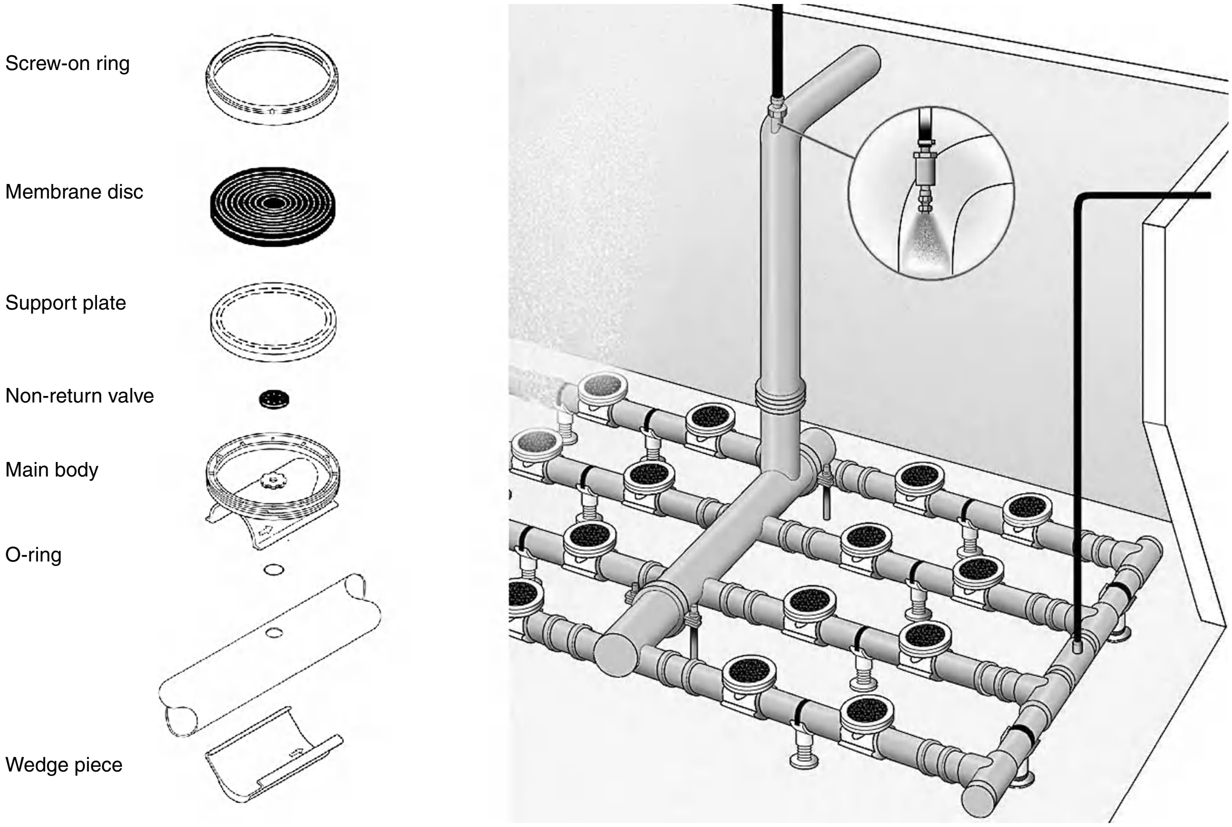

Figure 4. Typical membrane fine bubble diffuser details and installation.

membrane fine bubble diffuser for a fine bubble diffuser installation is shown in Fig. 4.

The mechanical and process design of fine bubble diffused air aeration systems can be quite involved. A dedicated section, therefore, expands on these systems.

BIBLIOGRAPHY

1. Hartley, K.J. (1985). *Operating the Activated Sludge Process*. GHD, Brisbane, pp. 75–77.
2. ASCE Standard No. ANSI/ASCE 2–91. (1993). *Measurement of Oxygen Transfer in Clean Water*, 2nd Edn. American Society of Civil Engineers, New York.
3. Metcalf & Eddy. (2003). *Wastewater Engineering: Treatment and Reuse*, 4th Edn. revised by G. Tchobanoglous, F.L. Burton, and H.D. Stensel, McGraw-Hill, New York, pp. 425–456.

FINE BUBBLE DIFFUSED AIR AERATION SYSTEMS

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DIFFUSER TYPES

Fine bubble diffusers are typically used for aerating activated sludge tanks in municipal wastewater treatment plants because medium or coarse bubble diffusers are not economical in medium depth tanks, which are prevalent in municipal applications.

Two types of fine bubble diffusers are available on the market:

- — rigid porous diffusers; and
- — elastic/rubber membrane diffusers.

A general comparison of rigid porous and rubber membrane diffuser systems is given in Table 1.

Rigid Porous Fine Bubble Diffusers

The first rigid porous diffusers were made of sintered ceramics such as sintered alumina; many diffusers are still made of this material. Its biggest advantage lies in its chemical inertness. Ceramic diffusers can be refired, for example, in a brick kiln, or acid cleaned to remove scaling and fouling and bring their permeability/head loss back to nearly new condition (1). Practical experience indicates that they need to be refired every 5 to 10 years and that this can be done only two to three times. However, refiring may not often be practical once tank downtime or total cost, including replacement of lost (broken) diffusers, is accounted for.

Alternative materials used to manufacture rigid porous diffusers include sintered HDPE granulate and round quartz sand in a phenol–resin matrix. These diffusers cannot be cleaned thermally because the temperatures

Table 1. Comparison of Rubber Membrane and Rigid Porous Diffusers

	Rubber Membrane Diffusers	Rigid Porous Diffusers
Continuous operation	Well suited	Well suited
Intermittent operation	Reasonably suited	Not suited
Turndown ratio	Large	Moderate
High water hardness	Scaling may lead to short membrane replacement intervals	Carbonate scaling can be controlled with in-line acid dosing
High water temperature	Not suited	Depending on diffuser material
High oil and grease concentrations	EPDM: not suited Silicone: well suited	Well suited
In-line cleaning	Bumping	Acid gas injection
Typical head loss	Higher	Lower
Typical oxygen transfer efficiency	Higher	Lower
Typical asset life	Replace membrane after 3 to 5 years Replacement of membrane brings diffuser back to new condition	Refire or acid clean after 5–10 years Refiring or acid cleaning can bring diffuser back to nearly new condition

in a kiln would destroy them. However, they can be acid cleaned and, due to the more regular and smoother geometry of the particles from which they are made, high-pressure hosing may have a greater effect than on diffusers made from genuine ceramic. The use of a resin matrix also makes it possible to include fouling inhibitors (bactericides) in the matrix and thus reduce bacterial growth on the diffuser and in its pores.

Rigid porous diffusers are manufactured in many shapes and types such as domes, cylinders, circular disks, and plates (noncircular disk). The method of mounting the actual porous diffuser element to the pipework is important in selecting a diffuser to provide flexibility for replacement, which is critical for converting a rigid porous diffuser system to a membrane diffuser system and vice versa, if required. Further, some suppliers offer features such as a nonreturn valve or a pressure sample port that can be integrated into the diffuser carrier. A nonreturn valve prevents intrusion of larger quantities of mixed liquor into the diffuser and the pipework, if the airflow should drop below the required minimum or should cease. A pressure sample port in the diffuser carrier in combination with a pressure probe in the header pipe and a static pressure measurement allows a determination of the dynamic wet pressure of the diffuser to judge whether a cleaning cycle is required.

The lifetime of rigid porous diffusers is determined mainly by

- — the lifetime of the bond between the diffuser body particles (disintegration);
- — reduction of the pore diameter by scaling (e.g., $CaCO_3$ precipitation);
- — reduction of the pore diameter by fouling (intrusion/growth of bacteria); and
- — blockage of pores due to dust and other particles in the air.

Due to blockage of its pores, the head loss of a rigid porous diffuser can only increase over its lifetime. At the same time, its oxygen transfer efficiency (OTE) may increase as the pores, and hence the air bubbles, produced become smaller, leading to reduced required air throughput. If they occur, these two effects may offset each other to some degree and may thus expand the useful life of the diffusers. There will, however, be a point where the aeration blowers cannot deliver sufficient quantities of air at the required, increased pressure any longer, and the wastewater treatment process becomes underaerated (oxygen deficient).

Rubber Membrane Fine Bubble Diffusers

Rubber membrane diffusers are made of a finely slotted rubber membrane mounted on a carrier, typically made of plastic. Most rubber membranes are made of EPDM because of its favorable physical properties and acceptable chemical resistance at a low price. However, the drawback of EPDM in wastewater applications is that its plasticizers are washed out over time by oils, grease, and solvents, which are always present in small quantities in wastewater and in compressed air, which in turn causes the membrane to become stiff over time and lose its ability to contract fully and close its pores when the air is cut off. The speed at which this process progresses is a function of various parameters; one of them is the oil and grease content of the wastewater. EPDM membranes are, therefore, unsuitable for wastewaters that have a high concentration of these constituents.

Alternative membrane materials that overcome some of the shortfalls and diffuser membranes are also available now in materials such as silicone rubber and polyurethane rubber. These materials are resistant to oil and grease in wastewater because they do not contain plasticizers.

Note that the resistance to oil and grease is not the only material characteristic where the various rubber types differ. Table 2 shows a number of physical parameters that demonstrate how different these materials are and that, for example, EPDM and silicone are not uniquely specified substances but can be produced to match different physical and chemical requirements. It can also be seen that EPDM varieties have higher tear resistance than the alternative materials; however, once a tear has formed, it will grow longer more easily than in the other materials.

An important aspect that is not captured in Table 2 is how the membranes perform over time ("aging"). EPDM membranes become stiffer, whereas silicone membranes tend to become softer. If not replaced before these effects become noticeable and with other effects,

Table 2. Examples of Diffuser Membrane Materials[a]

Material	EPDM (1)	EPDM (2)	Silicone (1)	Silicone (2)	Polyurethane
Plasticizer content, %	12	18	0	0	0
Tear resistance, MPa[a]	13	14.4	10	10.5	11
Ultimate elongation, %[a]	700	580	650	680	700
Tear strength, N/mm[b]	11.4	10.5	40	44.5	23

[a] Reference 2.

[a] DIN-53504.

[b] Various testing standards.

e.g., scaling, left aside, this different aging process may lead to slightly finer bubbles and an associated increase in OTE for EPDM membranes and slightly larger bubbles and an associated decrease in OTE for silicone membranes.

Due to the different properties and aging patterns of rubber membrane diffusers, compared with rigid porous diffusers, maintenance and cleaning are also different. A wash down with water is a typical means at water pressures often quite low to avoid damaging the membranes. Acid injection is rarely used to clean membranes. Rubber membrane diffusers can be "bumped" to remove scale, which is done by sharply increasing the airflow and then dropping back to a low (or nil) flow. By doing so, deposits on the diffuser surface break and loosen when the rubber membrane expands and are washed away.

The most common shapes of rubber membrane diffusers are circular discs, tubes of circular and noncircular cross section (e.g., cylindrical diffuser elements of a round cross section), and plates (noncircular disk).

Most diffuser types comprise a carrier and a separate membrane mounted on the carrier. Tube types have the diffuser membrane all around the carrier; the flat disk and plate types have a membrane sheet that is attached to the upper side of the carrier. Apart from these three main types of diffusers less frequently used designs also exist, such as diffuser tubes without an internal carrier where the membrane tubes are fixed to a support grid to hold them in place.

The most important difference between rigid porous diffusers and membrane diffusers is that membrane diffusers have built-in backflow prevention properties, which results from the elastic rubber membrane totally contracting when the air is cut off and thereby closing its pores.

Note that the membrane lifts off the carrier when pressurized and returns to its initial position and lies tightly on the carrier when the air is cut off. Further, all diffuser assemblies are designed so that the membrane closes the air entry ports in the carrier when it is resting, which is facilitated by the static head of the liquor above the diffuser. In addition to these nonreturn mechanisms, some disk diffusers include a nonreturn flap in the air entry port of the carrier. These properties make it possible to cut off the air supply to submerged diffusers without flooding the diffusers or the piping, which is a characteristic that is vital for diffused air aeration systems in sequencing batch reactors or in plants that have large diurnal load fluctuations, where diffusers have to be cut off at certain times.

The lifetime of rubber membrane diffusers is determined mainly by

- — operating temperature (higher temperatures, e.g., in tropical regions or in industrial applications, lead to a shorter lifetime);
- — the lifetime/residence time of the membrane plasticizer (leading to decreased membrane elasticity and increased head loss);
- — other aging effects on the rubber, such as UV radiation or oxidation;
- — chemically or biochemically induced hydrolysis of the rubber;
- — loss of pores self-closing properties from scaling (e.g., $CaCO_3$ precipitation) due to reduced elasticity and/or deposits in the pores;
- — reduction of the pore diameter by scaling (e.g., $CaCO_3$ precipitation);
- — reduction of the pore diameter by fouling (intrusion/growth of bacteria); and
- — blockage of pores due to dust and other particles in the air.

Over its lifetime, the head loss of an EPDM rubber membrane diffuser typically first drops when the membrane elongates slightly as a result of the expansion–contraction cycles experienced during operation. Once the head loss has reached its minimum, it can only increase from there on as a result of the above impacts. The OTE of rigid porous diffusers, may increase and lead to reduced air throughput requirements. The increased head loss can reach a point where the aeration blowers cannot deliver sufficient quantities of air at the required pressure. The increased operating pressure of the (then stiffer) diffuser also includes an increased risk of membrane failure.

Mixed Diffuser Systems

It is possible to combine rigid porous diffusers and rubber membrane diffusers in one installation. By doing so, some of the wastewater treatment plant's diffuser installation can benefit from the long lifetime of rigid porous diffusers, and some can benefit from the large turndown ratio of rubber membrane diffusers, for example,

- — rigid porous diffusers in the main nitrification zone and rubber membrane diffusers in a bivalent zone ("swing zone") that can be operated anoxic in summer to maximize nitrogen removal and aerobic in winter to compensate for the lower nitrification rate at lower temperatures by providing more aerobic tank volume and hence longer aerobic sludge age.

- a modified Ludzack–Ettinger process arrangement that has rigid porous diffusers in the main nitrification zone and rubber membrane diffusers in the last aerated zone to minimize aeration there and thus oxygen recycling back into the anoxic zone.
- a plant that has strong diurnal or seasonal load fluctuations where rigid porous diffusers cover the base load and additional rubber membrane diffusers can be switched on to cover the additional oxygen demand during peak hours or peak season.

Such systems have been built and are being operated successfully, but many factors have to be considered. The diffuser types need to be suitable for the particular wastewater, and the grid and control system layout also needs to be adapted. For example, because the head loss for the two diffuser types varies differently when the diffusers are aging, one must be aware that unless the airflow to each subsystem is automatically controlled separately (e.g., air supply valve modulating based on a DO reading) in each tank, the adjustment of the flow split between the two subsystems is a recurrent additional task for plant operators. Other factors are increased piping costs and increased spares storage.

DESIGN CONSIDERATIONS FOR DIFFUSED AIR AERATION SYSTEMS

Oxygen Transfer Efficiency

Aeration systems, in general, and diffused air aeration systems, in particular, are often compared on the basis of their SOTE, which is measured in a laboratory and refers to standardized conditions. Both the testing procedures and the reference conditions are set out in standards, such as the ASCE standard (3), which is probably, internationally, the most frequently used standard for this application.

The SOTE of diffused air aeration systems is a function of the average bubble diameter produced by the diffuser as well as of other parameters that are discussed further below. The dependence on bubble size is demonstrated by the following typical values for the SOTE, quoted in % oxygen transferred per meter of diffuser submergence:

- for coarse bubble systems: 2–3%/m;
- for medium bubble systems: 4–5%/m; and
- for fine bubble systems: 5.5–6.5%/m.

The SOTE can vary among suppliers and materials, and, even for a given diffuser system, it is still widely variable, depending on factors such as

- Specific air throughput per meter of diffuser length or square meter diffuser area: The SOTE decreases with increasing specific air throughput because the average diameter of the bubbles produced increases, which leads to a decreasing surface area to volume ratio for the gas bubbles.
- Floor coverage, the ratio of installed diffuser surface area to tank floor area: The SOTE increases with higher floor coverage and more even diffuser distribution, which is due to the decreased formation of “rolling” motion patterns in the liquor, which are typically observed in line aeration systems, where the liquor is accelerated upward by the rising bubbles from the aeration line (airlift pump principle) and flows back downward in the unaerated areas. These patterns lead to shortened detention time of the bubbles in the water and hence a decreased SOTE.
- strong currents in the basin due to mixers that may coalesce fine bubbles but may also add a horizontal flow component that increases the bubble detention time. The effect on the SOTE can, therefore, be detrimental as well as positive.
- tank depth: The effect of deep tanks on the design of aeration systems is quite complex and is discussed separately later.

Head Loss

Diffused air aeration systems require low head loss to be efficient. However, because the head loss is also a function of bubble size, a balance between head loss and oxygen transfer efficiency must be maintained to provide optimal aeration efficiency.

The increase in head loss from coarse to medium and fine bubble diffusers is usually compensated for by the associated increase in oxygen transfer efficiencies. The overall power requirements and, thus, operating costs in typical municipal wastewater applications are, therefore, typically lower for fine bubble diffusers than for coarser systems. When fine bubble diffusers start to clog, bubble size decreases, and oxygen transfer efficiency and head loss increase. In practice, these two effects may compensate for each other initially; in particular, for rigid porous diffusers, this effect is well documented (4). However, there is a point where the increased head loss cannot be compensated for any longer and the overall efficiency drops or where the blowers cannot any longer deliver the required quantities of air at the increased head.

Other impacts on the head loss of a diffuser are the material from which it is made, its condition (new/old, fouled, scaled, etc.), and the specific air throughput.

Deep Tanks

A tank is generally considered “deep” when its depth is 6 meters or more. The aeration of wastewater in deep tanks requires the designer to account for some physicochemical effects that come into play only in deep tanks (5).

The alpha factor (α) is basically not affected, but the SOTE is affected by

- the higher average static pressure and related higher solubility of oxygen, as can be deduced from Henry’s law (it increases the SOTE).
- the lower average oxygen content (partial pressure) in the bubble because its detention time in the liquor

is longer and hence more oxygen can be transferred from the bubble into the liquor, leading to a higher degree of oxygen depletion in the bubble. This effect decreases the SOTE.

- A potentially lower average bubble size due to higher total mass transfer from the bubble into the liquor because the solubility of air in water increases with pressure and the quantity of oxygen transferred per m^3 of air injected is also increased. This effect can be positive as well as detrimental. If the diffuser would produce relatively large bubbles, it helps to increase the bubble detention time and hence the SOTE. However, if the diffuser already produces small bubbles, the bubble surface becomes "stiffer," and mass transfer may be slower due to a slower surface renewal rate.

Overall, the effect is typically a lower SOTE per meter of diffuser submergence (%/m or $g/(Nm^3 \cdot m)$) compared with shallower tanks at the same specific air throughput and floor coverage. This effect can be compensated for to a certain extent by increasing the number of diffusers to increase floor coverage and decrease specific air throughput; however, this leads to increased capital and maintenance costs.

Published SOTE data typically refer to tank depth of around 3.5 to 5 meters, which is higher than the average SOTE for a deep tank. Care has to be taken when extrapolating from such data; preferably it should be avoided, and the supplier be contacted.

Normal aeration tanks show a pH drop of around 0.3 units depending on initial alkalinity/buffer capacity and the degree of nitrification and denitrification, which will be aggravated in deep tanks due to the increased solubility of CO_2 and reduced aeration air volumes, which in turn reduces the CO_2 stripping capacity of the system. A highly efficient diffuser system is not recommended for a deep tank because the more efficient the system is, the less air is required, and the more CO_2 builds up in the aerated liquor. Deep tanks are, therefore, often aerated by medium or coarse bubble diffusers or mechanical aeration systems because of their lower SOTE and associated higher air throughputs.

Fouling, Scaling, and Clogging of Diffusers

Fouling, scaling, and clogging can affect the performance of diffusers quite significantly. Fouling is mainly a function of how well a biofilm can be established on the diffuser surface. Some systems claim potential advantages of their diffuser system (ability to clean or inhibition of biofilm growth). Fouling and scaling should always be taken into account in the performance of rubber membrane and rigid porous diffused air aeration systems.

Fouling of rigid porous diffusers can be removed in-line by acid cleaning; an acidic gas such as HCl is dosed into the aeration air. However, in particular, in low alkalinity wastewaters, care has to be taken to avoid negative effects on the process due to impacts on the pH. For rubber membrane diffusers, diffusers are normally bumped to remove biofilms that may have formed. High-pressure water cleaning is an effective means of off-line biofilm removal from all diffuser types; ceramic diffusers offer the additional option of refiring.

The two main reasons for diffuser scaling are water hardness and chemical precipitation. The risk and severity of scale formation is easier to assess than fouling. Scaling from water hardness can be removed via acid cleaning and bumping; high-pressure water jetting, however, may not be effective. Scaling from phosphorus precipitation or other precipitation reactions may not lend itself as easily to acid cleaning or refiring but should, in most cases, still be removable to a sufficient extent by diffuser bumping.

Clogging is caused mainly by particles in the compressed air. These particles typically do not dissolve in acids nor can they be quantitatively removed by refiring. Clogging is, therefore, an irreversible process for rigid porous diffusers. Although diffuser bumping would probably push some of these particles through a rubber membrane diffuser, a good practice is to minimize dust and oil in the compressed air by installing appropriate filters.

The need for a cleaning cycle can be determined by measuring the head loss over a diffuser element, which can be done in-line. Measurement of the delivery pressure in the supply air header can also give an indication if temperature effects are considered and the delivery pressures are compared at similar air throughputs.

Note that the "bumping capability" of rubber membrane diffusers decreases when the membrane loses elasticity. Therefore, the effectiveness of bumping to remove fouling, scaling, or clogging decreases over time. Also, the more bumping treatment occurs, the more likely the diffuser is to fail.

Life Cycle Costs

Aeration systems, in general, are a prime example for an asset whose ongoing operating and maintenance costs exceed investment costs. A thorough life cycle cost analysis is critical to decide on the type of aeration system and supplier.

The major component of the operating costs of all aeration systems is the cost of electrical power. For flexible membrane diffuser systems, membrane replacement is a key contribution to life cycle costs. The factors affecting cost are

- the SOTE at the given floor coverage and typical air throughput;
- total replacement costs for membranes, including equipment and labor for installation;
- bankable guarantees on membrane lifetime;
- for existing systems: Effect of the head loss at typical air throughput on blower power consumption and hence on AE.

Other Design Aspects

In applications that have low process oxygen demands (for example, the last aerated section in a MLE process), the air quantities required to supply oxygen may become so small that satisfactory mixing cannot be achieved by the aeration system alone. In these instances, checking the calculated air demands with the air throughputs required for mixing is recommended. Aeration rates of

0.6 to 0.9 m^3/h per m^3 tank volume are suggested (6) for a diffused air aeration system where the diffusers are evenly distributed across the tank floor. For line aeration systems that have a spiral roll liquid motion, the suggested aeration rates are higher at 1.2 to 1.8 m^3/h per m^3 tank volume.

Where diffusers have to be selected for an existing wastewater treatment plant, consideration should be given to conducting on-site trials to determine the alpha factor. If a rubber membrane system is being considered, tests should be conducted to determine the performance of various membrane materials over time.

CONCLUSIONS

Fine bubble diffused air aeration is successfully used on many wastewater treatment plants, regardless of their size. It can provide significant advantages over other aeration systems in energy efficiency. Two main types of diffused air aeration systems are known, rigid porous systems and membrane systems. Of these, the latter offer, by far, better turndown properties. However, rigid porous systems are used more often again due to the longer lifetime of the diffuser element and the lower life cycle cost often associated with that.

Notwithstanding the common use of fine bubble diffused air aeration systems, their successful use depends on choosing the right application and designing the aeration system properly. In some applications, for example, deep tanks or shallow tanks, alternative aeration systems are often to be preferred, as discussed earlier.

BIBLIOGRAPHY

1. Hartley, K.J. and Gobbie, M.R. (1991). Fouling and Cleaning of Fine Bubble Ceramic Dome Diffusers. AWWA Australian Water & Wastewater Association, *Proc. 14th Federal Convention*. Perth, Vol. 1, pp. 109–116.
2. St. Schmidt-Holthausen. (2002). Supratec GmbH, correspondence.
3. ASCE Standard No. ANSI/ASCE 2–91. (1993). *Measurement of Oxygen Transfer in Clean Water*, 2nd Edn. American Society of Civil Engineers, New York.
4. Libra, J.A. et al. (2002). Comparison of the efficiency of large-scale ceramic and membrane aeration systems with the dynamic off-gas method. *Water Sci. Technol.* **46**(4–5): 317–324.
5. ATV. (1996). *Hinweise zu tiefen Belebungsbecken—Arbeitsbericht des ATV-Fachausschusses 2.6*. Korrespondenz Abwasser 6/96, pp. 1083–1086
6. WPCF. (1988). *Aeration—Manual of practice FD 13*. Water Pollution Control Federation, Alexandria, VA.

AIR STRIPPING

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Air stripping is a physical process that enhances volatilization of compounds from water by passing clean air through it. It is commonly used in treating groundwater contaminated with volatile organic compounds (VOCs) and in removing ammonia in wastewater.

An air stripping system creates air and water interfaces to enhance mass transfer of target compound(s) between the air and liquid phases. Several system configurations, including tray columns, spray systems, diffused aeration, and packed towers, are commercially available. Packed towers (also known as air strippers) are the most popular alternative for groundwater treatment.

A typical air stripper includes a liquid distribution system (e.g., a spray nozzle) at the top of the tower. It sprays influent water over the packing in the column. As the water trickles down, air enters the lower portion of the tower and is forced up through the column by a blower. Packing materials within the tower increase the surface area of the contaminated water that is exposed to air, thus maximizing the migration of VOCs from the liquid stream to the air stream. A sump at the bottom of the tower collects the decontaminated water. The exhaust from the top of the tower, which is commonly referred to as "off-gas," is either discharged to the atmosphere or directed to an off-gas treatment system.

The design of an air stripping system includes determining the diameter and height of the column, type and size of packing materials, air-to-water ratio, blower rating, and treatment of off-gas from the tower. The information needed for the design includes flow rates and quality of the influent water (contaminant concentrations, mineral content, pH, and temperature), quality of the influent air (temperature and contaminant concentrations), height restrictions on the tower; and restrictions on contaminant concentrations in the effluent water and air discharge from the tower.

Although air stripping is widely used to treat VOC-contaminated water, there are several limitations and concerns:

- Air stripping transfers only contaminants from water to air, and the contaminants are not destroyed. Consequently, treatment of the off-gas, which is laden with contaminants, is often necessary.
- Biological and inorganic fouling of packing may require pretreatment or periodic column cleaning.
- Air stripping is effective only for water contaminated by compounds of high vapor pressure and low solubility. Modifications of a conventional air stripping operation may be needed. The temperature of the influent liquid may need to be raised to increase the volatility of the target compound(s). For ammonia stripping, the pH of the water should be sufficiently high, in the range of 10.5 to 11.5, so that most of the ammonia is converted to a gas.
- The visual impacts associated with air strippers and the noise level of the air blower should also be considered. They are often viewed as nuisances when located in residential areas.

Removal efficiencies greater than 95% are typical for towers that have 4.6 to 6 meters (15 to 20 feet) of conventional packing and are removing compounds amenable to stripping, such as B/T/E/X, chloroethane, TCE, DCE, and PCE. When the height of the stripper may be a problem, alternatives such as installation of multiple columns in series, aeration tanks, or low-profile air strippers should be considered. Aeration tanks strip volatile compounds by bubbling air into a tank (diffused aeration) through which contaminated water flows, and their profiles are much lower. The low-profile stripper has a number of trays that are set almost horizontally. Water is cascaded over the trays to maximize air–water contact while minimizing vertical space. Equipment that can be added to the basic air stripper includes an air heater to improve removal efficiencies and automated control systems with sump level switches and safety features, such as differential pressure monitors, high sump level switches, and explosion-proof components.

LAND APPLICATIONS OF WASTEWATER IN ARID LANDS: THEORY AND CASE STUDIES

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Land application of wastewater is recommended by the Environmental Protection Agency as a method of recycling nutrients and organic matter while protecting freshwater resources (1). Wastewater has been applied to agronomic crops, rangelands, forests, and recreation areas, including parks and golf courses, and to disturbed lands such as mine spoils sites (2–5). Benefits from recycling wastewater include creating a supplemental irrigation source, thereby conserving drinking water, and reducing fertilizer costs because wastewater contains nitrogen and phosphorus (6). As wastewater moves through the soil profile, the soil and plants act as filters that trap and treat, through various mechanisms, waste particles and contaminants allowing the remaining water to drain through the soil profile (7,8). Wastewater provides an effective source of nutrients that vegetation roots can absorb and allow the plant to assimilate. The benefit of this system is both the effective remediation of wastes and the recycling of water, nutrients, and carbon via biomass production (4).

Previous studies have demonstrated the effectiveness of saline wastewater application to horticultural systems (9) and to agronomic crops such as cotton (*Gossypium hirsutum* L.), alfalfa (*Medicago sativa* L.), and cantaloupe (*Cucumis melo* L.) (10). Both studies have shown that plants take up and store salt ions in vegetative organs.

Conventional land application systems are accepted technology for many communities, but many communities lack the resources and infrastructure to support them. Any technology considered for implementation should have low capital input and low operating cost. The wastewater treatment system should also stimulate the local economy and be easy to maintain (11). Unfortunately, there is limited information to guide land managers in highly fragile arid and semiarid environments where wastewater may be the only source of supplemental irrigation.

A land application system design, as depicted in (Fig. 1), requires balancing the input of water required by plants against the amount of nitrogen that can be applied without adverse environmental impact (12,13). The wastewater application rate is governed by the total amount of nitrogen allowed to enter the groundwater. Typically, this is expressed as the amount of NO_3-N in the wastewater leached to the groundwater that cannot exceed 10 mg NO_3-N/L. Yearly water (Eq. 1) and nitrogen mass balance (Eq. 2) equations were used to develop the design criteria.

$$L_{w(p)} = \mathrm{PET} - P + W_p \tag{1}$$

where $L_{w(p)}$ = wastewater hydraulic loading rate (cm/mo);
PET = potential evapotranspiration rate (cm/mo);
P = precipitation rate (cm/mo);
W_p = design percolation rate (cm/mo);

$$L_{w(n)} = \frac{[C_p{}^*(\mathrm{P} - \mathrm{ET}) + (U^*4.4)]}{[(1-\mathrm{f})^*C_n - C_p]} \tag{2}$$

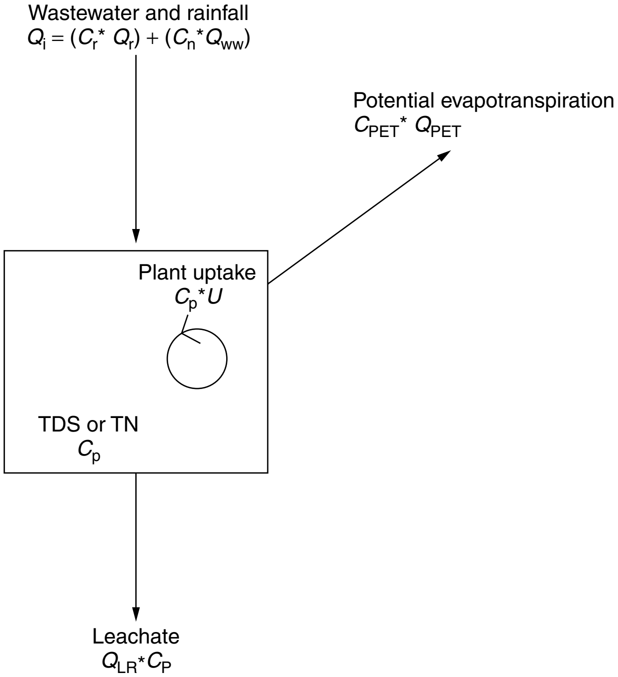

Figure 1. Mass flow diagram of the land application system with inputs, outputs, and process transformations where Q = flow; I = input; r = rainfall; ww = wastewater; LR = leachate; PET = potential evapotranspiration; C = Nitrogen concentration; r = rainfall; n = wastewater; p = percolating water; LR = leacheate; PET = potential evapotranspiration; U = Crop nitrogen uptake; TDS = Total dissolved solids; TN = Total nitrogen (12).

where $L_{w(n)}$ = allowable hydraulic loading rate (cm/yr);
ET = design PET rate (cm/yr);
P = design precipitation rate (cm/yr);
C_p = total nitrogen in percolating water (mg/L);
C_n = total nitrogen in applied wastewater (mg/L);
U = crop nitrogen uptake rate (kg/ha/yr); and
f = fraction of applied total nitrogen removed by denitrification and volatilization

Salt loading, soil salinity and its impact on plant survival and growth, must also be considered in plant selection. Salt loading is not incorporated into the design equations, but guidelines are provided in several sources (13,14). Most plants are intolerant to salt in the seedling stages than in more mature stages, so alternative sources of water may be required during the establishment period. When excess soluble salts accumulate in the rhizosphere, growth is reduced. Salt buildup can be controlled by applying additional irrigation water to leach salts below the root zone (15).

To use the limited amount and potentially saline wastewater, land managers must balance wastewater quality, crop water usage, nitrogen (fertilizer) requirements, and potential soil salinization. Crop coefficients can be calculated from local climate data to estimate evapotranspiration for particular crops from estimates of potential evapotranspiration (PET). Irrigation scheduling models have been developed for crop production in agronomic crops (16).

The following case studies explore the use of saline wastewater for pulpwood, nursery production, and wastewater treatment and disposal in arid regions (Table 1).

Ojinaga, Chihuahua, Mexico

Ojinaga, Chihuahua, Mexico is situated at the confluence of the Rio Grande and Rio Conchos on the U.S.–Mexican border (29.6°N 104.4°W). The climate of this part of the Chihuahuan Desert is arid; the annual rainfall is less than 250 mm, and approximately 75% of the rainfall occurs between June and October; annual potential evapotranspiration is 2450 mm. The maximum temperature is 50 °C, and the minimum temperature is −10 °C.

Municipal sewage is piped directly into an anaerobic lagoon, which acts as a settling pond for separating the solids from the waste stream and providing some reduction in waste strength. A 2-hectare (60,000 m^3) single-cell-anaerobic lagoon constructed in 1995 receives both industrial and municipal wastewater. Currently, one-half of the Ojinaga population is connected to the municipal wastewater system. According to Junta Municipal de Agua y Saneamiento (JMAS), the wastewater from Ojinaga is almost exclusively domestic. Industries in the area include a slaughterhouse and several cottage industries that contribute little in the way of metals or toxic organics. The contribution of the slaughterhouse wastewater is intermittent but high in organic waste. The influent is treated by a manual bar screen to remove large solids. Grit and materials that pass the bar screen are collected in the anaerobic cell by simple sedimentation with no active system for removing these materials. The single-stage anaerobic lagoon is designed to reduce biological oxygen demand (BOD), total suspended solids (TSS), and fecal coliform (FC) to some degree. Wastewater from this system flows to the land application unit for final treatment and disposal.

A pilot land application site (~1.1 ha total area) was established in April 1997 with black locust [*Robinia pseudoacacia* (L.)], clones of eucalyptus [*Eucalyptus camaldulensis* (Dehnh.)] and hybrid poplar [*Populus* (L.)]. Tree species selection was based on the criteria of drought tolerance, salt tolerance, and a short rotation cycle for wood fiber. Monitoring included wastewater effluent and groundwater quality characteristics, soils, and plant growth.

After 6 years, there was minimal overall impact on groundwater, no fecal coliform contamination or increase in NO_3-N, and about a 10% increase in salinity caused by high transpiration of the crop trees. The best tree species was *Eucalyptus* clone 4019. (Fig. 2). The growth rate exceeded the expected results and may allow harvesting on a 6-year rotation, which is 1 to 3 years faster than other studies with similar species. The advantages of commercial forestry include (1) providing a source of income and employment opportunities to the local economy, (2) improving abandoned saline agricultural lands, (3) maintaining irrigation district infrastructure, (4) diversifying the local economy, and (5) establishing an organization to produce wood fiber commercially. This endeavor could produce community-based jobs and have a positive cash flow for operation and maintenance. Ojinaga has been involved in master plan development for the past 3 years to develop a new treatment plant.

Table 1. Site Characteristics of Three Wastewater Use Studies

Parameter/Site	Ismailia, Egypt	Ojinaga, Mexico	Las Cruces, US
Soil type	Sand	Clay loam	Sand
Soil depth	10 m (to groundwater)	3 m (to groundwater)	3 m (to impervious layer)
Species	*Cupressus, Pinus*	*Populus, Eucalyptus*	*Larrea tridentata, Prosopis glandulosa*
Rotation	15–20 yr	6–7 yrs	n/a
Irrigation	Drip	Flood	Sprinkler
TDS	550	1950–2220	2500–3500
BOD	46	29–43	28
TKN	45	14–37	8–21

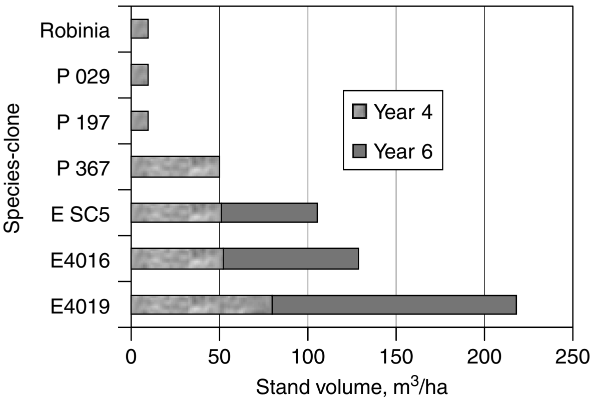

Figure 2. Ojinaga, Mexico, pulpwood stand volume 4 and 6 years after establishment.

Ismailia, Egypt

Ismailia, Egypt (30.60°N 32.29°E) built the Serrabium Wastewater Treatment Plant with Egypt and US AID support in 1995; it is operated by the Suez Canal Authority. The average mean temperature is 21.4 °C; monthly temperatures vary from 13.2 °C in January to 28.5 °C in July and August. Annual potential evapotranspiration rates are 2340 mm and annual precipitation is 25 mm. The treatment plant's designed capacity is 90,000 m^3/day, and the current flow is 80–85 thousand m^3/day. The amount of nitrogen in the wastewater is 45 mg/L, and groundwater depth is 10 m.

Pretreatment for the facility consists of three self-cleaning bar screens and two grit chambers. Flow is divided into two parallel treatment branches with three lagoons (aerated, facultative, and polishing lagoons) for each branch. The aerated lagoon has 20 aerators; 10 operate at any one time; the facultative lagoon has 10 aerators that are used only as needed to increase dissolved oxygen. The polishing lagoon is 3.5 m deep to facilitate the removal of fecal coliform bacteria and *Ascaris* eggs. The total detention time of the system is 11 days, designed to reduce BOD, TSS, *Ascaris* eggs, and fecal coliform bacteria.

The land application facility uses an area of 200 ha. The plants are drip irrigated with tertiary or secondary treated wastewater (90,000 m^3/day). The nursery at Serrabium Forest has a capacity to produce 100,000 seedlings/yr in polybags (12 × 15 cm) with a sand/clay/peat moss medium. Tree species produced are *Pinus pinea* (L.), *P. halepensis* (Mill.), *P. brutia* var. *eldarica* (Medv.), *Khaya senegalensis* (Desr.), *Cupressus arizonica* (Green), *C. sempervirens* (L.), *C. macrocarpa* (Hart.), *Morus alba* (L.), *Morus japonica* (Bail.), and *Cassia* sp. (L.). The wastewater is supplied to the site via an underground pipeline and is filtered through an in-line screen and then through several sand filters before it is delivered to the irrigation system.

There was no apparent soil layering or caliche development; however, root development appeared stunted in the upper 40 cm of the soil surface. Soils were saturated below the surface at the midpoint between trees indicating overapplication of wastewater and a potential risk of groundwater contamination. The stunted roots may have also resulted from the overirrigation of wastewater which may have contained some untreated dissolved organics which resulted in oxygen deficiency in the soil column.

Las Cruces, New Mexico, US

The study site located in Las Cruces, New Mexico, USA (32°18′ N, 106°55′ W) is semiarid the average rainfall is 220 mm, and approximately 50% of the annual rainfall occurs between July and September. The annual mean temperature is 15.8 °C, monthly temperatures vary from 5.5 °C in January to 26.6 °C in July. The potential evapotranspiration of the site is 1800 mm. The City of Las Cruces disposes of treated wastewater onto 36 ha of native Chihuahuan Desert vegetation including creosote bush *Larrea tridentata* (DC.) Cov. mesquite *Prosopis glandulosa* (Torr.) and annual and perennial forbs and grasses. The treatment plant designed capacity is 1500 m^3/day; current flows are 200 m^3/day applied to the 36-ha site.

The wastewater originates from tenants in an industrial park involved in dairy processing and metal wire fabrication. The total salinity (TDS) has reached as much as 4000 mg/L and is comprised mostly of sodium and chloride. (Fig. 3). The total nitrogen applied to the research application site in 2002 was 43.9 kg/ha. The wastewater

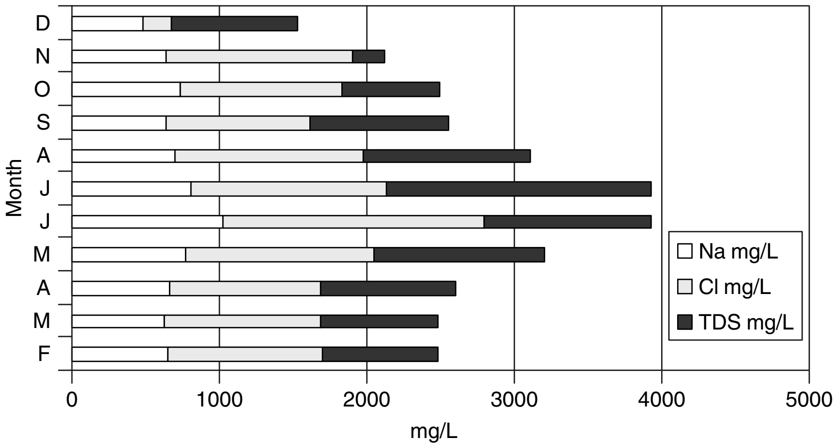

Figure 3. Las Cruces, NM, Effluent characteristics during first year of wastewater application.

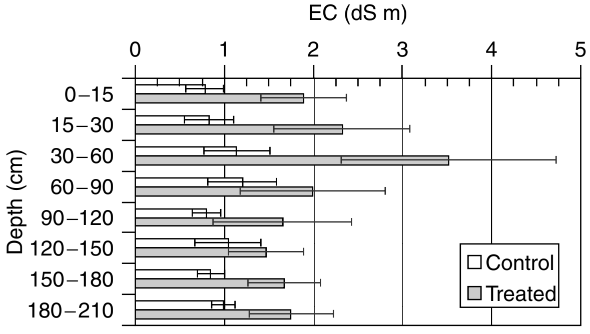

Figure 4. Electrical conductivity of soil vs. depth after 64 cm of wastewater application.

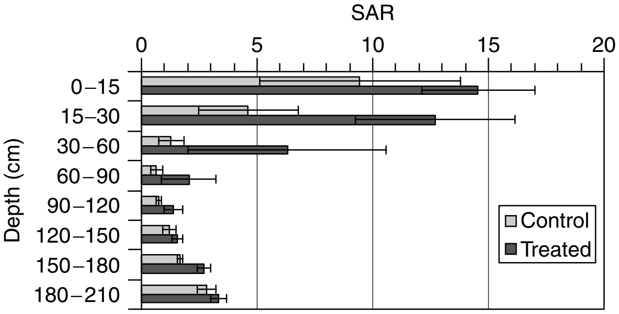

Figure 5. Sodicity measurements on soil after 64 cm of wastewater application.

is sent to a treatment train and then into aerated lagoons with a complete mix basin that has a fixed floor fine bubble diffuser system and a settling basin. The wastewater is then sent to a final holding pond before being land applied through a fixed head sprinkler system. After 64 cm of wastewater application during a growing season, there was an increase in soil salinity. Electrical conductivity (EC) peaked at 3.25 dS/m in the 30–60 cm sampling depth (Fig. 4). The sodium adsorption ratio (SAR) increased to a potential sodium hazard in the top 15 cm (Fig. 5). After 1 year, wastewater effectively deposited the salt ions in the top 60 cm; little or no salt accumulated in the lower depths. Further application will further deposit the salts beyond the root zone and limit growth reduction of the vegetation.

CONCLUSION

These wastewater land application case studies are located in arid regions that have minimal precipitation and high evapotranspiration. The applied water must be balanced against the needs of the plant and salt and nitrogen loading to ensure the development of a sustainable system. Therefore, the applied wastewater must meet the plant's water use needs. When seasonal plant demands are lower in the winter months, the wastewater must be applied at depths to prevent soil salinity increases in the rhizosphere. These interactions must be resolved through proper plant selection, site characteristic considerations, and water quality. The goals of the system in terms of the final product need to be incorporated into the process. These systems can be privately or publicly owned, but infrastructure and community support must be developed in advance and are essential to a project's success.

BIBLIOGRAPHY

1. U.S. Environmental Protection Agency. (1992). *Wastewater Treatment/Disposal for Small Communities Manual*. EPA.625-R-92-005. EPA, Washington, DC.
2. Sopper, W.E. and Kardos, L.T. (1973). Vegetation responses to irrigation with treated municipal wastewater. In: *Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland*. W.E. Sopper and L.T. Kardos (Eds.). The Pennsylvania State University Press, University Park, PA.
3. Sopper, W.E., Seaker, E.M., and Bastian, R.K. (Eds.). (1982). *Land Reclamation and Biomass Production with Municipal Wastewater and Sludge*. The Pennsylvania State University Press, University Park, PA.
4. Bastian, R.K. and Ryan, J.A. (1986). *Design and Management of Successful Land Application Systems*. *Proc. Utilization, Treatment, Disposal Waste Land*. Soil Science Society of America, Madison, WI, pp. 217–234.
5. Luecke, D.F. and De la Parra, C. (1994). From pollution to park. Experiment in Tijuana: A low-tech approach to wastewater management. *Calif. Coast Ocean* **10**(1): 7–19.
6. Al-Jamal, M.S., Sammis, T.W., Mexal, J.G., Picchioni, G.A., and Zachritz, W.H. (2002). A growth-irrigation scheduling model for wastewater use in forest production. *Agric. Water Manage.* **56**: 57–79.
7. Thomas, R.E. (1973). The soil as a physical filter. In: *Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland*. W.E. Sopper and L.T. Kardos (Eds.). The Pennsylvania State University Press, University Park, PA.
8. Watanabe, M.E. (1997). Phytoremediation on the brink of commercialization. *Environ. Sci. Technol.* **31**(4): 182–186.
9. Gori, R., Ferrini, F., Niece, F.P., and Lubello, C. (2000). Effect of reclaimed wastewater on the growth and nutrient content of three landscape shrubs. *J. Environ. Hortic.* **18**(2): 108–114.
10. Hoffman, W.C., Karpiscak, M.M., and Bartels, P.G. (1987). Response of cotton, alfalfa, and cantaloupe to foliar-deposited salt in an arid environment. *J. Environ. Qual.* **16**: 267–272.
11. Coate, C. (Ed.). (1998). *FORUM of the Association for Arid Lands Studies. Volume XV Number 1*. International Center for Arid and Semiarid Land Studies, Lubbock, TX.
12. Metcalf & Eddy, Inc. (1991). *Wastewater Engineering: Treatment, Disposal, and Reuse*. McGraw-Hill, New York.
13. Water Pollution Control Federation (WPCF). (1990). *Natural Systems for Wastewater Treatment*. Water Pollution Control Federation, Alexandria, VA.
14. Food and Agriculture Organization of the United Nations (FAO). (1992). CROPWAT—A computer program for irrigation planning and management. Irrigation and Drainage Paper No. 46. Rome, Italy, p. 126.
15. Sammis, T.W. and Herrera, E. (2000). *Leaching Requirements of Pecan and Fruit Trees, Guide H-644*. New Mexico State Agricultural Experiment Station, Las Cruces, NM.
16. Sammis, T.W., Mapel, C.L., Lugg, D.G., Lansford, R.R., and McGuckin, J.T. (1985). Evapotranspiration crop coefficients predicated using growing-degree-days. *Trans. ASAE* **28**(3): 773–780.

TECHNOLOGIES FOR ARSENIC REMOVAL FROM CONTAMINATED WATER SOURCES

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The majority of established arsenic removal technologies can be divided into three main categories, depending on the specific mechanism that is responsible for removing arsenic. These categories are usually referred as coagulation–precipitation, membrane, and sorption processes.

COAGULATION–PRECIPITATION PROCESSES

Three processes in this group have been developed for arsenic removal; aluminum or iron coagulation, lime softening, as well as a combination of iron and manganese removal with arsenic.

Coagulation Using Aluminum or Iron Salts

The coagulation/filtration process is considered a common water treatment technology, used to remove suspended, colloidal, and dissolved constituents from water sources or from wastewater. The coagulation process promotes the aggregation of suspended solids to form larger flocs, which can be subsequently separated/removed by sedimentation (settling) and/or filtration. Coagulation consists of three steps; coagulant addition and hydrolysis, particle destabilization, and interparticle collisions (floc growth). The first two steps, coagulant formation and particle destabilization, occur during initial rapid mixing, whereas the third step takes place during the following slow mixing, which enhances the flocculation of solids.

Aluminum (III) and iron (III) salts, such as aluminum sulfate (usually referred to as alum) or ferric chloride, are the most common coagulant reagents, used in water treatment (drinking or wastewater). Coagulation by aluminum or iron (III) salts, or a combination of them, such as the mixed sulfate salt, can also be used to remove dissolved inorganic contaminants such as arsenic from drinking water. The two primary mechanisms for removing dissolved inorganic contaminants are adsorption and occlusion. During adsorption, the dissolved contaminant attaches to the surface of a particle or precipitate. Occlusion occurs when the dissolved contaminant is adsorbed to a particle and then entrapped, as the particles continue to agglomerate. Several factors affect the efficiency of the coagulation process: coagulant dosage, pH, turbidity, natural organic matter, the presence of other anions or cations in the solution to be treated, the zeta potential of the system, and the temperature.

Most of the studies of arsenic removal have focused on As(V) treatment because As(V) can be removed more effectively than As(III) due to its speciation in aqueous solutions (i.e., the formation of dissociated/charged species). Furthermore, As(III) can be rather easily oxidized to As(V) by using a strong oxidant, such as chlorine. Ferric and alum salts are almost equally effective in removing arsenic on a molar basis, but when compared on a weight basis, ferric salts proved more effective than aluminum salts. These results occur because the iron hydroxides produced by the hydrolysis of ferric salts are less soluble than the respective aluminum hydroxides over a wide pH range. As(V) removal proved pH-independent in the pH range from 5.5–8.5, when coagulation took place from the addition of iron salts. When aluminum salts were used, arsenic removal decreased above pH 7. As(V) removal was independent of the initial arsenic concentration in the range of interest for drinking water treatment, and it correlated directly with coagulant dosage (1–3).

Lime Softening

Lime softening is commonly used for removing hardness from water. Hardness is due primarily to dissolved calcium and magnesium species. The addition of lime provides the necessary hydroxide ions, which increase the pH of water, resulting in calcium and magnesium removal by the formation of insoluble $CaCO_3$ and $Mg(OH)_2$ precipitates. Lime softening has also been applied successfully to remove heavy metals, radionuclides, dissolved organics, and viruses by adsorption and occlusion within the calcium carbonate and magnesium hydroxide produced. The typical lime softening treatment process train includes initial rapid mixing of lime, followed by flocculation of solids and separation by sedimentation (settling). These three steps are usually combined in one single unit, called a solids-contact softener. Filtration is usually used for subsequent treatment of the supernatant. Lime or a lime–soda mixture is used for softening, whereas the selection between them depends primarily on the specific type of hardness.

Relatively few studies have been conducted to evaluate the removal of arsenic during lime softening, indicating that arsenic removal is strongly pH-dependent. Removal of both As(III) and As(V) species is relatively small at pH values lower than 10. However, at a pH over 10.5, As(V) removal can reach almost 100%, whereas the removal of As(III) is about 75%. The presence of orthophosphates, as well as of carbonates, could limit the removal of arsenates by $Mg(OH)_2$ precipitates. If manganese is also present in the source water, some additional arsenic removal could be achieved through sorption onto the $Mn(OH)_2$ precipitate, although the formation of $Mn_3(AsO_4)_2$ solid was not considered a major mechanism. The initial arsenate concentration does not seem to affect the efficiency of the method in the range from 5–75 μg/L (2,3).

Combined Removal of Arsenic by Iron and Manganese

A number of processes, which are used to remove soluble iron and manganese cations from contaminated groundwater, involve oxidizing these ions, transforming them to the respective insoluble hydroxides, which can be further separated by sedimentation or filtration. Either iron or manganese ions can be oxidized by using a strong chemical reagent (oxidant), such as chlorine (4). Another way to oxidize iron and manganese cations is by biological

Figure 1. Common iron oxidizing bacteria of the *Gallionella* and *Leptothrix* genera.

oxidation, using so-called "iron oxidizing bacteria"; these facultative bacteria are indigenous to most groundwater (Fig. 1). Biological oxidation involves only preliminary aeration of groundwater to allow bacterial growth and then, the bacteria effectively oxidize iron and manganese to their insoluble hydroxides (5).

In both oxidation cases (chemical and biological), arsenic in the water can be subsequently sorbed onto the iron and manganese hydroxides formed (6). The following major steps have been suggested during iron and manganese oxidation, when used for simultaneous removal of arsenic:

(1) Indigenous "iron oxidizing bacteria" are colonized and immobilized on appropriate inert surfaces (filter media), such as granular sand or polymer beads, forming biofilm deposits and provoking the oxidation of soluble iron and manganese cations that form the respective insoluble precipitates.
(2) The precipitates are subsequently separated from the water by filtration.
(3) Arsenic attaches mainly to the iron hydroxides removed and to manganese oxides by adsorption and/or coprecipitation.

In this method, the initial concentration of iron seems to be critical because the efficiency of arsenic removal is increased by increasing the iron concentration (7). The initial concentration of arsenic does not affect the effectiveness of the method. During the application of biological oxidation for removing iron and manganese, the linear velocity does not affect arsenic removal up to 20–22 m/h (8). A typical biological iron removal (pilot-scale) plant is presented in Fig. 2.

Figure 2. Pilot plant unit, which was used for the biological oxidation and removal of iron and manganese (Umweltbundesamt, Institute for Hygiene of Water, Soil and Air, Berlin, Germany).

MEMBRANE PROCESSES

Two types of membrane processes remove arsenic efficiently from water sources: reverse osmosis and electrodialysis.

Reverse Osmosis

Two types of reverse osmosis units are used for arsenic removal: nanofiltration and hyperfiltration (Fig. 3).

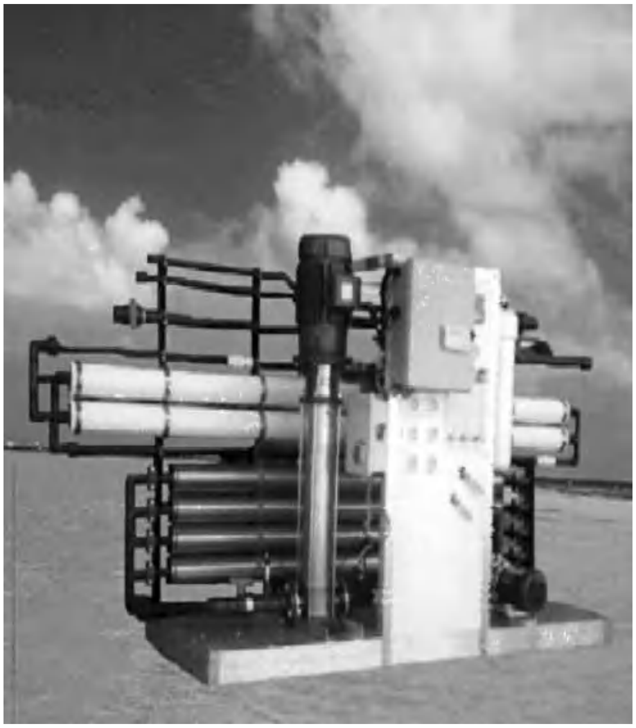

Figure 3. Typical commercial reverse osmosis unit used for drinking water treatment.

Nanofiltration is a relatively lower pressure reverse osmosis process that removes primarily the larger dissolved solids, compared to hyperfiltration. Nanofiltration is also known as a membranous softener because it removes divalent calcium and magnesium cations from water, which cause water hardness. Nanofiltration can also remove sulfates, as well as monovalent dissolved solids, such as chlorides and sodium.

Conversely, hyperfiltration operates at higher pressures, resulting in greater removal of all dissolved solids. A typical example of hyperfiltration is seawater desalination.

Nanofiltration and hyperfiltration are both effective for removing As(V), and the respective efficiencies are up to 95%, but when As(III) is present, a preoxidation step is usually required because As(III) removal efficiencies reportedly reach only 80%. The chemical reagents used to oxidize As(III), such as chlorine, are rather harmful to membranes, which is a major disadvantage of this oxidation method. Furthermore, reverse osmosis rejects/removes simultaneously large amounts of water, the desired product, which is another consideration for drinking water treatment applications (3).

Electrodialysis

Electrodialysis is another type of membrane process, using the passage of direct electric current through the aqueous solution to be treated and appropriate electrodes. Although the main applications of this method are to treat brackish waters, it can be also used for drinking water treatment. Dissolved solids exist as cations (positively charged, such as calcium and magnesium) and anions (negatively charged, such as sulfates and arsenic), so the cations can be moved toward the negatively charged electrode, and the anions to the positively charged electrode. The respective cell is divided into chambers, using specific ion exchange membranes that allow the selective passage of only cations or anions.

The problems in reverse osmosis also exist for electrodialysis. Strong oxidizing agents are usually harmful to the membranes. Large amounts of water are also rejected, eliminating the efficiency of the method. However, there has been little research on arsenic removal by electrodialysis (3).

ADSORPTION PROCESSES

Adsorption processes are another category of arsenic removal technologies; they are based on the adsorption of arsenic onto suitable adsorbing media. Two different technologies have been applied to remove arsenic, activated alumina and ion exchange.

Activated Alumina

Sorption onto activated alumina is considered mainly a physical (and to a lesser extent chemical) process, by which ions are removed from aqueous solutions by available adsorption sites on the surface of aluminum oxide. Activated alumina, usually prepared by dehydrating $Al(OH)_3$ at high temperatures, consists of amorphous and γ-aluminum oxide (Al_2O_3), usually placed in columns. Activated alumina removes arsenic in a number of cases. Although the process has not been yet fully characterized, it is believed that arsenic is adsorbed onto the surface of activated alumina mainly by electrostatic forces. A number of parameters affect the removal efficiency of this treatment method, such as arsenic oxidation state (i.e., tri- or pentavalent), the pH, the presence of other competitive anions, as well as the empty bed contact time (EBCT), which is the main operational/modeling parameter for column operation.

Similarly to the other previously presented treatment methods, As(V) can be removed more effectively than As(III), and the breakthrough point of 0.05 mg/L (the previous concentration limit for arsenic in drinking water) is reached after the treating 300 bed volumes (BV) for As(III), whereas for As(V) after 23,400 BV. The pH also affects the removal of arsenic significantly. Anions are better adsorbed below a pH of 8.2, which is the typical point-of zero charge for activated alumina. Below this value, the surface of activated alumina holds a positive charge, which can be balanced by adsorbing anions, such as arsenates. Several studies showed that As(V) removal is independent of pH in the range between 5.5 and 6. As(III) removal in that pH range is not equally efficient because As(III) is present as nonionic (molecular) arsenious acid (H_3AsO_3).

The presence of other competitive anions, such as phosphates and carbonates, can also affect the method's efficiency for arsenic removal because activated alumina has specific preferences for certain ions. Finally, the correlation between EBCT and arsenic removal is linear, and therefore, as EBCT is increased, the efficiency of arsenic removal is also increased (9,10).

Ion Exchange

Ion exchange is a physical/chemical process, by which ions held electrostatically on the surface of an appropriate solid phase can be exchanged with ions of similar charge from an aqueous solution. The solid phase is typically a synthetic ion exchange resin placed in columns and used preferably to remove particular contaminants of concern; certain natural products, such as zeolite, have been also used occasionally. Ion exchange is commonly used in drinking water treatment to remove hardness from water sources and also to remove nitrate, arsenate, chromate, and selenate anions from municipal water. Anion exchange resins are available in two main types, strong-base resin (SBA) and weak-base resin (WBA). Typically, SBA resins are used for arsenic removal because they tend to be more effective over a wider pH range than WBA resins.

Ion exchange does not remove As(III) because it occurs predominantly as uncharged species (H_3AsO_3) at the usual pH of most water sources. On the other hand, As(V) is negatively charged, and thus, it can be removed by appropriate ion exchange resins. When all the available sites on the resin have been exhausted, the bed can be regenerated by the passage of brine solution (chloride exchange).

The efficiency of the ion exchange process for arsenic removal is strongly affected by the presence of other competitive ions, such as total dissolved solids and sulfates. Other factors affecting the operating efficiency of the ion exchange process are the empty bed contact time, and the disposal of spent regenerant solutions (10).

Adsorptive Filtration Using Iron Oxide Coated Sand

This technology, relatively new in water treatment, is based on the adsorption of cationic metals and/or oxyanions onto the surface of iron oxide, and the particulate matter is simultaneously filtered from the water. Iron oxides form coatings on the surfaces of appropriate granular filter media placed in tanks or in columns, such as sand; subsequently, the modified material can act together as a filter and as an adsorber.

To remove oxyanions from contaminated water, the pH has to be adjusted below 7.2, which is the typical point-of-zero charge of iron oxides. Below this value, iron oxides are positively charged and can remove arsenic effectively. In this technology, As(V) is also treated more efficiently than As(III), because as discussed previously, As(III) is present as an uncharged species, up to pH 8. Above pH 8, As(III) starts to form anionic species, but iron oxides are also negatively charged at these high pH values; thus they cannot interact. Another crucial parameter for column operation is empty bed contact time. By increasing the respective contact time, arsenic removal is also increased. The initial arsenic concentration does not affect the efficiency of the method (11).

OXIDATION OF AS(III)

Arsenic can be removed from water by several technologies, but most of these techniques cannot remove As(III) effectively due to its speciation in water. Therefore, an oxidation step is usually required to transform As(III) into As(V). Oxygen is the preferred oxidant because using it avoids problems that other chemicals present, but the oxidation of arsenic by dissolved oxygen is very slow and therefore, cannot be effectively used. The most feasible oxidants today for arsenic removal are potassium permanganate and Fenton's reagent (a mixture of H_2O_2/Fe^{2+}). Chlorine or hypochlorites have also been used as oxidants of trivalent arsenic. Other techniques are UV irradiation and the use of ozone (9).

BIBLIOGRAPHY

1. Edwards, M. (1994). Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *J. Am. Water Works Assoc.* **86**(9): 64–78.
2. Fields, K., Chen, A., and Wang, L. (2000). *Report Arsenic Removal from Drinking Water by Coagulation / Filtration and Lime Softening Plants*. EPA/600/R-00/063. Cincinnati, OH.
3. Kartinen, E.O. and Martin, C.J. (1995). An overview of arsenic removal processes. *Desalination* **103**: 79–88.
4. Fields, K., Chen, A., and Wang, I. (2000). *Report Arsenic Removal from Drinking Water by Iron Removal Plants*. EPA/600/R-00/086. Cincinnati, OH.
5. Mouchet, P. (1992). From conventional to biological removal of iron and manganese in France. *J. Am. Water Works Assoc.* **84**(4): 158–166.
6. Lehimas, G.F., Chapman, J.I., and Bourgine, F.P. (1999). Use of biological processes for arsenic removal: A cost effective alternative to chemical treatment for As(III) in groundwater. Available at: www.saur.co.uk/poster/html.
7. U.S. E.P.A. (2000). Office of Groundwater and Drinking Water, Report Arsenic in drinking water-treatment technologies: Removal. Available at: www.epa.gov/OGWD/ars/ars4.html, Cincinnati, OH.
8. Seith, R. and Jekel, M. (1997). Bioxidation of AS(III) in fixed bed reactors. *Vom Wasser* **89**: 283–296.
9. Jekel, M.R. (1994). Removal of arsenic in drinking water treatment. In: *Arsenic in the Environment: Part I: Cycling and Characterization*. J.O. Nriangu (Ed.). John Wiley & Sons, New York, pp. 119–130.
10. Wang, L., Chen, A., and Fiels, K. (2000). *Report Arsenic Removal from Drinking Water by Ion-Exchange and Activated Alumina Plants*. EPA/600/R-00/088. Cincinnati, OH.
11. Benjamin, M.M., Sletten, R.S., Bailey, R.P., and Bennet, T. (1996). Sorption and filtration of metals using iron-oxide coated sand. *Water Res.* **30**: 2609–2620.

BIOCHEMICAL OXYGEN DEMAND

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BIOCHEMICAL OXYGEN DEMAND IN NATURAL AND ENGINEERED SYSTEMS

A vast number of organisms, primarily bacteria, survives and even thrives in an environment containing no oxygen. However, most living creatures with which we commonly interact are aerobic; they need oxygen to survive. Aerobic creatures include all of the higher life forms, such as fish, birds, mammals, and reptiles, as well as simpler species such as some bacteria and protozoa. The 4.7 billion year development of the earth and the evolution of species in response to this development have created many types of ecosystems; most support a balance between the demands of aerobic organisms for oxygen and the availability of oxygen. These "balanced ecosystems" are found in aquatic, terrestrial, and atmospheric biomes.

In a natural aquatic system, a large number of aerobic organisms exists. Interestingly, the higher life forms, fish, mammals, and shellfish, do not normally place a large oxygen demand on an aquatic system. Bacteria, and in particular those bacteria that decompose organic material, such as dead aquatic vegetation, for example, algae, can create a high oxygen demand due to the sheer number of organisms that reproduce in a short period of time. Aquatic bacteria that decompose organic material are endemic in the environment. Their populations are typically balanced by the natural system, and the available oxygen is generally sufficient; but human influences can upset this balance. The primary anthropogenic (human) sources of organic material in aquatic systems are sewage and other waste stream discharges. This increase in "food" can stimulate the growth of bacteria and can cause oxygen consumption at a rate greater than can be resupplied naturally. In addition to organic material, waste stream discharges along with overland runoff from agricultural fertilizers can increase the concentration of nutrients such as nitrogen and phosphorus in an aquatic system. This increased nutrient availability can stimulate the growth of aquatic vegetation, especially algae. When this vegetation dies, it serves as a source of organic material and stimulates aerobic bacterial growth and a corresponding oxygen demand. This process is called cultural eutrophication.

Certain chemical compounds (organic and inorganic) can also exert a demand for oxygen if the resulting combination of the chemical compound and oxygen forms a thermodynamically favorable spontaneous reaction. The *combined* biological and chemical requirement for oxygen in a waterbody is termed the biochemical oxygen demand (BOD). Material that makes up BOD can be either in dissolved or particulate (solid) form.

Whether BOD is considered a problem depends on two factors: the magnitude of the oxygen demand and the rate at which oxygen is resupplied to the water. The primary oxygen source in all natural waterbodies is the diffusion of molecular oxygen, O_2, from the atmosphere into water. This transfer of oxygen is limited by the solubility of oxygen in water (see Henry's law) and physical movement of oxygen molecules across the air–water boundary at the water surface.

MICROBIAL GROWTH

The life cycle for bacteria may only last a few days to weeks, but the growth rate can be rapid in response to the availability of some limiting factor. This rate of growth can be described, based on the growth factor that is in shortest supply, by using the empirical Monod model as follows:

$$\frac{dX}{dt} = \frac{\mu_m SX}{K_s + S} - k_d X \tag{1}$$

where X = concentration of biomass (mass/volume)
t = time
K_s = half saturation (limiting factor) constant (mass/volume)
k_d = endogenous decay (death) rate constant (time^{-1})
S = concentration of limiting factor (mass/volume)
μ_m = maximum growth rate of the organisms (time^{-1})

Limiting factors include an energy source (organic or inorganic), a carbon source to build new cell material, and nutrients.

MICROBIAL ENERGETICS

Microorganisms require a source of energy, a source of carbon, and nutrients to grow and reproduce. Microorganisms commonly obtain energy for metabolism via reduction—oxidation (redox) reactions. Redox reactions involve the transfer of an electron from a reduced compound to an oxidized compound. All complete redox reactions must contain a compound that becomes oxidized (loses an electron) and a compound that becomes reduced (gains an electron.) To gain energy, microorganisms oxidize a compound, which is called the "electron donor" because it loses an electron. The electron donor is also referred to as "food." Because electron transfer requires a complete electrical circuit, an electron acceptor is required to complete the transfer. The molecule that receives an electron is called the terminal electron acceptor (TEA).

Electron donors often consist of organic material found in sewage or natural systems, for example, dead aquatic vegetation. These highly reduced compounds contain more electrons and have a higher standard free energy than oxidized compounds that serve as TEAs (1). Inorganic compounds, such as ammonia and ferrous iron, can also serve as electron donors. The concentration of electron donor material in waste is sometimes referred to as the "strength" of the waste.

When oxygen is present in a particular system, it is commonly the preferred TEA over other oxidized compounds, such as nitrate and sulfate, because it is a stronger oxidizer. The chemical reduction half-reaction for molecular oxygen in aquatic systems can be summarized as follows:

$$2e^- + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow H_2O \tag{2}$$

This "consumption" of 1/2 mole of O_2 for every two electrons transferred from an electron donor is the source of the oxygen demand exerted on a system and often the cause of oxygen depletion in waterbodies that contain sewage or other waste discharges. Organisms that use oxygen as a TEA are called aerobic.

MICROBIAL COMPOSITION

In addition to using oxygen as a TEA, microbes also use oxygen as a nutrient. In this case, oxygen is incorporated directly into the cell structure. The microbial cell structure is commonly modeled as follows: $C_5H_7O_2N$ (1). Thus, two moles of oxygen are consumed for every mole of cells produced.

Reaction Kinetics

In a natural or engineered system, there are typically numerous chemical and biological reactions that consume oxygen. Consequently, it is difficult to estimate oxygen demand based on stoichiometry or a biological assay. One method for estimating the quantity of oxygen-demanding material in a waste is to make a gross measurement of the quantity of oxygen consumed by the waste via chemical and biological reactions. For domestic sewage and many natural systems, the gross rate of oxygen consumption over time (sum of chemical and biological reactions) is commonly modeled as the following first-order reaction:

$$\frac{d(\text{DO})}{dt} = -k\text{DO} \tag{3}$$

where DO = dissolved oxygen concentration (mass/volume, e.g., mg/L)
t = time
k = reaction rate (oxygen consumption rate) constant (time^{-1})

For a closed system, Eq. 3 can be integrated from time 0 to t, which yields the following:

$$\text{DO}(t) = \text{DO}_0 e^{-kt} \tag{4}$$

where $\text{DO}(t)$ = the dissolved oxygen concentration at a particular time (mass/volume)
DO_0 = the initial dissolved oxygen concentration (mass/volume)

This relationship is illustrated in Fig. 1, which indicates that there is an exponential decline in oxygen over time.

Similarly, the biochemical oxygen demand, BOD(t), at any time t can be defined as the quantity of oxygen *consumed* up to a given time (t) via chemical and biological reactions:

$$\text{BOD}(t) = \text{BOD}_{\text{ult}}(1 - e^{-kt}) \tag{5}$$

where BOD_{ult} = maximum or ultimate demand for oxygen that can be exerted under given conditions (mass/volume)

As illustrated in Fig. 2, BOD(t) increases exponentially over time until BOD_{ult} is reached.

Many compounding factors influence BOD, but a significant environmental condition is the temperature of the system. Standard methods have been established for sampling and measuring BOD for comparison and analysis, but a temperature correction is typically required to correlate these laboratory results with field conditions. The correction is determined by using the relationship presented as Eq. 6 (see Ref. 2) and is applied to k (reaction rate constant). This correction is empirical and accounts for changes in both chemical and biological components of the reaction rate constant:

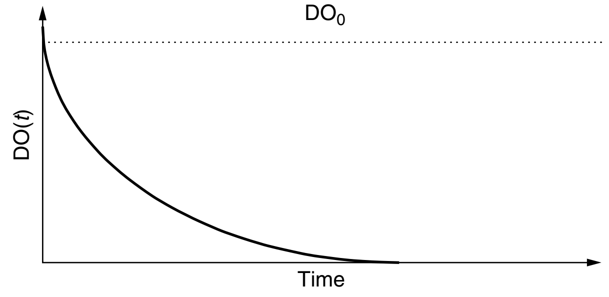

Figure 1. Change in dissolved oxygen with time.

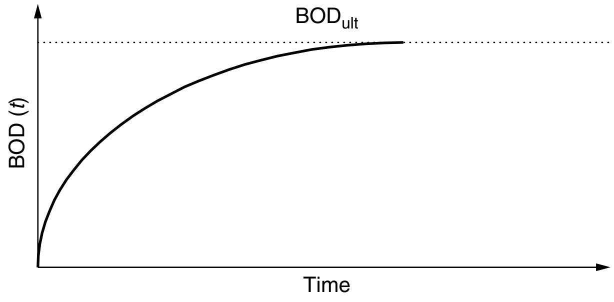

Figure 2. Exertion of BOD in a system.

$$k_{\text{temp}} = k_{20}\theta^{(T-20)} \tag{6}$$

where k_{20} = reaction rate constant at 20 °C
T = temperature (°C)
$\theta = 1.135$ when $4\,°\text{C} \le T \le 20\,°\text{C}$ (3)

MEASUREMENT OF BOD

The BOD test is one method for quantifying the concentration of oxygen-demanding material in a waste. In this test, the quantity of oxygen consumed by the waste over a period of 5 days is measured. This measurement includes all viable oxygen-consuming chemical and biological reactions. The standard procedures for BOD measurement are detailed in *Standard Methods for the Examination of Water and Wastewater* (4). The basis of the Standard Methods procedure is measurement of the change in dissolved oxygen concentration in a standard size container after 5 days of incubation under a set of standard environmental conditions (i.e., sealed from the atmosphere, 20 °C, dark conditions). The resulting change in DO is related to the total biochemical oxygen demand of the waste. If the "strength" of the waste is high (high BOD), the standard sample may consume all available oxygen in the sealed sample before the end of the incubation period and yield inconclusive results. In such cases, the sample water is diluted with aerated water to ensure that a nonzero value of DO is measured at the end of the 5-day incubation. The BOD experiment is illustrated in Fig. 3. The water is aerated to saturate it with oxygen (see Henry's law for a discussion of saturation). A seed (freeze-dried microorganisms) can be added to ensure that sufficient microorganisms are present to consume the waste (electron donor). If used, a seed will place an additional oxygen demand on the sample, which must also be considered.

The samples are placed in an incubator at 20 °C for 5 days and are shielded from sunlight to minimize the influence of photosynthesis on the dissolved oxygen concentration. The following relationship is used to

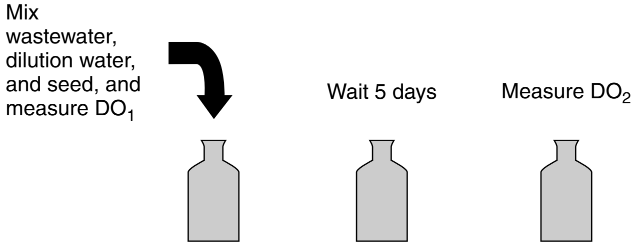

Figure 3. BOD experiment.

calculate the BOD (5) of a sample in which no seed is added:

$$\mathrm{BOD} = \frac{(\mathrm{DO}_1 - \mathrm{DO}_2)}{P} \tag{7}$$

where

$$P = \frac{V_{\mathrm{waste}}}{V_{\mathrm{waste}} + V_{\mathrm{dilution}}}$$

DO_1 = dissolved oxygen concentration of waste/dilution mixture immediately after preparation (mass/volume)
DO_2 = dissolved oxygen concentration of waste/dilution mixture immediately after a 5-day incubation (mass/volume)
V = volume

The BOD (4) is typically less than $\mathrm{BOD}_{\mathrm{ult}}$ for most wastewaters. However, the BOD (4) is typically used for water quality standards and engineering designs. The total demand for oxygen ($\mathrm{BOD}_{\mathrm{ult}}$) by the water body can be determined from the BOD (5) measurement using Eq. 5 and t equal to 5 days.

CONTROL STRATEGIES

For centuries, rivers and lakes have been used as receptacles for human waste. These wastes are major sources of organic material, which can stimulate the growth of aerobic bacteria. In addition, waste streams can contain reduced chemical compounds that react with dissolved oxygen. Contrary to popular belief, the primary purpose of sewage treatment is not to rid the waste of harmful pathogens (though an important side benefit), but to ensure that the carbon and sometimes the nutrient contribution of the sewage to the receiving waterbody does not create a situation where lack of oxygen becomes limiting to aquatic life.

The most common Environmental Protection Agency (EPA) approved control strategy is removal of oxygen-demanding material from waste streams before the discharge enters a natural watercourse. Solid organic material is removed by settling processes (primary treatment), and dissolved organic material is removed through accelerated biological activity (secondary treatment). In secondary treatment, bacteria that are commonly present in domestic waste are provided with sufficient oxygen (a process called aeration) to consume dissolved organic material. In addition, as the organisms reproduce, additional dissolved organic material in the waste is converted into biomass, which is then separated (typically by gravity settling) from the water.

Following secondary treatment, various biological and chemical techniques can be employed (tertiary treatment) to remove additional "contaminants" such as nitrogen, phosphorous, and heavy metals. Primary and secondary treatment of municipal wastewater is required by law in the United States. The requirement for tertiary treatment is determined, case-by-case, based on a combination of total contaminant being discharged in the waste stream and the receiving waterbody's ability to assimilate the contaminant.

BIBLIOGRAPHY

1. Grady, C.P.L., Daigger, G.T., and Lim, H.C. (1999). *Biological Wastewater Treatment*, 2nd Edn. Marcel Dekker, New York.
2. Droste, R.L. (1997). *Theory and Practice of Water and Wastewater Treatment*. John Wiley & Sons, New York.
3. G. Tchobanoglous and F.L. Burton (Eds.). (1991). *Wastewater Engineering—Treatment, Disposal and Reuse*, 3rd Edn. Metcalf and Eddy, Inc., McGraw-Hill, New York.
4. AWWA. (1995). *Standard Methods for the Examination of Water and Wastewater*, 19th Edn. A.D. Eaton, L.S. Clesceri, and A.E. Greenberg (Eds.). American Water Works Association, American Public Health Association, and Water Environment Federation, Washington, DC.

READING LIST

Bitton, G. (1999). *Wastewater Microbiology*, 2nd Edn. Wiley-Liss, New York.

Davis, M.L. and Cornwell, D.A. (1998). *Introduction to Environmental Engineering*, 3rd Edn. McGraw-Hill, New York.

MOLECULAR BIOLOGY TOOLS FOR MONITORING BIODIVERSITY IN WASTEWATER TREATMENT PLANTS

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INTRODUCTION

The group of organisms most directly associated with wastewater treatment is bacteria. They dominate all other groups, both in numbers and biomass, and lead to mineralization and elimination of organic and inorganic compounds (1). Therefore, it seems a natural progression to study the biodiversity and ecology of these organisms in relation to wastewater treatment.

In recent years, molecular methods have been used to study microbial community structure and function due to the revelation that the majority of microbes in the environment are unculturable on standard laboratory agars and conditions (2). It is thought that the percentage of culturable organisms is in the range of 1–10% of the total community; the figure for the number of bacteria described so far is thought to be approximately 1% (3). Taking this into consideration, the use of molecular methods has provided a far more objective and unbiased picture of the total community in wastewater systems.

The methods available can be used in various ways to provide separate pieces of information. Some are used to give a profile of the total community at the site, whereas others identify the organisms performing a specific function. Another set of methods focuses on fluorescent probing of specific whole cells. More recently, new technologies have emerged, which are substrate based, labeling organisms according to their catabolic potential.

COMMUNITY PROFILING METHODS

Community profiling methods produce rapid surveys, which provide us with a phylogenetic profile of the microbial population at a particular site. The speed of application and specificity of these techniques can be used to assess the community composition across space, through time, down pollution gradients, and under various treatments.

Methodologies that provide "molecular fingerprints" are most commonly based on polymerase chain reaction (PCR) amplification of 16S rRNA genes. The 16S rRNA gene is essential as it encodes for a subunit of the prokaryotic ribosome, and therefore is present in all prokaryotic life forms. The equivalent gene in all eukaryotes is the 18S rRNA gene. The gene contains variable regions, which allow identifying organisms down to various taxonomic levels. Fingerprinting studies can also be carried out by amplifying particular functional genes and subsequently analyzing the evolution and phylogeny of enzymes of particular interest.

Denaturing Gradient Gel Electrophoresis

Denaturing gradient gel electrophoresis (DGGE) has been used successfully in many investigations of community structure. It is now one of the most widespread and well-established methods used in obtaining culture independent microbial profiles.

DGGE is based on analytical separation of DNA fragments of identical or near-identical length based on their sequence composition (4). Separation is based on the changing electrophoretic mobilities of DNA fragments migrating in a gel containing a linearly increasing gradient of DNA denaturants. Changes in fragment mobility are associated with partial melting of the dsDNA in discrete regions, the so-called melting domains. Each band shown on the gel represents a taxonomic unit in the environment, and the band intensity can be associated with the species' abundance within it. Once the gel has been visualized, it is also possible to cut out bands directly for sequencing.

The methodology derives from one used in the medical sciences (4) and was subsequently modified for microbial community analyses (5), where the procedure is performed on the total community nucleic acid. An example of a DGGE gel is shown in Fig. 1 (6). The communities shown were extracted from various points of a diesel-contaminated groundwater remediation system.

DGGE is an efficient and inexpensive method of analyzing a community structure and diversity. It also allows higher phylogenetic resolution than many other community analysis methods. Furthermore, one has an advantage in being able to excise bands for sequencing. The only drawback of the method is that only sample sets of up to 50 can be analyzed on one gel, as gel-to-gel comparisons can be difficult.

Length Heterogeneity PCR

More recently, other methods have become available, such as length heterogeneity PCR (LH-PCR); (7). LH-PCR works by exploiting the natural variation in length of the 16S rDNA gene due to group-specific "variable regions" of microbial community members (8). The PCR is carried out using one fluorescently labeled primer, and the amplicons lengths are then separated on a sequencer, where the resultant peaks, comparable with DGGE gel bands, represent various phylogenetic groups. An example of an LH-PCR output can be seen in Fig. 1, where peaks shown represent various phylogenetic groups in a community in a diesel-contaminated groundwater sample.

LH-PCR is reliable for determining the identity of organisms down to class/subclass level and allows processing large sample sets where samples are directly comparable due to an internal size standard run on the sequencer. One drawback of LH-PCR is that organisms can be effectively identified down only to class/subclass level and single peaks may represent multiple bacterial genera within the same taxonomic subclass (e.g., γ-*Proteobacteria*). LH-PCR is especially suitable for tracking known community members through time or during different treatments. In time, this method will become more reliable when the databases available for various environmental samples are improved.

Terminal Restriction Fragment Length Polymorphism (tRFLP)

tRFLP has been used as a reliable community profiling technique by sizing variable length restriction fragment digest patterns of amplified 16S rDNA (9). The method is similar to LH-PCR but involves an endonuclease restriction step and gives a higher phylogenetic resolution based on the specific sequence variance within the 16S rRNA gene.

tRFLP is reliable for determining the identity of organisms down to group level and, in parallel with LH-PCR, it allows processing large sample sets where samples are directly comparable; an example is shown in Fig. 1. The problem of identifying organisms below group level is somewhat mitigated by tRFLP. It must be emphasized that the choice of enzyme for digests to resolve bacterial taxonomic groups during tRFLP analyses is critical and requires some a priori knowledge of the bacterial groups in the samples for effective phylogenetic targeting.

THE USE OF MOLECULAR PROBES IN COMMUNITY ANALYSIS

Rather than providing a community fingerprint, these methodologies are used to probe for certain known community members. These methods require some a priori knowledge of the population or can be used to determine whether an organism is present. A molecular probe is applied, which hybridizes with the DNA or RNA of the specific organism. The probe can be applied *in situ* or *ex situ*. These methods are powerful tools, which avoid the possible biases of cloning and PCR amplification techniques, and can yield a more direct measure of the target groups of interest.

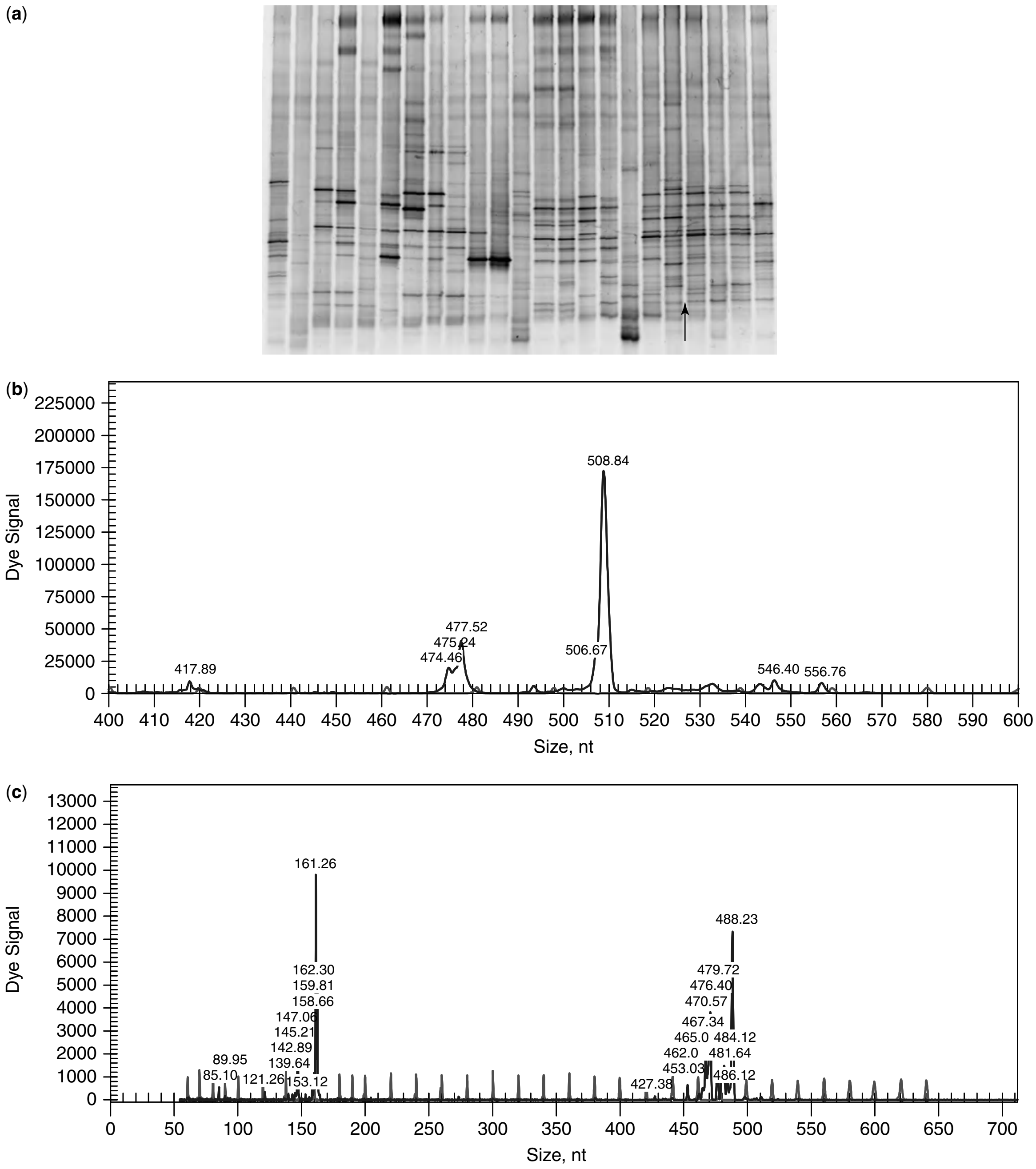

Figure 1. (**a**) DGGE profile showing samples taken from a groundwater diesel remediation system. (**b**) An example of an LH-PCR output. (**c**) An example of a tRFLP output. Both outputs correspond to lane 20 on the DGGE gel.

DNA Microarrays

A DNA microarray (a DNA microchip or DNA chip) is an orderly, high-density matrix of hundreds (or thousands) of individual longer cDNA probes or short oligonucleotides bound directly or indirectly to a solid surface (10). Unlike membrane hybridization, the chip is a high-density format that allows simultaneous hybridization of a labeled DNA or RNA target to a large set of probes, thus providing high throughput. Most applications have been in cell biology such as applied to drug discovery or to monitor gene expression patterns in pure culture, but more recently, the technology has been used successfully in environmental studies (11). Microarrays are a useful tool for high turnover screening of large numbers of samples. They are, however, rather expensive to construct.

Reverse Sample Genome Probing

Reverse sample genome probing (RSGP) uses the entire genome of a microorganism as a specific probe that allows detecting it in the environment. Whole genome probes have been used to detect *Mycobacterium, Mycoplasma, Chlamidia, Bacteroides, Pseudomonas, Sphingomonas,*

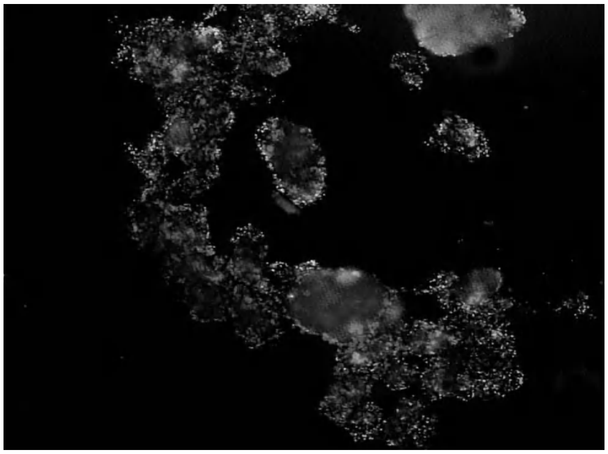

Figure 2. FISH probing of *Thauera* species in a wastewater treatment system. The *Thauera* specific probe is labeled in red. The species Eub358 is shown in green.

and *Campylobacter* species. A good example of the use of this method was looking for sulfate-reducing organisms in contaminated oil fields (12).

Fluorescent *In Situ* Hybridization of Whole Cells

Whole cell *in situ* hybridization with fluorescently labeled oligonucleotides in community analysis was first developed in the late 1980s (13). The procedure involves fixing the environmental sample to permeabilize the cells while maintaining their morphological integrity. The cells are then immersed in hybridization solution containing fluorescently labeled oligonucleotide. After washing to remove unbound probes, the sample is viewed by epifluorescence microscopy. Cells that show specific hybridization with the fluorochrome-labeled probe can be identified and enumerated, as shown in Fig. 2.

THE USE OF LABELED SUBSTRATES TO PROBE FOR ORGANISMS

In addition to community profiling methods and the use of specific oligonucleotide probes, substrate-based procedures have been developed that are culture independent and can be employed *in situ*. These methods, in particular, employ stable isotopes, such as ^{13}C, to determine exactly which organisms are involved in the breakdown of specific contaminants. These methods allow identification of the organisms involved in processing the contaminating compound and are some of the most sophisticated methods used in the field.

Polar Lipid-Derived Fatty Acid-Based SIP

^{13}C labeled substrate is pulsed into the microbial community in the environment and results in labeling polar lipid-derived fatty acids (PLFAs) from assimilating organisms. PLFAs are then extracted, separated, and analyzed for ^{13}C enrichment by isotope ratio mass spectrometry (IRMS). Because specific phylogenetic groups produce signature PLFA profiles, the stable isotope enrichment of certain PLFAs reveal which organisms were dominating the metabolism of the labeled substrate.

The first PLFA-SIP investigation was carried out by Boschker et al. (14), who identified the microorganisms responsible for oxidizing the greenhouse gas methane in a freshwater sediment.

DNA Stable Isotope Probing

More recently, nucleic acids have been used in SIP studies. These methods are more user-friendly because sequence information is so widely available, and nucleic acid extraction from environmental samples is easy.

Stable isotope labeled DNA can be isolated from mixed microbial communities based on the increase in buoyant density from isotopic enrichment. Density centrifugation in cesium chloride gradients was used to separate "heavy" for natural DNA, and 16S rDNA clone libraries constructed from heavy DNA were sequenced to obtain the identity of organisms assimilating the ^{13}C labeled substrate used in the study. This technique has been used to attribute methanol to use particular *Proteobacteria* in an oak forest soil (15).

RNA Stable Isotope Probing

Due to the fact that DNA synthesis is associated only with cell replication, the amounts of DNA synthesized in the duration of a ^{13}C pulse may be low in a natural environment with low cell replication. The use of RNA in SIP, however, offers the same sequence-based resolution but avoids the limitations of labeling due to its high turnover rate. The procedure is performed as DNA-SIP above, and reverse transcription of the heavy RNA to identify organisms is added. RNA-SIP has been applied to an operative industrial phenol-degrading wastewater treatment system to identify organisms responsible for metabolizing phenol (16). Figure 3 shows the fractionation of natural and heavy ^{13}C labeled RNA. The fractionation,

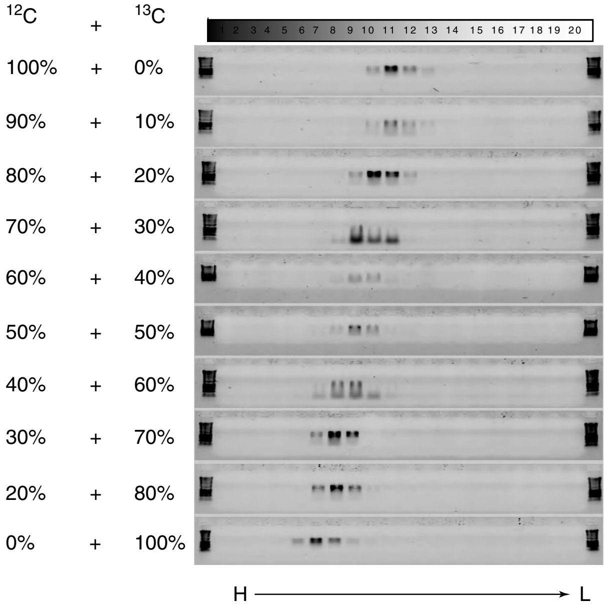

Figure 3. The appearance of natural (^{12}C) and heavy (^{13}C labeled) RNA shown in RNA-SIP. The top gradient fractions contain the natural weight RNA, and the heavy RNA becomes apparent as we move down the fractions (17).

extraction, and subsequent sequencing of the heavy RNA resulted in identifying the dominant phenol degrader in a wastewater system as a *Thauera* species.

Fluorescence *In Situ* Hybridization and Secondary Ion Mass Spectrometry

Recently, investigations in which individual cells or mixed aggregates of cells in methane-consuming communities were identified by fluorescence *in situ* hybridization and, subsequently, analyses for ^{13}C content by secondary ion mass spectrometry (18). The natural abundance of ^{13}C in methane is low, thus enabling the association of cells harboring depleted ^{13}C signatures with methane consumption.

All SIP techniques outlined before are sophisticated methods of associating an organism with a specific function, their catabolic potential. The one problem of SIP is that the labeled substrates are hard to obtain and may require custom synthesis, which is a rather costly process.

BIBLIOGRAPHY

1. Amann, R., Lemmer, H., and Wagner, M. (1998). Monitoring the community structure of wastewater treatment plants: a comparison of old and new techniques. *FEMS Microbiol. Ecol.* **25**: 205–215.
2. Amann, R.I., Ludwig, W., and Schleifer, K.H. (1995). Phylogenetic identification and *in situ* detection of individual microbial cells without cultivation. *FEMS Microbiol. Rev.* **59**: 143–169.
3. Cox, C.B. and Moore, P.D. (2000). Biodiversity. *Biogeography: An Ecological and Evolutionary Approach*, 6th Edn. Blackwell Science, New York.
4. Myers, R.M., Maniatis, T., and Lerman, L.S. (1987). Detection of localisation of single base changes by denaturing gradient gel electrophoresis. *Methods Enzymol.* **155**: 501–527.
5. Muyzer, G., De Wall, E.C., and Uitterlinden, A.G. (1993). Profiling of complex microbial populations by denaturing gradient gel electrophoresis analysis of polymerase chain reaction-amplified genes coding for 16S rRNA. *Appl. Environ. Microbiol.* **59**: 695–700.
6. Ciric, L., Whiteley, A., Manefield, M., Griffiths, R., Philp, J., and Bailey, M. (2003). Approaches for analyzing the diversity of diesel degrading microbial communities. *Proc. 2nd Eur. Bioremediation Conf.*, pp. 449–452.
7. Suzuki, M., Rappé, M.S., and Giovannoni, S.J. (1998). Kinetic bias in estimates of coastal picoplankton community structure obtained by measurements of small subunit rRNA gene PCR amplicon length heterogeneity. *Appl. Environ. Microbiol.* **64**: 4522–4529.
8. Whiteley, A.S., Griffiths, R.I., and Bailey, M.J. (2003). Analysis of the microbial functional diversity within water stressed soil communities by flow cytometric analysis and CTC+ cell sorting. *J. Microbiol. Methods* **54**: 257–267.
9. Liu, W.T., Marsh, T.L., Cheng, H., and Forney, L.J. (1997). Characterisation of microbial diversity by determining terminal restriction fragment length polymorphisms of genes encoding 16S rRNA. *Appl. Environ. Microbiol.* **63**: 4516–4522.
10. Service, R.F. (1998). Microchip arrays put DNA on the spot. *Science* **282**: 396–399.
11. Guschin, D.Y., Mobarry, B.K., Proudnikov, D., Stahl, D.A., Rittmann, B.E., and Mirzabekov, A.D. (1997). Oligonucleotide microchips as genosensors for determinative and environmental studies in microbiology. *Appl. Environ. Microbiol.* **63**: 2397–2402.
12. Voordouw, G., Voordouw, K.J., Jack, T.R., Foght, J., Fedorak, P.M., and Westlake, D.W.S. (1992). Identification of distinct communities of sulfate-reducing bacteria in the oil fields by reverse sample genome probing. *Appl. Environ. Microbiol.* **58**: 3542–3552.
13. DeLong, E.F., Wickham, G.S., and Pace, N.R. (1989). Phylogenetic strains: ribosomal RNA-based probes for the identification of single microbial cells. *Science* **243**: 1360–1363.
14. Boschker, H.T.S., Nold, S.C., Wellsbury, P., Bos, D., de Graaf, W., Pel, R., Parkes, R.J., and Cappenberg, T.E. (1998). Direct linking of microbial populations to specific biogeochemical processes by ^{13}C-labelling of biomarkers. *Nature* **392**: 801–805.
15. Radajevski, S., Ineson, P., Parekh, N.R., and Murrell, J.C. (2000). Stable-isotope probing as a tool in microbial ecology. *Nature* **403**: 646–649.
16. Manefield, M., Whiteley, A.S., Griffiths, R.I., and Bailey, M.J. (2002). RNA stable isotope probing: A novel means of linking microbial community function to phylogeny. *Appl. Env. Microbiol.* **68**: 5367–5373.
17. Manefield, M., Whiteley, A.S., Ostle, N., Ineson, P., and Bailey, M.J. (2002). Technical considerations for RNA-based stable isotope probing: An approach in associating microbial diversity with microbial function. *Rapid Commun. Mass Spectrom.* **16**: 2179–2183.
18. Orphan, V.J., House, C.H., Hinrichs, K.-U., McKeegan, K.D., and DeLong, E.F. (2001). Methane-consuming Archaea revealed by directly coupled isotopic and phylogenetic analysis. *Science* **293**: 484–486.

BIOSOLIDS

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Wastewater treatment processes remove organics, inorganic materials, and contaminants in sludge. Biosolids are treated municipal wastewater sludge that can be beneficially used, especially as a soil amendment, in accordance with standards.

The Water Environment Federation (WEF) has adopted a policy of encouraging the use of the word 'biosolids' in place of sludge to promote public acceptance of reused materials. Land application of biosolids has been and continues to be successfully implemented by many countries. Many countries have rules and regulations associated with biosolids reuse and disposal. Almost all rules are based on reducing pathogens and pollutants. However, rules and regulations vary in different countries. Criteria and methods of obtaining results to determine the use of biosolids also vary.

The United States EPA Standards (US EPA, 1993,1995) for using sludge includes pathogen requirements, vector attraction reduction requirements, and pollutant ceiling concentrations. In accordance with them, two classes of requirements—Class "A" and Class "B" were accepted as rules. To achieve Class "A" (pathogen) requirements, either the density of fecal coliform bacteria in the sludge shall be less than 1000 most probable number (MPN) per gram of total solids, or the density of *Salmonella* sp. bacteria shall be less than 3 MPN per 4 grams of total solids. In addition, the sludge must contain less than one unit of plaque-forming virus and less than one helminth ova per 4 grams of total solids.

Class "B" sludge product must meet one of three alternative requirements. In the first of these, the geometric mean of the density of fecal coliform (expressed either by MPN or colony-forming units per gram of total solids) for seven samples must be less than 2,000,000. The geometric mean is the antilogarithm of the arithmetic average of the logarithms of seven samples. Alternatively, the sludge may be classified as Class "B" by being treated by a process to significantly reduce pathogens (PSRP) or by a process determined to be equivalent to PRSP by the permitting authority.

Class "A" sludge is prone to regrowth of pathogenic bacteria, such as *Salmonella* sp., after treatment because it lacks an adequate density of competitive organisms. Concerns for regrowth led to several additional requirements. First, pathogen reduction must be achieved prior to or at the same time that certain vector attraction reduction requirements are met. Second, pathogen density requirements must be met when the biosolids are used or disposed of, not when sludge is treated. Third, Class "A" biosolids applied to the land for vector attraction reduction must be applied within 8 hours after discharge from the pathogen treatment process.

Class "B" biosolids cannot be sold or given away in a bag or other container for land application. Biosolids, which meet Class "B," can be applied to agricultural land, forests, public contract sites, or reclamation sites. Land application of Class "B" has restrictions for the harvesting of crops and turf, grazing of animals, and public access.

These restrictions are designed to provide time for the natural environment to reduce the pathogenic organisms in the biosolids. Food crops that touch the biosolids/soil mixture and are aboveground cannot be harvested for 14 months after application of biosolids to land. Root crops cannot be harvested for 20 to 38 months after biosolids application. In this case, the lowest time period applies if biosolids remains on the land surface for 4 months prior to incorporation into the soil, and the higher value applies when it does not. Class "A" and Class "B" biosolids have some vector attraction reduction requirements for land application.

The disposal alternatives are based on the treatment level provided. The most common methods for achieving Classes "A" or "B" biosolids include digestion, composting, thermal drying, and alkaline stabilization.

DIGESTION

Several sludge digestion technologies that consist of anaerobic and aerobic processes are widely used.

Anaerobic Digestion

Anaerobic digestion is a biological process of reducing volatile solids by microorganisms in the absence of oxygen; it reduces odor and pathogen content. Digesters are cylindrical reservoirs with conical bottoms; the upper section of the reservoir has a sealed cover with a device for collecting gas. One-stage and two-stage digesters are in use. In two-stage digesters, the first stage has covered heated reservoirs, and the second stage has open, unheated reservoirs.

Two types of anaerobic digestion processes are in use—mesophilic and thermophilic. Mesophilic processes function in the temperature range of 32–35 °C. The thermophilic process is operated at a higher temperature (50–55 °C) to reduce organic solids and pathogen content further. The process can use conventional standard rate and high-rate digesters with solid retention time from 30–60 days to 10–20 days. To produce Class "B" biosolids, digested sludge has to meet one of the following: reduce volatile solids by a minimum of 38%, or demonstrate that further anaerobic digesting of a portion of the sludge in a bench-scale lab unit for 40 additional days at a temperature between 30 and 37 °C will reduce the volatile solids by less than 17%.

The end products of anaerobic digestion are biosolids, gas, and water. The following gas composition can be expected: methane —60 to 75%; carbon dioxide —16 to 40%; nitrogen, hydrogen, and oxygen —0.4 to 6%. The average heat of combustion of this gas is 21 million joule/m^3. Depending on the chemical composition of the sludge, the liberation of gas varies from 5 to 20 m^3 per m^3 of sludge or 1 m^3 for every 1 kg of a disintegrated sludge's organic content.

Anaerobic digestion requires energy in the form of heat and electricity. Supplying this energy can be expensive unless part of the energy required is received directly from using the gas. When less than 10–12 m^3 of gas is liberated per 1 m^3 of sludge, the resulting heat balance may be negative. If the gas obtained is in excess of 12 m^3 per 1 m^3 of sludge, it may be used in boilers, heating systems, and so on.

Methane is characterized by explosion hazard and may poison people, if the gas leaks. The volume of gasholders is determined in accordance with gas production and the demand schedule. The volume of gasholders is approximately equal to 2–4 hours of gas production.

Aerobic Digestion

Aerobic digestion is a process of oxidation of the organic part of sludge by microorganisms in special tanks in the presence of oxygen (air aeration of sludge). Aerobic digestion has been widely used in wastewater treatment plants (WWTP) for many years. The purpose of aerobic sludge digestion is to stabilize raw sludge and produce biosolids for further treatment and disposal. Equipment for aerobic digestion is simpler, with in design and operation than that for anaerobic digestion. The more useful sludge aerobic digestion processes are conducted in open structures of the aeration tank type. The duration of the volatile part of solids oxidation depends on the food/microorganism ratio, temperature, intensity and quantity of aeration, and also on wastewater composition and technological demand. This process is more useful for digesting and stabilizing thickened activated sludge.

The detention time to reduce volatile solids and stabilize a mixture of waste activated sludge and raw primary sludge may be 10–15 days at an operating temperature of 20 °C (68 °F). Traditionally, digesters have been designed for a detention time of 20–30 days. However, to meet Class "B" sludge regulations by aerobic digestion, Federal Regulations (40 CFR 257) require detention times of 40 and 60 days at temperatures of 20 °C and 15 °C (68 °F and 59 °F), respectively, and reduction of volatile solids by a minimum of 38%. Long aerobic digestion times require large tank volumes. To reduce tank volumes, the solids concentration can be increased by gravity, belt, or drum thickeners.

Aerobically digested biosolids should be settled for 1.5–5 hours in a sedimentation zone inside the aeration tank or settling in sedimentors. The supernatant BOD is about 100 mg/L, and the COD varies from 350 to 700 mg/L. The moisture content of the biosolids is 95–98% after sedimentation.

Oxidation of the organic part of sludge releases about 3.6 kcal of heat per gram of volatile suspended solids (VSS) in aerobic autoheating mesophilic digestion or autothermal thermophilic aerobic digestion. Temperature control is important in both processes. These processes use heat, created by biochemical oxidation of the organic substances by air introduced into the reactors. The processes are realized in hermetically sealed reactors. The heat balance has to take into account heat loss to surroundings, effluent gas, effluent sludge, and so on.

Autothermal thermophilic aerobic digestion (ATAD) systems for sludge stabilization and disinfection include two hermetically sealed reactors which can be operated with an existing anaerobic digester (prestage ATAD) or operated as conventional ATAD. By using the ATAD process for heat balance, activated sludge has to be thickened to 5% or more of dry solids using belt or rotary drum thickeners. Technological schemes include waste-activated sludge holding and buffer tanks, thickeners, pumps, heat exchangers, reactors, treated sludge holding tanks, and communications. Depending on the temperature and process duration, ATAD can be used to produce Class "B" or "A" biosolids. Class "A" biosolids should be heated to 55–60 °C and aerated for about 10 days. Class "B" aerobic and anaerobic digested biosolids may be converted to Class "A" by maintaining a temperature of at least 70 °C for a minimum of 30 minutes. This can be done by inserting hot air or gases directly into the digested biosolids or by using heat exchangers.

COMPOSTING

Composting of domestic waste and manure has been used for thousands of years. However, the production of compost from wastewater sludge of large-scale municipal wastewater treatment plants began in the 1960–1970s.

Composting can be performed as aerobic or anaerobic biothermal processes which release heat during the decomposition of organics. Aerobic biothermal processes release almost 30 times more heat than anaerobic processes. That is why aerobic processes are used more often. The composting process reduces the organic material in the sludge by approximately 25–30%. During composting, the heat generated by the decomposition of the organic portion of the sludge, reduces the moisture content of the sludge, stabilizes the sludge, and renders the residual harmless by transforming it into usable biosolids.

The heat generated by decomposition of 1.0 kg of organic material averages 20–21 million joules (Mjoule). This generated heat drives the biothermal process and moves the composting process from the mesophilic phase (25 to 40 °C) to the thermophilic phase (55 to 65 °C). Most pathogens are destroyed during the thermophilic phase.

The generated heat also facilitates the evaporation of moisture. Approximately 4.0 Mjoule of heat will evaporate 1.0 kg of moisture (taking into account heat losses and heating of the compost material). Thus, decomposition of 1.0 kg of organic material facilitates the removal of approximately 5.0 kg of moisture from the sludge (21 Mjoule/4 Mjoule/kg of water).

Before composting, it is necessary to dewater sludge. Dewatering reduces the volume of sludge, and it also decreases the amount of moisture to be evaporated by the composting process.

The aerobic process can be performed by using different systems—windrow, aerated static piles, or in-vessel. Sludge is composted together with bulking materials, such as saw dust, wood chips, peat, paper product waste, and ready compost, which provide the mixture with the necessary moisture, porosity, and carbon content.

For vector attraction reduction requirements and to achieve Class "B" biosolids during composting, the temperature has to be above 40 °C (104 °F) for a minimum of 14 days and average more than 45 °C for the same period. To obtain Class "A" compost, the US EPA requires that the temperature in the piles have to be at least 55 °C (131 °F) for 3 days.

Windrow piles or trenches are effective, but mixing and turning does not provide enough air, that is why anaerobic conditions (sometimes) take place in these devices, which generates odors. More often aerated static pile composting is used. Piles have been made by mixing dewatered sludge with wood chips or saw dust. Arrangements of dewatered sludge and amendments prior to mixing follow recycled wood chips (or saw dust) on the floor, dewatered sludge on the top, or when fresh, wood chips (or saw dust) or recycled compost. To prevent heat loss and protect against insects and rodents, piles are covered by ready compost.

In aerated static piles, perforated pipes mounted underneath the composting pile provide aeration. Pipes are covered with layers of sand, gravel, or bulking material and are connected to blowers.

Aerated static pile composting is an effective process. It is easy to operate and does not require high personnel qualification. Compost is a dry, disinfected, and stabilized product. However, the speed of the process depends on several factors, such as bulking materials; proportion of bulking materials to dewatered sludge; efficacy of mixing bulking materials with dewatered sludge; temperature, moisture, and porosity of the mixture; mass of the mixture being composted; quantity of air and duration of aeration; correction between C and N; quantity of recycling compost and bulking material, and toxicity to biological decomposition.

The moisture content of mixed sludge-bulking material has to be 60–67%. The quantity of air is 10–25 m^3/hour per ton of volatile solids. Increased air allows an increase in process speed, but excess air decreases the process speed and temperature. Aeration begins 5–10 days after starting the process and lasts 25–30 days for 8 hours every three days. The index of aeration is the concentration of CO_2. When the concentration of CO_2 increases to more than 7% of gas volume, inhibition of microorganisms and a decrease in temperature occur. At the beginning of the process, the carbon to nitrogen (C:N) ratio is 30:1–34:1 in a pile with saw dust and 25:1–27:1 in a pile with ground bark. Compost is cured for 1–3 months. In the United States, more than 200 composting facilities are in operation now, mostly aerated static piles. But windrow and in-vessel composting also takes place.

Windrow piles are turned with mobile equipment every 3–5 days until the temperature is maintained at 55–65 °C and composted for a period of 3 to 5 weeks, when cured and stored in piles for 1–2 months. The process is based on constructing a windrow from a mixture of dewatered sludge, bulking agent, and recycled compost that provides composting material of proper moisture content, porosity, and carbon source for microorganisms.

Composting processes such as windrow, static piles, aerated static piles, and different types of in-vessel (vertical towers, vessels, reactors, containers, and so on) are widely used in Europe, Japan, and other countries. In-vessel composting processes are accomplished inside enclosed containers that provide a completely controlled environment, temperature, aeration, and odor control. However, in-vessel systems are more complicated and expensive than windrow or aerated static piles and require qualified personnel.

THERMAL DRYING

Thermal drying is designed to disinfect and decrease the weight and volume of wastewater sludge. Thermal drying permits economical sludge transportation from treatment plants and subsequent use.

Thermal drying of sludge is conducted in drying systems consisting of a drying device (dryer) and auxiliary equipment, which includes furnaces with a fuel supply system, feeders, cyclones, scrubbers, blowing equipment, conveyors and bins, as well as monitoring and measuring instruments and automatic control equipment.

To reduce fuel required, sludge should be dewatered before thermal drying by using belt process, centrifuges, or plate presses. For thermal drying of sludge, use fluidized bed dryers, drum dryers, opposite jet dryers, dryers with peripheral discharge of the dried sludge, or Pelletech drying systems. In dryers, the drying temperature should reach 500–800 °C, and drying time is approximately 10–15 minutes.

The Pelletech dryer is a vertically oriented multistage unit that uses steam or thermal transfer fluid in a closed loop to achieve 90% or greater dry solids content in the product. This process minimizes formation of dust and oversized chunks. Pelletizing and drying involves heat and mass transfer, mixing, combustion, conveying, classification, and evaporation.

Thermal dryer sludge is a Class "A" biosolid when sludge achieves 75% dry solids concentration, if no unstabilized primary is present, and 90% of dry solids content, if unstabilized primary sludge is present, by direct or indirect contact with hot gases. Either the temperature of the sludge particles exceeds 80 °C (176 °F) or the wet bulk temperature of the gas in contact with the sludge as the sewage sludge leaves the dryer exceeds 80 °C (176 °F).

The thermal drying process exceeds Class "A" biosolids regulations and can be used for soil improvement without additional restrictions; the solids can be bagged or sold in bulk as fertilizer to landscape contractors or the general public.

ALKALINE STABILIZATION

To produce biosolids that meet pathogen and vector attraction reduction requirements, wastewater treatment plants often use alkaline stabilization. For sludge stabilization, which meets Class "A" or "B," quicklime or hydrated lime are used. Lime is added to sludge before or after dewatering. If quicklime is added to sludge, it initially reacts with water to form hydrated lime. This reaction is exothermic and releases approximately 15,300 cal/g mole (27,500 Btu/lb/mole). The reaction between quicklime and carbon dioxide is also exothermic, releasing approximately 43,300 cal/g mole (78,000 Btu/lb/mole). To achieve Class "A" pathogen reduction, the quantity of added lime is determined so that the pH of the sludge and lime mixture is raised to 12 or greater for 72 hours; the temperature of the sludge during this period must be higher than 52 °C for 12 hours or longer. In addition, air-dried resultant biosolids have to achieve greater than 50% solids content. This process is often called sludge pasteurization. The lime pasteurization process provides a higher level of pathogen reduction than lime stabilization and the result is biosolids that meets Class "A" requirements.

For vector attraction reduction that meets Class "B," the mixture of sludge and lime has to be raised to pH 12 for at least 2 hours and remain over pH 11.5 for an additional 22 hours, all without further alkali addition.

Disinfection of sludge with quicklime or hydrated lime is widely used in Europe to reduce odor, pathogens, and putrefaction of the sludge. Lime stabilization can be part of a sludge conditioning process prior to dewatering (prelime stabilization) or following a dewatering step (postlime stabilization). As a rule, lime is stored in silos and mixed with sludge by various types of mixers.

BIOSOLIDS USE

Biosolids are often used as an organic-mineral nitrogen-phosphorus-potassium fertilizer, soil amendment, or soil conditioning material. Biosolids may be used as a fertilizer on agricultural lands, forests, public contact sites, reclamation sites, rangeland, pastures, lawns or home gardens, or as Class "A" biosolids that are given away in a bag or other container for application to land. Biosolids contain necessary macro- and micronutrients for plant growth. Biosolids may be considered a lime fertilizer when the lime is used for sludge stabilization or pasteurization. The mineral part of biosolids is usually represented by combinations of calcium, silica, aluminum, and iron. Several types of micronutrients are present in biosolids, which increase the speed of many biochemical reactions during plant growth. Most micronutrients can be considered microfertilizers. For example, copper increases the harvest of wheat on marshy and sandy soils. Manganese contributes to increasing the harvest of beets, corn, and some other agricultural crops. A deficiency in iron and zinc in plant growth causes serious breaches in vital activities of plants, specifically related to fruit plants, grape, and cotton plants. Boron is very important for crops such as flax, sugar beets, cotton, feed legumes, peas, clover, alfalfa and several other fruits, berries, and vegetable crops. Micronutrients also contribute to assimilation of organics from the sludge by plants. However, the increased concentration of microelements exercises a negative influence on the growth and quality of plants.

According to the standards for biosolids use, it is necessary to reduce pathogens as mentioned above, but it is not enough. It is very important to determine the pollutants concentration in biosolids, which have to be less than limits and whether biosolids meet cumulative pollutant loading rates (kg/ha) and annual polluting loading rates to soil (kg/ha-year).

Several microelements are essential and some not essential for plants and animals, depending on their doses. Some of them are heavy metals that require some restrictions in use. Among them are arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium and zinc. Some chemicals, such as barium, beryllium, carbon disulfide, dioxins, and phenol, should be considered hazardous enough to be a potential threat to the health of people and wildlife. The United States currently regulates nine chemical pollutants, but the EPA has already considered regulating six more pollutants. There are special rules and regulations in several economically developed countries that restrict the content of heavy metals in biosolids used as fertilizers and also restrict doses of embedding biosolids in soils.

The requirements for heavy metal content in biosolids become less restrictive when using the soils for shrubs, flowers, for fast-growing trees, like willows, for development of low productive soils and their recuperation, for reinforcement of ravines and hillsides, and for planting trees and shrubs on former industrial waste sites.

If biosolids contain more pollutant concentrations than the requirements of standards, these biosolids should be buried in landfills or incinerated. To reduce expenditures for incineration, sludge organics should be used as fuel.

CONCLUSION

Biosolids are treated wastewater sludge that can be beneficially used as a soil amendment. When considering the use of biosolids, how and where biosolids may be used and how they should be prepared for use corresponding to the requirements of Standards should be determined.

Several processes for sludge treatment such as different methods of digestion, thermal, biothermal, or chemical treatment provide reduction of pathogens and vector attractions to achieve Class “A” or “B” biosolids. Aerobic and anaerobic digestion of sludge are widely used processes of sludge stabilization and produce biosolids that meet Class “B” sludge regulations. Autothermal thermophilic digestion systems operated in hermetically sealed reactors allow production of Class “A” biosolids.

Thermal drying, lime stabilization, and lime pasteurization are used to destroy pathogens, eliminate odor, reduce most of the water content and the volume of sludge, and lower transportation costs of biosolids. These processes are in use for Class “A” or “B” biosolids.

Composting is an effective way of stabilizing and reducing pathogens in sludge. Many utilities use wastewater sludge composting systems, such as windrow, aerated static piles, and in-vessel.

Composting delivers high quality product, which has macro-and micronutrients and can be used as a soil conditioning material, amendment, or fertilizer—either as Class “A” or “B.”

Biosolids, after appropriate treatment, may be used as a fertilizer on agricultural lands, forests, public contact sites, reclamation sites, rangeland, pastures, lawns, or home gardens. It should be determined if Class “A” or Class “B” pathogen requirements can be reached and also if the sludge meets one of the vector attraction reduction criteria. After that, pollutant concentration and doses of embedding biosolids in soils should be determined.

Extensive use of dewatered and disinfected biosolids received from municipal wastewater treatment plants as fertilizers will contribute to the solution of the problem of their effective, economical, and ecologically acceptable removal and disposal.

READING LIST

Outwater, A.B. (1994). *Reuse of Sludge and Minor Wastewater Residuals*. CRC Press, Boca Raton, FL.

Epstein, E. (1997). *The Science of Composting*. Technomic, Lancaster, PA.

Shimp, G. and Childress, B. (2002). Improving the process. *Civ. Eng.* **72**(9): 74–77.

Haug, R.T. (1993). *The Practical Handbook of Compost Engineering*. Lewis, Boca Raton, FL.

Lue-Hing, C., Zenz, D.R., and Kuchenither, R. (1992). *Municipal Sewage Sludge Management*. Vol. 4, Technomic, Lancaster, PA.

Manual of Practice #8. (1992). *Design of Municipal Wastewater Treatment Plans*. Vol. 2. WEF, ASCE Manual and Report of Engineering Practice #76.

Porteous, J. (1998). Controlled aerobic digestion of thickened sludge. *Water Eng. Manage.* August: 26–28.

Pelletier, R.A., Slooh, D.S., and Lothrop, T.L. (2001). To lime or not to lime. . . that is the question. *Fl. Water Resour. J.* February: 37–38; 40.

Spellman, F.R. (1996). *Wastewater Biosolids to Compost*. Technomic, Lancaster, PA.

Turovskiy, I.S. (1999). Beneficial use of wastewater sludge biosolids in Russia. *Fl. Water Resour. J.* May: 23–26.

Turovskiy, I.S. (2001). Technological improvements for the aerobic digestion of sludge. *Water Eng. Manage.* August: 33–36.

Turovskiy, I.S. and Westbrook, J.D. (2002). Wastewater sludge composting.*Water Eng. Manage.* October: 29–32.

U.S. EPA. (1999). *Biosolids Generation, Use, and Disposal in the United States*. EPA530-R-99-009.

U.S. EPA. (1989). *Summary of In-vessel Composting of Municipal Wastewater Sludge*. EPA625/8-89-016.

U.S. EPA. (1993). *The Standards for the Use or Disposal of Sewage Sludge. Title 40 of the Code of Federal Regulation 503*. Federal Register 58 FR 9248 TO 9404. U.S. EPA, Washington, DC.

Wave, H.H. (2003). *U.S. Filter's Mag.* **2**(2): 40.

INTEGRATED CAPACITY BUILDING NEEDS FOR WATER SUPPLY AND WASTEWATER SANITATION

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INTRODUCTION

Sustainable development is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (1). This was the unifying theme of the 1992 Earth Summit in Rio de Janeiro that produced Agenda 21, Blueprint for Sustainable Development. To do most of what the new sustainable development paradigm challenges society to do requires us to strengthen our collective capacity to respond to those challenges and opportunities. "Capacity building is the sum of efforts needed to develop, enhance and utilize the skills of people and institutions to follow a path of sustainable development" (2). A UNDP program, Capacity 21 (2), seeks to build capacity to implement Agenda 21 (3). At the core of integrated watershed management (IWM) lies the engineered human water supply and wastewater sanitation cycle, operating within the hydrologic constraints of the surface watershed and aquifer system (Fig. 1). We must remember, however, that although water resources are the prima facie focus, water cycling depends on a functioning ecosystem comprising interactions of air, soil, climate, forests, and biodiversity.

It is evident from the simplified schematic diagram of the water cycle that this is a complex system that has many types of capacities needed to sustain the sociopolitical, economic, and technological networks it entails. In a typical settlement, there are diverse users of water/producers of wastewater. In a typical watershed, there are many such settlements of varying size and productive activity, comprising people living in water-producing zones (aquifer recharge zones, upland forest zones) and those who consume most water and produce most wastewater (cities and major farming/irrigation zones).

One common focus for societal capacity building is education and training, centered on strengthening human resources. Another common clientele for capacity building is government institutions. Howe (4) has identified key institutional water management requirements for a watershed scale: (1) coordinated management of surface water and groundwater resources, (2) coordinated management of both water quantity and water quality, (3) provision of incentives for greater economic and technical efficiencies in water use, and (4) protection of public values associated with water service (e.g., reliable, safe, clean, affordable supply). To achieve this, the water institutions must develop the following characteristics (after 1):

- the capacity to coordinate water plans with other agencies (e.g., urban planning, agriculture, public health, environment, industrial);
- the capacity to solve water problems creatively using a variety of options and approaches (e.g., laws, pricing, taxes, tradable supply and/or pollution permits, subsidies);
- the foresight to separate roles and responsibilities for water resource planning and management activities

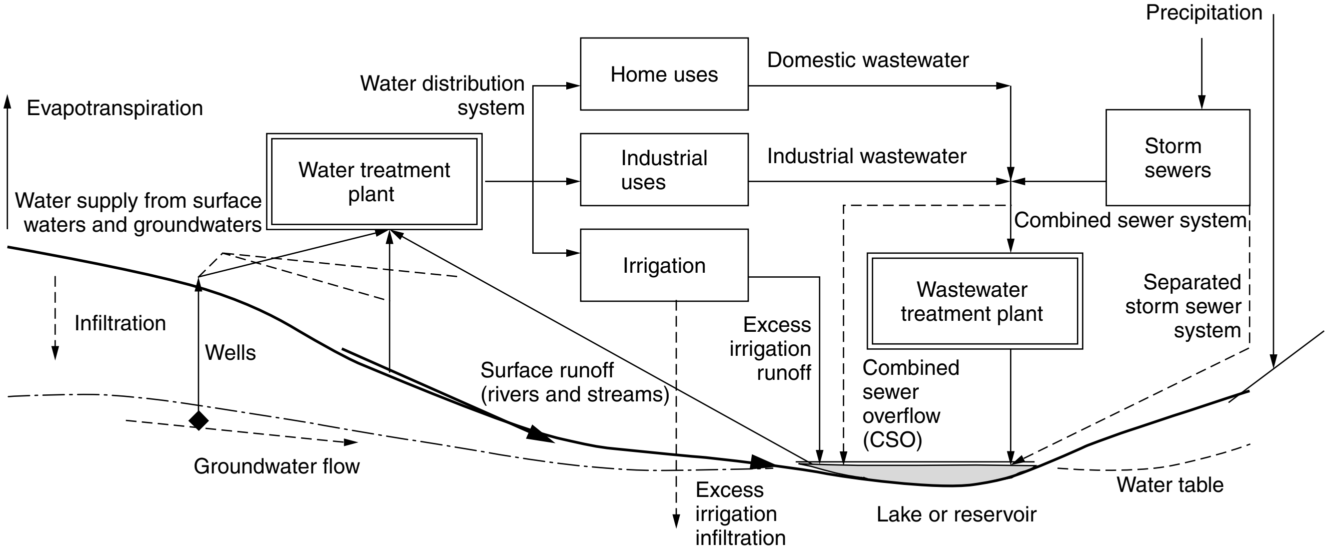

Figure 1. The water supply–wastewater sanitation cycle constrained within the hydrologic cycle. This schematic reveals a complex physical and administrative system that requires an integrated approach to capacity building, especially on the watershed scale.

from construction activities (i.e., avoid conflicts of interest);
- the multidisciplinary capacity to undertake multicriteria/multiobjective planning and evaluation of alternatives;
- devolve decision-making power to the lowest practical level—national, state/regional (provincial), local or municipal—consistent with the scale of the water issue;
- capacity and willingness to use appropriate participatory methods involving different stakeholders at different stages of a project (preplanning/conceptual, planning and design, implementation, maintenance, monitoring and evaluation);
- ability to reward innovation and adapt to changing conditions and priorities.

Wherever capacities are missing or weak, a process of integrated multiobjective, multidisciplinary capacity building is needed, a very common requirement worldwide.

Laws and regulations express societal norms and values and are crucial instruments that help us respond to the challenge of water sustainability. Designing and implementing such responsive legal instruments also reveals the need for an integrated capacity building approach. These legal instruments should (after 5)

- Encourage administration at the appropriate hydrologic scale: watershed, multiwatershed and/or aquifer system.
- Foster internalization of the values and ethics of sustainable resource development.
- Encourage integrated approaches to water supply and sanitation, ecology, and public health.
- Prevent water allocation/usage policy-making from fragmenting among agencies.
- Promote integrated appraisals, notably environmental, economic, and sociopolitical impacts assessment of alternative actions.
- Enforce reward and penalty incentives that encourage sustainability.

And to achieve this, de facto, they should also

- encourage integrated capacity strengthening of governmental institutions, NGOs, community associations, and businesses to transition into more sustainable policies and practices, and work collaboratively.

Current practices of natural resource management and current development policies do not exploit the codependency between coupled water sustainability topics such as (1) water quantity management (e.g., conservation, higher efficiency, and demand management through equitable pricing), (2) water quality management (e.g., standards demanded by diverse users and uses), and (3) aquifer recharge protection and upland forest conservation. This occurs mainly because there is no systematic way to do this that accommodates diverse stakeholder interests and concerns and bridges institutional barriers while strengthening the required social and technological assets (6). Existing methods—with very few notable exceptions—are largely ineffective and not adaptive to changing sociopolitical and geophysical conditions. A recent body of work called participatory integrated capacity building (PICB) addresses this challenge.

PARTICIPATORY INTEGRATED CAPACITY BUILDING

What is participatory integrated capacity building (PICB)? From 1998–2000, local working groups in collaboration with the Mexican National Water Commission (CNA), coordinated by Downs (7), developed a PICB approach to urban water planning and management. Following an analysis that compared relatively sustainable development projects worldwide during the past 10–15 years (those yielding a steady stream of benefits *after* external support was removed) with a much larger number of *un*sustainable projects, six broad synergistic categories of capacity building emerged as critical components for success: (1) strengthening political and financial commitment; (2) strengthening human resources, including education, training, and awareness-raising; (3) strengthening information resources for policy-making (e.g., monitoring and GIS tools for data integration); (4) strengthening policies, regulations, enforcement, and verification; (5) applying appropriate technology and basic infrastructure (e.g., for water and wastewater treatment); and (6) stimulating local enterprise development (i.e., support products and services that provide socioeconomic sustainability. Each one builds on those before it with positive feedback.

This six-story framework is made up of elements that are operational, that is, for which we can design an action plan (Table 1). Table 1 was synthesized from fieldwork, workshops, and literature, notably Alaerts et al. (8), UNDP (9), UNCED (10,11). Although Table 1 considers the needs of an urban area, the same six levels can be extended to determine the needs of periurban and rural areas of the watershed. This integrated approach can be applied on different scales and contexts of settlement, so it can, in theory, also be applied to networks of settlements that comprise a watershed as a whole.

Using Table 1 (or a rural, periurban, or watershed-scale version of it) as our diagnostic template, local working groups undertaking strategic planning can assess existing capacity, then prioritize elements using several criteria, including cultural acceptability, potential cost-effectiveness, and strategic importance to solving the priority problems that have been identified as objectives. In the case study (7), strategic planning was carried out to identify the capacity-building needs of three pilot cities: Mérida, Yucatán; Ciudad Juárez, Chihuahua; and Atizapán de Zaragoza in the State of México. The project was successful in developing strategic work plans that were used to leverage support for the ongoing implementation phase. The main lesson learned in the field was that horizontal multistakeholder processes worked well, even where the norm is nonproductive competition among social groups. The author also saw the need to strengthen sociopolitical support and seed

Table 1. PICB Elements for Sustainable Water Supply and Sanitation in an Urban Context[a]

#	Element Name	Description
		Level 1. Strengthen sociopolitical support and seed financial support
1.1	Sociopolitical support	Build local, state, and federal political support, and commitments of in-kind support (labor and materials).
1.2	Seed finance	Obtain seed funding then leverage other funds for capital projects
		Level 2. Strengthen education and awareness-raising
2.1	Water and sanitation education at the community and school levels	Awareness-raising of water and sanitation issues in the community and the community's rights, obligations, and roles. Education of children at kindergarten, primary, secondary, and preparatory school levels.
2.2	Promotion of a sustainable water and sanitation culture	Use of media instruments and campaigns (TV, radio, print, Web) to promote water savings, efficiency and sanitation goals, and fair pricing. Encourage recognition of water as an economic good and provider of ecological services.
2.3	Train the local trainer	Train local trainers for community, scholastic, and professional education to remove dependency on external experts and make training self-sufficient (links to 2.1 and 2.5).
2.4	Education at university level	Local/regional university education at undergraduate and postgraduate levels to form skilled young professionals and researchers who support water management.
2.5	Professional training	Training in specialist technical and administrative topics for public and private sector participants in water management.
		Level 3. Strengthen information and monitoring to inform policy
3.1	Integrated data collection, processing, and interpretation for informed decision making	Design integrated collection, processing, and interpretation of key water, public health and ecology data, implement it, and integrate information in a GIS format for easy access and decision support.
3.2	Analysis by certified laboratories	Build capacity of laboratories to provide quality-assured analysis of key indicators from 3.1 (links to 2.4, 2.5, 3.1). Instigate locally accessible certification via partnerships with U.S. or Canadian institutions.
3.3	Periodic sustainability diagnosis	Check progress of the sustainability/capacity-building process at intervals for decision-making. Links to 3.1, 4.1.
3.4	Make applied research more cost-effective using a regional applied research network	Facilitate and instigate improved communication and collaboration among researchers to eliminate duplication of effort. Identify, quantify, and prioritize risks. Develop interventions and communication programs with water/sanitation stakeholders.
3.5	Regional institutional network	Facilitate and instigate improved communication and collaboration among public and private institutions (e.g., public health, water, ecology, urban planning).
3.6	Multistakeholder forum for decision making	Facilitate and instigate improved communication and collaboration among representatives from the community, public sector, private sector, and academia to take joint decisions.
		Level 4. Strengthen policy making, regulations, and compliance
4.1	Pollution prevention and reduction policies	Statutory endorsement of sustainable pollution prevention/reduction goals by political leaders at regional, national, state, and local levels.
4.2	Responsive regulatory framework	Review and improve the water supply and sanitation regulatory framework at the municipal, state, and federal levels to make them responsive to municipal, state, and federal needs.
4.3	Regulatory compliance program	Design, develop, and implement a compliance program, including verification and incentives with emphasis on voluntary compliance.
4.4	Tariff and rights schemes	Review and improve the legal and judicial schemes used to assign pollution tariffs and rights. Implement schemes with user buy-in. Equitable supply pricing and allocation for basic needs.
		Level 5. Strengthen basic sanitation infrastructure
5.1	Sustainable water supply	Improved coverage and quality of safe drinking water supply, increasing user's willingness to pay and financial viability of service. Combine sustainable use of groundwater and surface water with demand management and wastewater reuse.
5.2	Wastewater handling/disposal	Best appropriate available technologies (BAATs) for domestic, industrial, and agricultural wastewaters. Includes a spectrum from small-scale rural 'ecological' sanitation to treatment plants with reuse of effluent and viable biosolids.
5.3	Pollution prevention and waste minimization	Design, develop, and implement pollution-prevention programs including pretreatment of industrial effluents, source reduction, and alternative process technologies.
5.4	Solid waste handling/disposal	BAATS for solid waste, including landfill and safe incineration with energy cogeneration.
5.5	Stormwater drainage	Effective evacuation of rainwater and flood prevention. Includes avoidance of stagnant water bodies that harbor disease vectors.

(*continued overleaf*)

Table 1. (*Continued*)

#	Element Name	Description
	Level 6. Strengthen local enterprise development for support products and services	
6.1	Utility company performance	Improve utility company's effectiveness and efficiency at the technical (e.g., leak detection, metering) and administrative levels (e.g., billing)
6.2	Water supply tariffs and rights scheme	Review and improve the legal and judicial schemes used to assign water supply and sanitation tariffs by capacity to pay and rights to water by use priority (direct links to 4.1, 5.3)
6.3	Water supply and sanitation service quality	Improve water supply and sanitation service quality (e.g., continuity, pressure and water quality), in turn boosting users' willingness to pay and economic sustainability
6.4	Develop local water supply and sanitation market	Stimulate local and external provision of products and services to support the water and sanitation sector. Emphasize local providers' participation.
6.5	Stimulate sector investment	Stimulate enterprise development. Provide regulatory and fiscal incentives.

[a] Reference 7.

financial support (Level 1 of Table 1) from the outset and not wait for work plans to be designed. A related issue was to remove any dependency on external, nonlocal support and so make success contingent *primarily* on community resources complemented by some federal support for the first phase of implementation that addressed priority actions.

It is worth noting that the sixth PICB level—enterprise development and the 'market'—recognizes water as an economic good that should be priced according to users' ability to pay. For subsistence communities, a full public subsidy is appropriate to cover basic needs. Overprivatization risks occur when water services are run purely for profit, and marginalized communities unable to pay incur crippling water debts (12). This has occurred in South Africa and touches a nerve in many other places where water is viewed as both a public good and a human right that should not be controlled by commercial interests. We also recognize that the issue of user willingness to pay for water services is cultural (habits of free water) and also one of poor service quality: Why should a person pay for water that is not clean and only comes intermittently? Experience in one pilot site for the PICB project—Ciudad Juárez, a water-scarce, rapidly growing city across the border from El Paso, Texas—demonstrates that even low-income users *are* willing to pay for a reliable, good quality water and sanitation service in a way that allows public utilities to break even on costs.

Significantly, the Ciudad Juárez case was one in which the community of water users was involved in planning and designing from the outset such that a strong sense of ownership of the water supply and sanitation infrastructure was developed. When special interests attempted to take control of the project, the community mobilized to prevent this, one of the few instances of successful public mitigation of corruption in Mexico. This lends credence to our hypothesis that PICB can weather political instabilities and corrupt power plays and also change the public's sense of power over its destiny, restoring faith in the public process and partnerships with responsible institutions. In this way, the three types of sustainability—economic, social, and environmental—are satisfied through a societal capacity building process.

The other caveat to the sixth (and most controversial) level is that PICB places emphasis on *local* providers of products and services such that local entrepreneurs have incentives and opportunities to compete fairly in the water market with external suppliers. External suppliers too often supply inappropriate technological solutions to developing countries where the capacity to operate and maintain the foreign plant is weak or nonexistent. Unfortunately, there are far too many cases, for example, of wastewater treatment plants and analytical laboratories that have been abandoned because of a lack of personnel trained to operate and maintain them (6,7).

OPERATIONAL CONSIDERATIONS

Operational sustainability is a function of integrated capacity building (7). Experience of this capacity building project (7) revealed the need to be clear and concise about the objectives and rationale behind what appears to be a very ambitious and complex process. Integrated watershed management—any environmental management problem—must pass through three key stages *before* any capacity building occurs (although when projects are done in a participatory way, one can argue that societal capacity is already being built). These preplanning stages are (1) a baseline survey of existing conditions and priority needs; (2) problem formulation based on the assessment—identification of priority watershed problems; and (3) project objectives, often policy questions that seek to design and implement 'sustainable solutions' to priority problems. Once preferred solutions/management options are chosen for each priority problem using a multicriteria method (e.g., environmental and social impacts assessment, ESIA), the integrated capacity required *to sustain* each solution is determined. The way PICB fits into typical watershed project stages is shown in Fig. 2.

A participatory, integrated approach to capacity building has one major strategic advantage. Solutions of priority environment–development problems share significant amounts of capacity building requirements. For example, marginalized communities often face coupled sets of problems: (1) unsafe water supply; (2) inadequate wastewater and solid waste sanitation; (3) inadequate water-related disease detection, prevention, and control; (4) grossly inefficient irrigation; and (5) no conservation/mitigation of soil erosion caused by surface runoff. By addressing them

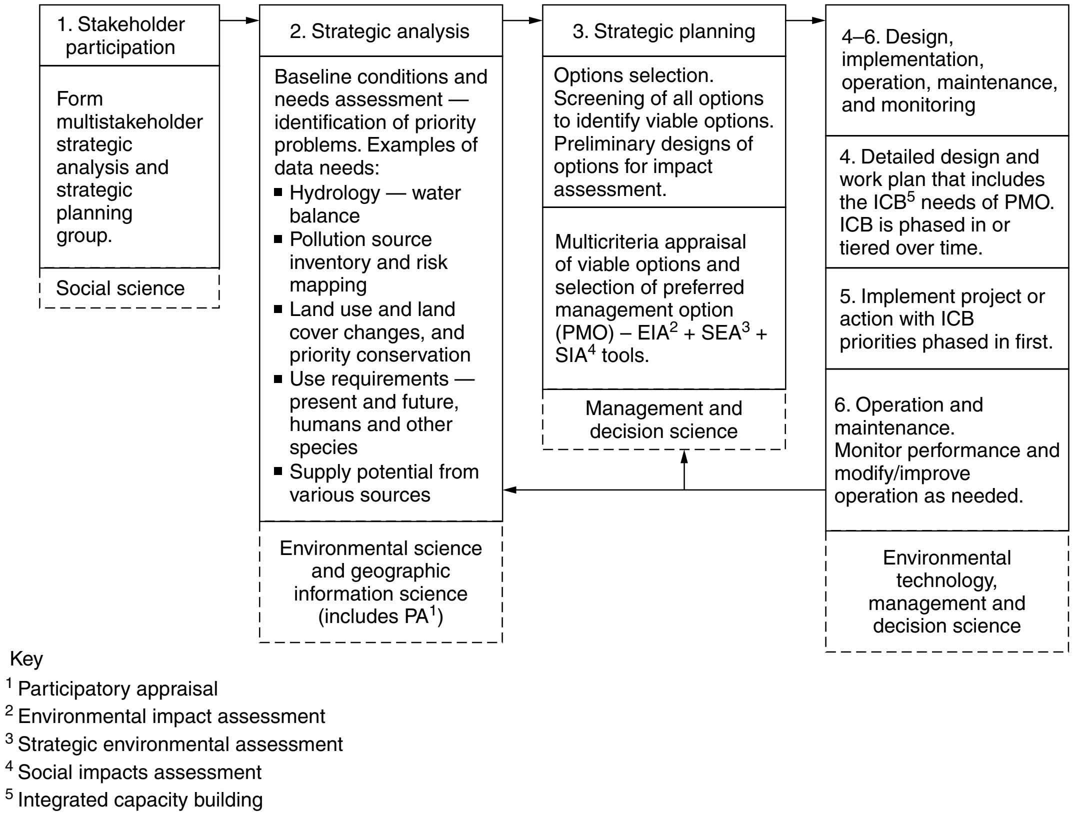

Figure 2. The key role of integrated capacity building (ICB) in sustainable watershed planning and management (6).

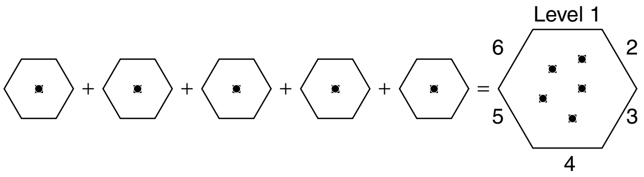

Figure 3. Strategic economies of scale emerge. Six levels of participatory integrated capacity building (PICB) support preferred solutions to five hypothetical priority problems. The integrated six levels are shown as hexagons, solutions as centered dots—the hexagons sustaining the dots. The final plan is shown as a large hexagon of integrated capacities sustaining the five coupled water-centered priority problems. The 'hexagonal' process of integrated capacity building is iterative, cyclical, continuous, just as the process of Fig. 2 is adaptive to new needs and priorities.

collectively, significant economies of scale emerge in the required societal capacity, as shown in Fig. 3.

MULTICAPITAL CONTEXT

Capacity building that supports sustainable development may also be viewed in the theoretical context of investments in, and returns on, strengthening different kinds of capital. Scoones (13) identifies five categories of capital assets that sustain human livelihoods:

1. *Natural Capital*: land, water, wildlife, biodiversity;
2. *Social Capital*: groups, networks, institutions of people;
3. *Human Capital*: skills, knowledge, healthy people;
4. *Physical Capital*: basic infrastructure that supports shelter, transportation, energy, water supply and sanitation, health care, education, and communications;
5. *Financial Capital*: income, savings, credit.

This means that to sustain water resources and watersheds requires the support of all five types of capital and further reinforces the concept that capacity building to strengthen this capital must be multifarious and integrated. Although the concept of capital is human-centered, it can be viewed in the context of ecosystem management, where humans are integral, supermodifying parts of the system. Watersheds are logical ecosystem delineations based on surface hydrology and topography.

Social capital is worthy of special note. Social capital is considered in institutional capacity building, but commonly, formal government agencies are addressed by donors. The central government in developing countries is often given funding from development agencies to build its capacity. Local nongovernmental organizations (NGOs) and community-based organizations (CBOs) typically have to rely on volunteer personnel and donations to function and build capacity. Universities still tend to build their own capacities through academic research grants, though some do partner with NGOs, CBOs, and local government to carry out projects that have clear practical goals. Empirical evidence points strongly to community-based natural resource management and participatory processes as keys to social sustainability. But how can this be done on the watershed scale required for ecological sustainability? The answer lies in strengthening the social capital of the watershed by forming collaborative networks of communities, principally CBOs, local NGOs, local (municipal) government, and local universities. When this is done, human capital and financial capital are also strengthened and become aligned with the mutual gains and common imperatives of watershed stewardship. For example, often in developing countries, marginalized rural agroforesters occupy the upper reaches of the watershed and become, de facto, 'producers' of water resources for downstream users because their actions affect zones of upland precipitation, groundwater recharge, and runoff. Both 'producers' and users share the common interest of watershed sustainability, and both must be involved in strategic planning. By networking and through capacity building coordinated by NGOs, marginalized communities can gain the social capital/political power they need to negotiate for mutual gains with influential user groups and government agencies. In Mexico, for example, the country has been divided into 26 watershed councils that administer water services to 100 million Mexicans. Unfortunately, the sustainability of this approach is called into question by the lack of participation by 'producers' and the clear domination of demand-driven policy-making by influential industrial and agricultural users. This is a useful example because it is a common equity issue in many countries that undermines watershed/ecosystem sustainability in three ways:

- conceptually, because equity issues are at the core of sustainable development;
- thermodynamically, because water-producing zones drive the water cycle; and
- practically, because without effective stakeholder participation, neither can diverse interests be reconciled, nor required integrated societal capacity be built.

CLOSING REMARKS

The concepts and practices of sustainable development, integrated watershed/ecosystem planning and management, equitable stakeholder participation, capital assets, and integrated capacity building are closely connected. The process may appear complex because of its multifaceted nature, but a strategic approach allows us to identify the most important issues, negotiate mutual gains for diverse stakeholder interests, and exploit the considerable economies of scale that emerge. Another advantage of integrated capacity building is that as well as mutual gains, the process delineates responsibilities, roles, and contributions as a collaborative socioecological enterprise.

BIBLIOGRAPHY

1. WCED (World Commission on Environment and Development). (1987). *Our Common Future*. Oxford University Press, New York.
2. UNDP (United Nations Development Programme). (2001). About Capacity 21. Available at: www.sdnp.undp.org/c21.
3. UNCED. (1992). *Earth Summit 1992—the United Nations Conference on Environment and Development*. The Regency Press, London, UK.
4. Howe, C. (1995). *Guidelines for the Design of Effective Water Management Institutions Utilizing Economic Instruments*. Report presented at Workshop on the use of economic principles for the integrated management of freshwater resources, United Nations Environment Programme (UNEP), Nairobi, Kenya.
5. Smith, D. and Rast, W. (1998). Environmentally sustainable management and use of internationally shared freshwater resources. In: *Watershed Management—Practice, Policies and Coordination*. R.J. Reimold (Ed.). McGraw-Hill, New York, p. 294.
6. Downs, T.J. (2002). A participatory integrated capacity building approach to the theory and practice of sustainability—Mexico and New England Watershed Case Studies. In: *International Experiences on Sustainability*. W.L. Filho (Ed.). Peter Lang, Frankfurt am Main, pp. 179–205.
7. Downs, T.J. (2001). Making sustainable development operational: Capacity building for the water supply and sanitation sector in Mexico. *J. Environ. Plann. Manage.* **44**(4): 525–544.
8. Alaerts, G.J., Blair, T.L., and Hartvelt, F.J.A. (Eds.). (1991). *A Strategy for Water Sector Capacity Building*, *IHE Report Series* 24. International Institute for Hydraulic and Environmental Engineering (IHE), Delft, The Netherlands and UNDP, New York.
9. UNDP (United Nations Development Programme). (1998). *Capacity Building for Sustainable Management of Water Resources and Aquatic Environment: A Strategic Framework for UNDP*. UNDP Water Strategy, UNDP, New York.
10. UNCED (United Nations Conference on Environment and Development). (1992). Transfer of environmentally sound technology, cooperation and capacity building, Agenda 21, Chapter 34. Available at: www.un.org/esa/sustdev/agenda21.
11. UNCED. (1992). National mechanisms and international cooperation for capacity building in developing countries, Agenda 21, Chapter 37. Available at: www.un.org/esa/sustdev/agenda21.
12. Gleik, P., Wolff, G., Chalecki, E.L., and Reyes, R. (2002). *The New Economy of Water: The Risks and Benefits of Globalization and Privatization of Fresh Water*. Pacific Institute, Oakland, CA.
13. Scoones, I. (1998). *Sustainable Rural Livelihoods: A Framework for Analysis*. Working Paper 72, Institute of Development Studies, Brighton, UK.

WASTEWATER CHARACTERIZATION

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An understanding of the nature of wastewater is fundamental to the design and operation of wastewater collection, treatment, and reuse facilities. Wastewater is characterized in terms of its physical, chemical, and biological composition. Greater emphasis is being placed on wastewater characterization because of its changing characteristics and the imposition of stricter limits on wastewater discharges that are used beneficially. Thorough characterization of wastewater in the design and optimization of biological treatment processes is increasingly important due to the advent of process modeling. Process modeling for activated sludge, as it is currently conceived, requires experimental assessment of kinetic and stoichiometric constants.

The principal physical properties and the chemical and biological constituents of wastewater and their significance are as follows.

PHYSICAL CHARACTERISTICS

Physical characteristics are those characteristics that respond to the senses of sight, touch, taste, and smell. The most important physical characteristic of wastewater is its total solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Other important physical characteristics include particle size distribution; turbidity; color; transmittance; temperature; conductivity; and density, specific gravity, and specific weight. Table 1 illustrates common physical characteristics, their analyses, and importance in wastewater treatment.

CHEMICAL CHARACTERISTICS

The chemical constituents of wastewater are typically classified as inorganic and organic. Inorganic chemical constituents of concern include nutrients, nonmetallic constituents, metals, and gases. Organic chemical constituents of concern are BOD, COD, and specific organic compounds.

Inorganic Chemical Characteristics

The sources of inorganic nonmetallic and metallic constituents in wastewater derive from background levels in the water supply, from the additions resulting from domestic use, from the addition of highly mineralized water from private wells and groundwater, and from industrial use. Because the concentration of various inorganic constituents can greatly affect the beneficial uses for the waters, the constituents in each wastewater must be considered separately. Table 2 illustrates the common inorganic chemical characteristics, their analyses, and importance in wastewater treatment.

Organic Chemical Characteristics

Organic compounds or organics are normally composed of combinations of carbon, hydrogen, and oxygen, together with nitrogen in some cases. Many organics are soluble in water. Most natural organics consist of decay products of organic solids, synthetic organics are usually the result of wastewater discharges or agricultural practices. The organic matter in wastewater typically consists of proteins (40–60%), carbohydrates (25–50%), and oils and fats (8–12%). Along with the proteins, carbohydrates, fats and oils, and urea, wastewater typically contains small quantities of a very large number of different synthetic molecules, whose structures range from simple to complex.

Organic constituents of interest in wastewater are classified as aggregate and individual. Aggregate organic constituents are comprised of a number of individual compounds that cannot be distinguished separately. Laboratory methods commonly used today to measure aggregate

Table 1. Common Analyses Used to Assess the Physical Constituents in Wastewater

Test[a]	Abbreviation/Definition	Use or Significance of Test Results
Total solids	TS	To assess the reuse potential of wastewater and to determine the most suitable type of operations and processes for treating it
Total volatile solids	TVS	
Total fixed solids	TFS	
Volatile suspended solids	VSS	
Fixed suspended solids	FSS	
Total dissolved solids	TDS (TS-TSS)	
Volatile dissolved solids	VDS	
Total fixed dissolved solids	FDS	
Settleable solids		To determine those solids that will settle by gravity in a specified time period
Particle size distribution	PSD	To assess the performance of treatment processes
Turbidity	NTU[b]	Used to assess the quality of treated wastewater
Color	Light brown, gray, black	To assess the condition of wastewater (fresh or septic)
Transmittance	% T	Used to assess the suitability of treated effluent for effluent disinfection
Odor	TON[c]	To determine if odors will be a problem
Temperature	°C or °F	Important in the design and operation of biological processes in treatment facilities
Density	ρ	
Conductivity	EC	Used to assess the suitability of treated effluent for agricultural applications

[a] Details of various tests may be found in Reference 1.

[b] NTU = nephelometric turbidity unit.

[c] TON = threshold odor number.

Table 2. Common Analyses Used to Assess the Inorganic Chemical Constituents in Wastewater

Test[a]	Abbreviation/Definition	Use or Significance of Test Results
Free ammonia	NH_3	Used as a measure of nutrients present and the degree of decomposition in the wastewater; the oxidized form can be taken as a measure
Organic nitrogen	Org N	
Total Kjeldahl nitrogen	TKN (Org N + NH_4^+)	
Nitrites	NO_2^-	
Nitrates	NO_3^-	
Total nitrogen	TN	
Inorganic phosphorus	Inorg P	
Total phosphorus	TP	
Organic phosphorus	Org P	
pH	$pH = -\log[H+]$	A measure of the acidity or basicity of an aqueous solution
Alkalinity	$HCO_3^- + CO_3^{2-} + OH^- - H^+$	A measure of the buffering capacity of wastewater
Chloride	Cl^-	To assess the suitability of wastewater for agricultural reuse
Sulfate	SO_4^{2-}	To assess the potential for the formation of odors and may impact the treatability of waste sludge
Metals	As, Cd, Ca, Cr, Co, Cu, Pb, Mg, Hg, Mo, Ni, Se, Na, Zn	To assess the suitability of wastewater for reuse and for toxicity effects in treatment. Trace amounts of metals are important in biological treatment
Specific inorganic elements and compounds		To assess the presence or absence of specific constituents
Various gases	O_2, CO_2, NH_3, H_2S, CH_4	To assess the presence or absence of specific gases

[a] For test details, see Reference 1.

Table 3. Common Analyses Used to Assess the Organic Chemical Constituents in Wastewater

Test[a]	Abbreviation/Definition	Use or Significance of Test Results
Five-day carbonaceous biochemical oxygen demand	$CBOD_5$	A measure of the amount of oxygen required to stabilize a waste biologically
Ultimate carbonaceous biochemical oxygen demand	UBOD (also BOD_U, BOD_L)	A measure of the amount of oxygen required to stabilize a waste biologically
Nitrogenous oxygen demand	NOD	A measure of the amount of oxygen required to oxidize biologically the nitrogen in the wastewater to nitrate
Chemical oxygen demand	COD	Often used as a substitute for the BOD test
Total organic carbon	TOC	Often used as a substitute for the BOD test
Specific organic compounds and classes of compounds	MBAS[b], CTAS[c]	To determine the presence of specific organic compounds and to assess whether special design measures are needed for removal

[a] For test details, see Reference 1.

[b] MBAS = Methylene blue active substances

[c] CTAS = cobalt thiocyanate active substances

organic matter (typically greater than 1 mg/L) in wastewater include BOD, COD, and TOC. Both aggregate and individual organic constituents are of great significance in the treatment, disposal, and treatment of wastewater. Table 3 illustrates common organic chemical constituents, their analyses, and importance in wastewater treatment.

BIOLOGICAL CHARACTERISTICS

The biological characteristics of wastewater are of fundamental importance in controlling diseases caused by pathogenic organisms of human origin and because of the extensive and fundamental role played by bacteria

Table 4. Common Analyses Used to Assess the Biological Constituents in Wastewater

Test[a]	Abbreviation/Definition	Use or Significance of Test Results
Coliform organisms	MPN (most probable number)	To assess the presence of pathogenic bacteria and the effectiveness of the disinfection process
Specific microorganisms	Bacteria, protozoa, helminths, viruses	To assess the presence of specific organisms in connection with plant operation and for reuse.
Toxicity	TU_a and TU_c,	Toxic unit acute, toxic unit chronic

[a] For test details, see Reference 1.

and other microorganisms in decomposing and stabilizing organic matter in nature and wastewater treatment plants. Most species of pathogens such as bacteria, viruses, and protozoa can survive in wastewater and maintain their infectious capabilities for a significant period of time. Table 4 illustrates common biological characteristics, their analyses, and importance in wastewater treatment.

BIBLIOGRAPHY

1. APHA. (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edn. American Public Health Association, Washington, DC.

READING LIST

Metcalf & Eddy. (2003). *Wastewater Engineering: Treatment, Disposal, Reuse*, 4th Edn. McGraw-Hill, New York, pp. 10, 30, 31.

CHEMICALLY ENHANCED PRIMARY TREATMENT OF WASTEWATER

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Chemically enhanced primary treatment (CEPT) is a wastewater treatment process in which small doses of chemical compounds are added to wastewater in order to increase the operating efficiency of sedimentation basins. The chemicals cause the suspended particles to clump together via the processes of coagulation and flocculation. The particle aggregates, or flocs, settle faster and thus enhance the treatment efficiency, which is measured as the removal of solids, organic matter, and nutrients from the wastewater. The chemicals utilized in CEPT are the same ones commonly added in potable water treatment (e.g., metal salts and/or organic polymers).

CEPT allows the sedimentation basins to operate at twice the overflow rate (defined as the flow per unit area in the sedimentation basin) of conventional primary treatment, while maintaining higher removal rates of total suspended solids (TSS) and biochemical oxygen demand (BOD). (The increase in BOD removal by CEPT is usually larger than that of suspended solids because of the removal through precipitation of colloidal BOD.) The treatment infrastructure is thus smaller, which reduces capital costs. The capital costs of a CEPT plant are approximately 25% of the capital costs of a conventional secondary treatment plant of equal capacity, while the operational costs are one-half those of a conventional secondary treatment plant (1). Additionally, CEPT provides the opportunity for either reducing the size of subsequent biological treatment units, or increasing the capacity of existing conventional treatment plants.

Table 1. Comparison of Removal Efficiencies (1)

Treatment Method	TSS, %	BOD, %
Conventional primary treatment	55	35
Conventional primary + biological secondary treatment	90	85
Chemically enhanced primary treatment	85	55

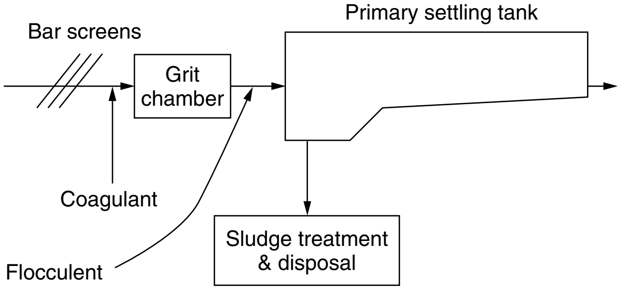

Figure 1. Schematic of conventional primary treatment and CEPT. (The addition of a flocculent in the form of organic polymers is optional.)

CEPT is almost as efficient as secondary treatment with respect to removal efficiencies (Table 1). CEPT may be implemented using a dedicated "CEPT tank" (i.e., a settling tank specially designed for CEPT) or by retrofitting a conventional primary treatment facility or stabilization ponds (2–5). The latter two incarnations of CEPT are relevant when upgrading overloaded existing systems (6).

A conventional primary treatment process consists of bar screens, a grit chamber, and a settling tank (Fig. 1). To upgrade a conventional primary treatment facility to a CEPT facility, all that is needed is the addition of a chemical coagulant (and optionally a flocculent). With CEPT's high surface overflow rate, the sedimentation basins will not need to be large when compared to conventional primary sedimentation basins (7).

CEPT has been used for over one hundred years, yet it is not as commonly found as would be expected upon analysis of its performance. The misconception is that CEPT dramatically increased sludge production. However, CEPT is used today with a minimal coagulant dosage (10–50 mg/L), and the chemicals themselves make only a slight contribution to the total sludge production. The greatest portion of the increase of sludge production is due to the increased solids removal in the settling tank.

CEPT does not preclude secondary or tertiary treatment. It makes any subsequent treatment smaller and less costly due to the increased efficiency. CEPT is a relatively simple technology providing a low-cost and effective treatment, which is easily implemented over existing infrastructure (6,8,9). CEPT is also one of the least expensive wastewater treatment processes in which the effluent can be effectively disinfected.

BIBLIOGRAPHY

1. National Research Council. (1992). *Wastewater Management in Urban Coastal Areas*. National Academy Press, Washington, DC.

2. Ødegaard, H., Balmer, P., and Hanaeus, J. (1987). Chemical precipitation in highly loaded stabilization ponds in cold climates: Scandinavian experiences. *Water Sci. Technol.* **19**(12): 71–77.
3. Hanaeus, J. (1991). Chemical precipitation in ponds for wastewater treatment. *Vatten* **47**(2): 108–116.
4. Hanaeus, J. (1991). Sludge accumulation in ponds for wastewater treatment using alum precipitation. *Vatten* **47**(3): 181–188.
5. Hanaeus, J. (1991). *Wastewater Treatment By Chemical Precipitation in Ponds*. [Ph.D. thesis]. Lulea University of Technology, Lulea, Sweden.
6. Harleman, D.R.F. and Murcott, S.E. (1992). *Upgrading and Multi-Stage Development of Municipal Wastewater Treatment Plants: Applicability of Chemically Enhanced Primary Treatment*. Tech. rep., World Bank.
7. Harleman, D.R.F., Harremöes, P., and Yi, Q. (1997). Hong Kong Harbor cleanup: international panel reviews plans for treatment upgrade. *Water Environ. Technol.*, 47–50.
8. Harleman, D.R.F. and Murcott, S. (2001). CEPT: challenging the status quo. *Water* **21**: 57–59.
9. Harleman, D.R.F. and Murcott, S. (2001). An innovative approach to urban wastewater treatment in the developing world. *Water* **21**: 44–48.

GETTING OUR CLEAN WATER ACT TOGETHER

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City of Wyoming, Michigan
Wyoming, Michigan

Sometimes, having ideas or understanding ideas takes a long time. Maybe it is like fine wine. This idea was born in the current business climate of mission statements, defining the product, public perception, reality and principles and practices of Total Quality Management (TQM—which has reached the stage of maturity where an individual can now be a Certified Master TQMer). The idea: our industry's main product is clean water. No duh! (Not a TQM phrase.) This may not be a great revelation to anyone except maybe me. So what is my point? It is simply a question, "Why do we call them wastewater plants when the main product is clean water?" This could be rephrased to say "What cookie factory calls itself the flour, lard, baking soda, raisin, cinnamon, chocolate chip factory'?" This is the topic of this article.

As I began to think about this idea, I kept asking myself why we did not call the end product "clean water" right from the start. I can understand the use of the term "wastewater treatment plant" but not the shortened term "wastewater plant" now in common use. The subtle implication is that somehow "wastewater" is the product. It was starting to bother me. The message is inconsistent. There is something subliminally wrong with giving a negative connotation to something that does not deserve it. The well-worn axiom may fit here: If it walks like a duck and swims like a duck and quacks like a duck, it's a duck. I came to the conclusion it was time to call a duck "clean water." We spend a great deal of time and money trying to convince the dozens of students and the visiting public how well we clean it—just to call it "wastewater."

Before proceeding, I need to thank the author or authors of the word "wastewater" (you know, the word that is never recognized by your spell checker until you add it). Incidentally, if Virgil Langworthy, a Michigan resident and long-time water professional, is not the originator of the word, he can certainly be credited with being one of the early purveyors of it in the early 1960s. "The reason for the change" he said, "was the bad perception of the term 'sewage.'" And this was before TQM.

The word "wastewater" is far better than "sewerage" or "sewage" and was a great addition to our descriptive word quiver for our evolving industry language. These words have served us well over recent years, but the time has come to add and use the term "clean water" as the focus or our business. I must hasten to add that these traditional words should not be abandoned but further defined and applied when these new definitions warrant their use. "Wastewater" should now properly be redefined "as the used water leaving a household or industry and entering a sewer system." It could be also used as another way to describe plant influent but NOT what leaves a plant.

I read once that traditional Eskimo culture has more than 30 terms in its language to describe snow. The words were needed to describe the varying conditions of the harsh climate. We add more words to language to communicate concept, especially where we spend great amounts of time and study. One additional example would be the in computer industry. How many of us knew what "W.Y.S.I.W.Y.G." was in the early 1980s? (For those unfamiliar with that term, it was an acronym for "What you see is what you get," but it lost its periods and made its way into the dictionary as a genuine word.)

I decided to put action to my thoughts and began to use "clean water plant" in conversation with my co-workers and neighboring plants. Surprising resistance to the idea came from some of my brothers in drinking water plants who said things like "You are the 'dirty water people' and we are the 'clean water people'." The other comment was "if you use the term 'clean water' at a wastewater plant, the public will be confused." My response is simply to point out how frequently after a tour of the wastewater plant many people comment "I always wondered where my drinking water came from" when they leave. At that point, I feel like a total failure as a public educator. I do not think the public cares about our heterohydrophobic (fear of different kinds of water) distinctions, as long as they are receiving good service.

If there is confusion about the use of the term, it is because we in the clean water industry have failed to appropriate it and use it. The United States Congress gave us the "clean water" title 25 years ago with the passage of the Clean Water Act (CWA) which set discharge standards for WASTEWATER PLANTS since 1972. They then passed the Safe Drinking Water Act (SDWA) a few years later for DRINKING WATER PLANTS. What are we waiting for? Is not more than 25 years long enough to wait and see if the 800-pound gorilla (CWA) sitting in our living room is here to stay permanently? NEWS FLASH: He's *here to stay and while we were waiting, his whole family moved in and one of them, some say, is bigger and uGLIer (GLI is*

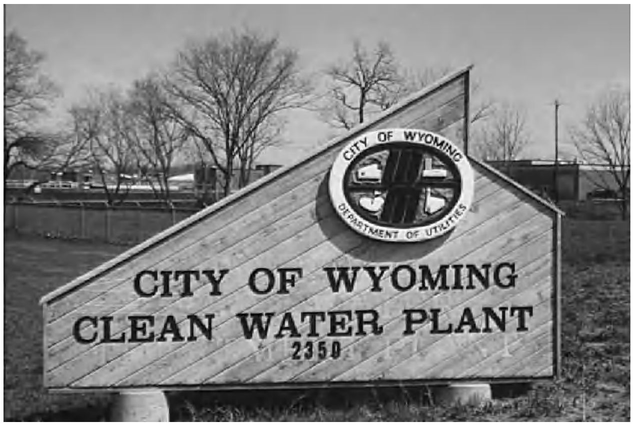

Figure 1. Sign at Wyoming waste water treatment plant.

an intentional reference to the Great Lakes Initiative). And they all want bananas!

Our society wants clean water, and it takes lots and lots of bananas to make it happen and keep it happening. We are giving society clean water now and we need to continue this good work, BUT make sure we acknowledge it is discharged from a Clean Water Plant. We all know bananas do not grow on trees (or is that money), and we do know how demanding gorillas can be. A word to the wise: feed the gorillas and suggest family planning.

In summary, I propose a global renaming of our "wastewater treatment plants" to "clean water plants." The drinking water plants are left with titles such as "safe drinking water plants," "drinking water plants," and/or "water filtration plants." I know of no drinking water plants that use the term "clean water" in their title. So, it is time to drive this idea out of the giant parking lot of ideas whose time has not yet come onto the freeway of ideas in everyday usage. I know the City of Wyoming, Michigan's Clean Water Plant is already on the freeway entry ramp hoping to see you at our clean water destination—the banana plantation (Fig. 1).

INADEQUATE TREATMENT OF WASTEWATER: A SOURCE OF COLIFORM BACTERIA IN RECEIVING SURFACE WATER BODIES IN DEVELOPING COUNTRIES—CASE STUDY: EASTERN CAPE PROVINCE OF SOUTH AFRICA

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INTRODUCTION

Sanitation, in its broadest meaning, refers to the formulation and application of measures designed to protect public health. It also covers the purification of wastewater and sewage before it is returned to the water cycle. Usually, wastewater treatment involves collecting the wastewater in a central, segregated location (the wastewater treatment plant) and subjecting the wastewater to various treatment processes (biological treatment and disinfection of the final effluent). The characteristics of these wastes, which are significant in pollution, are the suspended solids, oxygen demand of the organic matter (BOD), the coliform bacteria, and other pathogenic micro-organisms (1).

The presence of coliform bacteria in drinking water is the most common reason for the violation of the water standards. Coliform bacteria have a long history in water quality assessment, mainly because of their association with fecal pollution and relatively easy and rapid detection. Some members of the group are almost conclusively of fecal origion, whereas others may also multiply in suitable water environments (2,3). The South African General and Special Standards stipulate that treated sewage should comply with a standard of nil fecal coliforms/100 ml (Act 96 of May 18, 1984 No. 9225, Regulation 991). The efficiency of a wastewater treatment plant in removing harmful micro-organisms from the influent is therefore of utmost importance. Failure to remove such micro-organisms will result in harmful pathogens returning into the receiving surface water body. Being a major source of pathogens that are carried in water, monitoring sewage for pathogens has been demonstrated to be an excellent epidemiological tool for determining what diseases may be prevalent in the community at any one moment (4).

In the developing world, much of the population consumes untreated and nonpiped drinking water. Typically, people collect water from any available source and store it in a vessel or a container in the dwelling for domestic and potable use, often without treatment or protection from further contamination. It is therefore not surprising that an estimated 15–30% (5) of community gastrointestinal diseases in developing countries are attributed to unsafe drinking water, with studies indicating similar percentages (15–20%) of waterborne diarrheal diseases (6). These problems could be attributed to the unavailability of proper sanitation methods or when the existing methods are not functioning adequately (7). Severe problems with the microbial quality of water could be expected, especially in rural and informal settlements. In these areas, widespread scarcity, gradual destruction, and increased pollution of water sources exists. The situation is aggravated by the existence of many insufficient, poorly operated or maintained sanitation services (8). Fecal contamination of water supplies by untreated and/or inadequately treated sewage effluents entering rivers and dams that serve as the source of municipal water supplies create conditions for the rapid spread of pathogens, a problem encountered in both the developing and the developed parts of the world (9).

Although the Eastern Cape province of South Africa, where this study was conducted, is predominantly rural in composition, both rural and urban sectors can be found within the province. The Eastern Cape Province is one of South Africa's poorest provinces, where the official poverty rate in 1998 was at least 70%, and only a quarter of all households possessed an inside water tape (10). Although great strides have been made in effort to provide access to clean water, many small villages still lack safe water supplies (11), whereas large communities have water treatment plants, which fail to provide potable water of high quality to their consumers (12). The areas without water supplies use water directly from available and often contaminated sources without any treatment. In both cases, communities are therefore exposed to water-related diseases. This situation also pertains in most of the communities in the poor areas of developing countries.

The aim of this study was to evaluate the efficiency of the urban, semiurban, and the rural wastewater treatment plants for the removal of coliform bacteria in order to establish the relationship between the microbiological quality of the final effluent and that of the receiving water body, which may further influence infection and disease in the community. Our intention was to provide information that could assist water authorities in developing countries to address problems in the management of wastewater treatment plants in terms of microbiological standards of the effluent as set down by official guidelines, such as those in South Africa (13,14). Two of the four wastewater treatment plants used during the present survey, i.e., in Alice and Fort Beaufort, serve predominantly rural areas, whereas the other two wastewater treatment plants, i.e., East London and Dimbaza, serve urban and semiurban communities, respectively.

MATERIALS AND METHODS

Study Sites

Four wastewater treatment plants that serve the Buffalo City and Nkonkobe Municipal areas in the Eastern Cape Province of South Africa were used in the present study. The wastewater treatment plants are located in urban (East London–East Bank Reclamation Works), semiurban (Dimbaza), and rural areas (Alice and Fort Beaufort). The activated sludge system is the biological wastewater treatment used in all plants, followed by chlorination of the final effluent.

The final effluent from the East Bank Reclamation Works is discharged into the Indian Ocean between Nahoon and Eastern Beach at Bats Cave and into a pond for the irrigation of a nearby golf course. Supernatant liquor from the sedimentation tanks is channeled into a fish pond located within the plant premises. The Dimbaza wastewater treatment plant discharges its final effluent into a stream that empties into the Tembisa sewerage dams. The Alice wastewater treatment plant is situated on the banks of the Tyume River, which is also used as the receiving water body for the final effluent from the plant. The final effluent from Fort Beaufort Sewage Works is discharged into the Kat River. All these final effluents or receiving water bodies are often used by the communities for one or various purposes, which include domestic, agricultural, or recreational purposes.

Sample Collection

Wastewater samples were collected weekly from different stages (the raw influent, the aerobic zone, the clarifier, the final effluent, and the receiving water body) of the four plants between August and October 2003. For the microbiological quality analyses, sampling was done aseptically into sterile glass bottles. For the effluent samples, sodium thiosulphate (*ca* 17.5 mg/L) was added to bottles before autoclaving. The samples were then placed in ice bags and transported to the base laboratory at the University of Fort Hare for analyses within 2–4 h after collection.

Analyses of Wastewater and Receiving Water Body Samples

Free Chlorine Residual. The concentrations of free chlorine residual in the treated effluents were determined using a multiparameter ion-specific meter (Hanna BDH-laboratory).

Coliform Counts. The membrane filtration technique was considered, but the method proved to be too sensitive for the analyses of the samples. Consequently, the standard spread plate procedure was used during the study period. Three different selective media, namely Chromocult coliform agar (Merck), Fluorocult *E. coli* 0157: H7 agar (Merck), and Sorbitol–MacConkey agar (Mast Diagnostics) were used for the isolation of coliforms and other *Enterobacteriaceae* (Table 1). The agars were prepared according to the manufacturer's instruction. Water samples were analyzed for the above microorganisms using internationally accepted techniques (15). The enumeration of coliforms was based on the color of colonies corresponding to presumptive coliforms as indicated in Table 1.

Identification of Coliform Isolates. Bacterial colonies from the influent, final effluent, and the receiving water

Table 1. Summary of the Various Bacterial Colonies and Presumptive Coliform Strains Isolated from Different Culture Media

Culture Medium	Presumptive Bacterial Strain	Color of the Colony
Chromocult coliform agar	*Citrobacter freundii*	Salmon to red
	Escherichia coli	Blue to violet
	Salmonella enteritidis	Colorless
Fluorocult *E. coli* 0157:H7 agar	*Proteus Mirabilis*	Brown
	Enterobacter aerogenes	Yellow
	Escherichia coli 0157:H7	Colorless
	Salmonella typhimurium	Yellow with black center
Sorbitol–MacConkey agar	*Escherichia coli 0157:H7*	Colorless

body samples differing in size, shape, and color were randomly selected from different plates and transferred onto the same medium by streak plate technique and incubated at 37 °C for 24 h. These were further isolated on MacConkey agar (Biolab) by the same method and incubated at 37 °C for 24 h, thereafter they were further purified by the same method at least three times using nutrient agar biolab before gram staining was done. Oxidase tests were then conducted on those colonies that were gram negative. The 20E API kit was used for the oxidase-negative colonies and the strips were incubated at 37 °C for 24 h. The strips were then read and the final identification was secured using API LAB PLUS computer software (BioMérieux, Marcy l'Etoile, France).

RESULTS

Concentration of Free Available Chlorine (Residual) in the Final Effluents

The concentrations of the free chlorine residuals fluctuated in all the plants with the exception of the East London wastewater treatment plant (Table 2). Chlorine overdosing occurred during the first two months of the study period (August and September) in the Fort Beaufort plant and in September in the Dimbaza plant. A constant concentration of free chlorine residual was noted during the whole study period in the East London plant, whereas low concentrations of free chlorine residuals were noted in the final effluent of the Alice wastewater treatment plant (Table 2). Although the 1996 South African Guidelines do not specify any standard for the concentration of free chlorine residual in the treated effluent, this study considered those for domestic water supplies, which recommend ranges of 0.3–0.6 mg/l as ideal free chlorine residual concentration and 0.6–0.8 mg/l as good free chlorine residual concentration with insignificant risk of health effects (14). With the exception of the final East London treated effluents, none of the wastewater plant treated effluents complied with the above-mentioned recommended limits for domestic water supplies.

Performances of Wastewater Treatment Plants for the Removal of Presumptive Coliforms

The four wastewater treatment plants were investigated for their efficiency for the removal of coliforms. The enumeration of coliforms in each zone of different wastewater treatment plant was done in order to assess whether there was in fact a decrease in the number of presumptive coliforms as the wastewater flowed through the treatment processes, a practice that also served to identify possible malfunctioning in any of the wastewater treatment plant zones.

Table 2. Concentrations of Free Chlorine Residual in the Final Effluents from during the Study Period (Ranges) (No. of the Samples for Each Plant; 12)

Wastewater Treatment Plant	Chlorine Residual (mg/l) Ranges	Chlorine Residual (mg/l) Means
Dimbaza	0.93–2.5	1.85
East London	0.59–0.66	0.58
Alice	0.03–0.66	0.24
Fort Beaufort	0.16–4.33	2.07

In general, a gradual removal of presumptive coliforms was observed through the different zones of the wastewater treatment plants. The data, however, reflected variations with regard to both the patterns and the efficiency of each plant for the removal of coliform micro-organisms (Figs. 1 and 2).

In the influent samples, both the Dimbaza and East London wastewater treatment plants had higher mean coliform counts (ranging between 4.6 log cfu/ml and 6.6 log cfu/ml for Dimbaza and between 5.3 log cfu/ml and 7 log cfu/ml for East London) than those found in Alice (5–6 log cfu/ml) and Fort Beaufort (4.8–6.2 log cfu/ml). This observation results from the fact that both Dimbaza and East London are urban and semiurban areas, respectively, and they are also both industrialized and, hence, much more densely populated than Alice and Fort Beaufort. Results in Figs. 1 and 2 also show that, although in Dimbaza, East London, and Alice wastewater treatment plants, a noticeable decrease in the mean coliform counts was observed in the clarifier zone, high mean coliform counts were still noted in the Fort Beaufort wastewater treatment plant, which was because of the absence of a functional clarifier.

The mean ranges for coliforms (0–0.2 cfu/ml) in the Dimbaza wastewater treatment's final effluent complied with the South African General and Special Standards, which stipulate that treated sewage effluents must have a standard of nil fecal coliforms (Act 96 of May 18, 1984 No. 9225, Regulation 991). The Dimbaza's effluent was also within the limits set for agricultural purposes (irrigation), which are ≤10,000 count/100 ml for fecal coliform and ≤1 counts/100 ml for *E. coli* (16). In East London, Alice, and Fort Beaufort wastewater treatment plants, the mean coliform ranges in the treated effluent samples were 1.5–2.9 log cfu/ml, 0.8–2.6 log cfu/ml, and 0.6–2.9 log cfu/ml, respectively. These results suggest that the general microbiological qualities of these effluents did not comply with the limits set by the South African Authorities, especially in terms of fecal coliforms.

Generally, an increase occurred in presumptive coliform counts from the final effluent samples to the receiving water body samples of the Dimbaza, Alice (presumptive *E. coli* being the exception), and Fort Beaufort wastewater treatment plants, whereas a decrease occurred in the mean counts of all presumptive coliforms from the East London water receiving body samples (Fig. 2). The means for coliforms in the receiving water bodies ranged between 0.2 and 1.5 log cfu/100 ml for Dimbaza, between 0 and 2.5 log cfu/100 ml for East London plant, between 0.25 and 3 log cfu/100 ml for the Alice plant, and between 1.5 and 3.25 log cfu/100 ml for Fort Beaufort. The results suggest that the receiving water bodies of all the plants did not comply with the limits set for domestic (0–10 counts/100 ml for total coliform, 0 counts/100 ml for fecal coliforms) and recreational (0–130 counts/100 ml for fecal coliform, *E coli* 0–130 counts/100 ml) use (13,14,17).

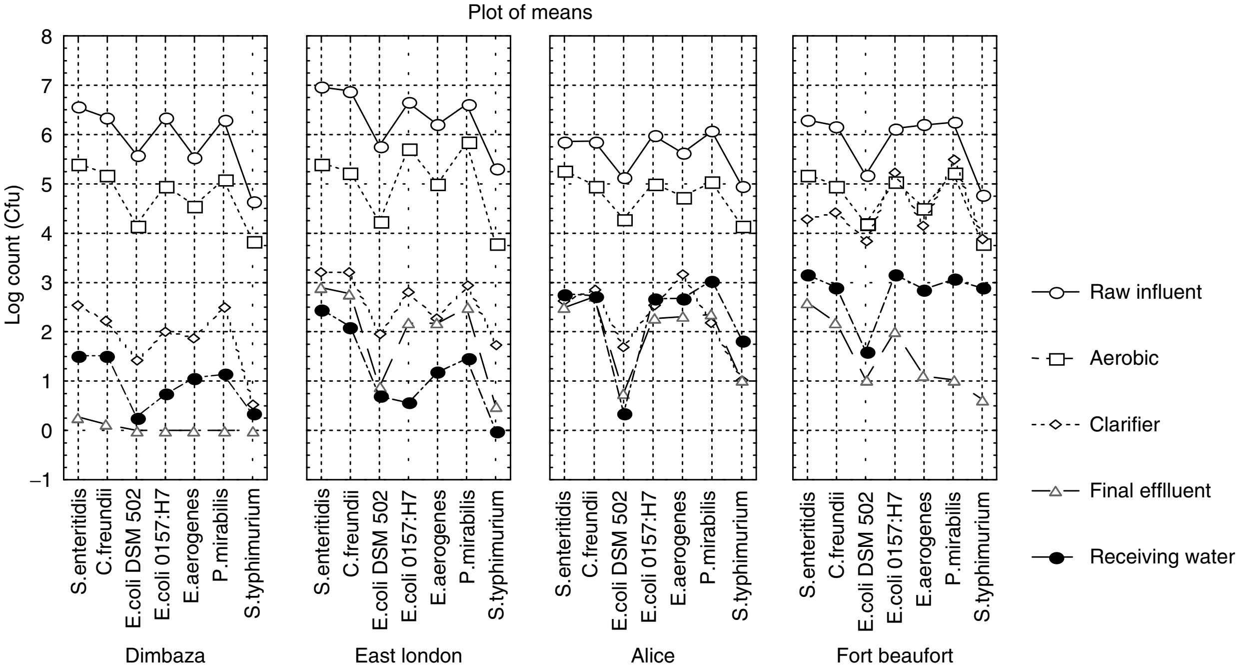

Figure 1. Plot of mean counts for presumptive coliforms obtained from the different zones of the Dimbaza, East London, Alice, and Fort Beaufort wastewater treatment plants and their water receiving bodies.

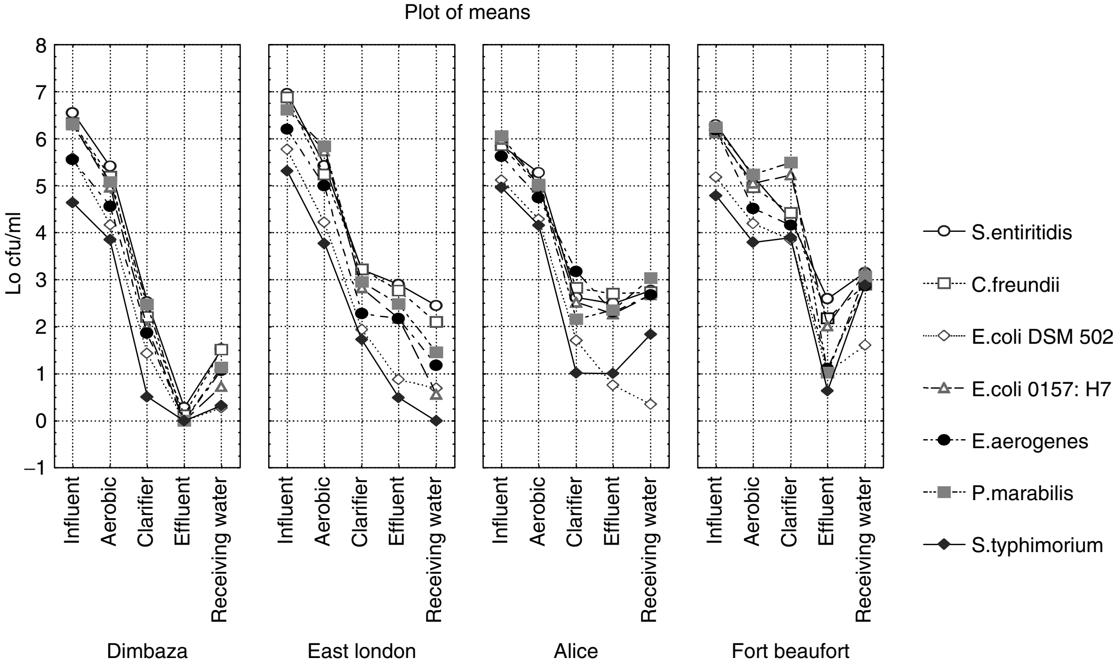

Figure 2. Performance of the different wastewater treatment plants for the removal of the presumptive coliform bacteria.

Identification and Bacterial Isolates

According to the API 20E system, the oxidase test and the gram staining test, species of *Proteus* were not among the identified organisms that belonged to the presumptive coliform species (Table 3). However, species of *Escherichia* (Dimbaza: influent; East London: receiving water body; Alice: influent and final effluent; Fort Beaufort: influent, final effluent, and receiving water body), *Citrobacter* (Alice: influent, final effluent, and receiving water body; East London: influent and receiving water body; Alice: influent; Fort Beaufort: influent and final effluent), and *Salmonella*

Table 3. Bacterial Isolates Identified from the Influent, Effluents, and Receiving Water Body Samples Analyzed (Number of Samples: 12 for each Stage of the Plant)

Wastewater Plants	Water Sources	Bacterial Isolate Identified
Dimbaza	Influent	*Aeromonas hydrophila, Citrobacter freundii, Escherichia coli, Klebsiella ornithinolytica, Vibrio cholerae, Vibrio parahaemolytica, Serratia liquefaciens*.
	Effluent	*Citrobacter freundii*
	Receiving body	*Citrobacter freundii, Enterobacter aerogenosa, Salmonella arizonae, Serratia odorifera*
East London	Influent	*Aeromonas hydophila, Chromo violaceum, Citrobacter freundii, Enterobacter aeogenosa, Klebsiella ornithinolytical, Pseudomonas putida, Vibrio fluvialis, Serratia ficaria, Serratia odorifera, Chromo violaceum.*
	Effluent	*Aeromonas hydophila, Chromo violaceum, Klebsiella ornithinolytica, Pseudomonas putida, Serratia odorifera, Serratia ficaria, Vibrio fluvialis.*
	Receiving body	*Aeromonas hydrophila, Citrobacter freundii, Escherichia coli, Klebsiella oxytoca, Klebsiella ornithinolytica, Morganella morgani, Vibrio fluvialis*
Alice	Influent	*Aeromonas hydophila, Citrobacter freundii, Enterobacter cloacae, Escherichia coli, Klebsiella ornithinolytica, Klebsiella oxytoca, Klebsiella ozaenae, Kluyvera* spp., *Pseudomonas putida, Vibrio cholerae*
	Effluent	*Aeromonas hydophila, Escherichia coli, Klebsiella ornithinolytica, Enterobacter amnigenus, Klebsiella ozaenae, Klebsiella oxytoca, Kluyvera* spp., *Pseudomonas putida*
	Receiving body	*Aeromonas hydophila, Enterobacter amnigenus, Klebsiella ornithinolytica, Klebsiella oxytoca, Pseudomonas aerogenosa, Pseudomonas putida*
Fort Beaufort	Influent	*Aeromonas hydrophila, Citrobacter freundii, Escherichia coli, Klebsiella ornithinolytica, Klebsiella oxytoca, Pasteurella pneumoniae, Salmonella arizonae, Serratia odorifera, Vibrio fluvialis.*
	Effluent	*Aeromonas hydrophila, Citrobacter freundii, Escherichia coli, Klebsiella oxytoca, Vibrio fluvialis*
	Receiving body	*Aeromonas hydrophila, Escherichia coli, Enterobacter cloacae, Pseudomonas putida, Shewan putrefaciens, Vibrio fluvialis*

(Dimbaza: receiving water body; Fort Beaufort: influent) were identified in some zones of the plants. Other organisms belonging to 11 other different species were also identified from different zones of the plants. These species included *Aeromonas* (Dimbaza: influent; Alice, East London, and Fort Beaufort: influent, final effluent, and receiving water body), *Klebsiella* (Dimbaza: influent; East London and Fort Beaufort: influent, final effluent, and receiving water body; Fort Beaufort: influent and final effluent), *Serratia* (Dimbaza: influent and receiving water body; East London: influent and effluent; Fort Beaufort: influent), *Enterobacter* (Dimbaza: receiving water body; East London: influent; Alice: influent, effluent, and receiving water body; Fort Beaufort: receiving water body), *Pseudomonas* (East London: influent and effluent; Alice: influent, effluent, and receiving water body; Fort Beaufort: receiving water body), *Vibrio* (Dimbaza: East London and Fort Beaufort: influent; Alice: influent, effluent, and receiving water body), *Chromo* (East London: influent and effluent), *Morganella* (East London: receiving water body), *Kluyvera* (Alice: influent and effluent), *Erwinia* (Alice: receiving water body), and *Shewanella* (Fort Beaufort: receiving water body) (Table 3). The efficiency of the Dimbaza wastewater treatment plant was also confirmed with the identification tests when compared with the other three plants. Among the 7 species identified from the Dimbaza's influent, only *Citrobacer freundii* was still prevalent in the treated final effluent and also in the receiving water body. It is obvious from the results in Table 3 that the final effluent was not the source of organisms such *Enterobacter aerogenosa, Salmonella arizonae*, and *Serratia odorifera* identified from the receiving water body. *Aeromonas hydrophila*, which was found to be the dominant strain in all influents, was still prevalent in the East London, Alice, and Fort Beaufort's treated effluents and received water bodies.

DISCUSSION

Access to a clean, pathogen-free water supply is a major priority for any community if it is to remain disease-free. In today's highly urbanized society, the best way to achieve this objective is to recycle water by treating used or wastewater through a treatment plant system. The efficiency of wastewater treatment plants in removing pathogenic micro-organisms from their final effluents can only be achieved by disinfection. According to White (18), the most prevalent practice of disinfection is free chlorine, which is also the practice in many developing countries. Disinfection with chlorine is always influenced by indicator organism concentration, disinfection concentration, contact time, temperature, and pH. The availability of the free chlorine residuals in the final effluents gives an indication of the efficacy of the disinfection process and thus a rapid indicator of the probable microbiological safety of the treated effluent.

In terms of the concentration of free residual in the effluents, results indicated the availability of free chlorine residual in all the wastewater plants, although in some plants (Fort Beaufort and Dimbaza, Table 2) these concentrations exceeded the limit recommended by water authorities, which are in the range of 0.3–0.6 mg/l as ideal free chlorine residual concentration and 0.6–0.8 mg/l as good free chlorine residual concentration for insignificant risk of health effects (14). In contrast to the other plants, the free chlorine concentrations complied with (East London) or were lower than the standards (Alice) (Table 2).

Although free chlorine was available in the various final effluents, with the exception of the Dimbaza plant, which showed a removal of coliform organisms at 85.71%, the results suggest that the microbiological quality of the final effluent in East London, Alice, and Fort Beaufort plants exceeded the standards for domestic and recreational use. The results also indicated that the effluents from all the plants were also one of the sources of coliforms in the receiving water bodies. In the Dimbaza plant, the *Citrobacter freundii* found in the final effluent also appeared in the receiving water body. In the Alice, Fort Beaufort, and East London wastewater treatment plants, 62.5%, 60%, and 43% of the organisms found in the final effluent were also prevalent in the receiving water body, respectively (Table 3). The results suggest that the microbiological quality of the effluents examined poses a serious health risk to the community, which is consistent with the findings of previous investigators, such as Muyima and Ngcakani (9), who pointed out that fecal contamination of drinking water supplied by untreated or inadequately treated sewage effluents entering rivers and dams that serve as the source of municipal water supplies creates conditions for the rapid spread of pathogens. It also became clear from the findings that the main reason behind the inefficiencies shown by the wastewater treatment plants for the removal of the coliforms stem from inadequate disinfection practices and/or inadequate maintenance of the facilities, as observed with the Fort Beaufort plant. Although the East London wastewater treatment plant was technically well equipped with five aerators and six clarifiers, this equipment was under repair during the study period and not all the clarifiers were in a working condition. This fact has been reiterated by Pearson and Idema (19), who, commenting on the disinfection of effluents in many cases in the developing countries, stated that a high level of reliability of water supply schemes, particularly the treatment process, is the exception rather than the rule. The authors further pointed out that various factors such as cost, operator training, and problems with maintenance of the infrastructure could be contributory factors to these problems.

A number of different species of potentially pathogenic micro-organisms were isolated from both the final effluents and the receiving water bodies of the different wastewater treatment plants. Although differences existed with the types of species isolated from the various effluents, potentially pathogenic organisms were isolated from all the effluent and receiving water body samples in various degrees of preponderance (Table 3). *Aeromonas hydrophila*, for example, was found as the dominant micro-organism identified from final effluents and receiving water bodies in East London, Alice, and Fort Beaufort wastewater plants. *Aeromonas* can be infectious, producing focal or systemic infections of varied severity. The most common clinical infection that has been associated with this organism is diarrhea (20–23). The preponderance of *A. hydrophila* in the final effluents and receiving water bodies is cause for much concern, because it is common for communities in the Eastern Cape to use the effluent receiving water body such as a river (in Alice and Fort Beaufort), a dam (Dimbaza), or ocean beach (East London) as a water source for drinking, bathing, washing (i.e., clothes, dishes, etc.), or recreational purposes (i.e., swimming) and the final effluent as a water source for irrigation purposes. The microbiological quality of these water sources could influence infection and disease in the communities.

CONCLUSIONS

A relationship existed between the microbiological quality of the final effluent and that of the receiving water body, and the relationship was such that the better the quality of the final effluent, the better the quality of the receiving water body. From the results, it could also be deduced that the appearance of coliform bacteria in the receiving water body, although no evidence exists of such in the final effluent, means that the source of pollution was from a source outside of the wastewater treatment process.

The disinfection practices and guidelines in terms of chlorine residual concentrations were found not to be sufficient for the removal of coliforms from the effluent. Although the chlorine residual concentration may fall within the recommended limits for no risk, the occurrence of coliforms could still be detected in the final effluent. This study, therefore, suggests that other factors, such as the chlorine demand of the water, the contact time, the initial indicator organisms, or the use of powerful disinfectants, be considered by the operators in wastewater treatment plants for the treatment of the effluents before they are discharged into the receiving water bodies.

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BIBLIOGRAPHY

1. Eckenfelder, Jr., W.W. and O'Connor, D.J. (1961). *Biological Waste Treatment*. Pergamon Press, New York, pp. 1, 7.
2. Grabow, W.O.K. (1996). Waterborne diseases: Update on water quality assessment and control. *Wat. SA.* **22**(2): 193–197.
3. Mnqumevu, B.V. (1998). Detection of faecal coliform bacteria and heterotrophic plate count bacteria attached to household containers during storage of drinking ground water in rural communities. B.Sc. (Honors) Thesis, Department of Biochemistry and Microbiology, University of Fort Hare, Alice, South Africa.
4. Moore, B. (1948). Monthly bulletin. *Ministry of Health* **7**: 241.
5. Payment, P., Richardson, L., Siemiatycki, J., Dewar, M., and Franco. (1991). A randomized trial to evaluate the risks of

gastrointestinal diseases due to consumption of drinking water meeting current microbiological standards. *Am. J. Publ. Hlth.* **81**: 703–708.

6. Quick, R. et al. (1999). Diarrhea prevention in Bolivia through point-of-use disinfection and safe storage: a promising new strategy. *Epi. Infect.* **122**: 83–90.
7. Fatoki, O.S., Gogwana, P., and Ogunfowokan, A.O. (2003). Pollution assessment in the keiskamma river and in the impoundment downstream. *Water S.A.* **1**(2): 183.
8. Venter, S.N. (2001). Microbial water quality in the 21st Century. *S.A. Water Bull.* January/February.
9. Muyima, N.Y.O. and Ngcakani, F. (1998). Indicator Bacteria And Regrowth Potential Of The Drinking Waterin Alice, Eastern Cape, Department of Biochemistry and Microbiology, University of Fort Hare. *Water SA.* **24**: 1.
10. Mey, J. (1998). *Poverty and Inequality in South Africa*. Report prepared for the Executive Deputy President and Inter-Ministerial Committee for poverty and inequality, Durban.
11. Momba, M.N.B., Malakate, V.K., and Theron, J. (2004). Abundance of pathogenic Escherichia.coli, Salmonella typhimurium and Vibrio cholerae in Nkonkobe drinking water sources. *J. Water Health*. Submitted for peer review.
12. Momba, M.N.B., Tyafa, Z., and Makala, N. (2004). Rural water treatment plants fail to provide potable water to their consumers: the Alice water treatment plant in the Eastern Cape Province of South Africa. *S. African J. Sci.* **100**: 307–310.
13. Department of Water Affairs and Forestry (DWAF). (1996). *South African Water Quality Guidelines*, 2nd Edn. Vol. 1: Domestic Use. Pretoria, South Africa.
14. Department of Water Affairs and Forestry (DWAF), Department of Health and Water Research Commission. (1998). *Quality of Domestic Water Supplies*. Vol. 1: Assessment Guide. *Water research Commission* No: TT101/98 ISBN No: 1 86845 416 9.
15. American Public Health Association. (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th Edn. AWWA. Water Environmental Federation, Washington, DC.
16. Department of Water Affairs and Forestry (DWAF). (1996). *South African Water Quality Guidelines*, 2nd Edn. Vol. 4: Agricultural Use and Irrigation. Pretoria, South Africa.
17. Department of Water Affairs and Forestry (DWAF). (1996). *South African Water Quality Guidelines*, 2nd Edn. Vol. 2: Recreational Use. Pretoria, South Africa.
18. White, G.C. (1992). *Handbook of Chlorination and Alternative Disinfectants*. Van Nostrand, New York.
19. Pearson, I. and Idema, G. (1998). An assessment of common problems associated with drinking water disinfection. *WRC* No. 649/1/98.
20. Davis, W.A., Kane, J.G., and Garagusi, V.F. (1978). Human *Aeromonas* infections: a review of the literature a case report of endocarditis. *J. Med.* **57**: 267–277.
21. Agbonlahor, D.E. (1983). The role of *Aeromonas* in acute diarrhoeal diseases in Nigeria. *Cent. Afric. J. Med.* **29**: 142–145.
22. Bhat, P., Shantnakumari, S., and Rajan, D. (1984). The characterization significance of *pleisionomasshigelloides* and *aeronomas hydrophilla* isolated from an epidemic of diarrhea. *Indian J. Med. Res.* **52**: 1051–1060.
23. Watson, I.M., Robinson, J.O., Burke, V., and Grace, M. (1985). Invasiveness of *Aeromonas* spp in relation to biotype. *J. Clinic. Microbiol.* **22**: 48–51.

DENITRIFICATION IN THE ACTIVATED SLUDGE PROCESS

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Denitrification in the activated sludge process is the use of nitrate ions ($NO_3{}^-$) by facultative anaerobic (denitrifying) bacteria to degrade soluble carbonaceous BOD (cBOD). Although denitrification most often is observed in the secondary clarifier, denitrification occurs whenever an anoxic condition exists. Denitrification in the secondary clarifier often is referred to as "clumping," "rising sludge," and "dark sludge rising." Clumping is highly undesired, because it results in poor compaction of solids, loss of solids, increased operational costs, and possible permit violations.

Besides the anoxic condition known as clumping, an undesired anoxic condition can occur in the sewer system and other treatment units and a desired anoxic condition can be produced in a denitrification tank or designated anoxic tank. A denitrification tank is used to satisfy a total nitrogen discharge limit, while a designated anoxic tank is used to improve process performance. Desired process performance includes destruction of undesired filamentous organism growth and strengthening of floc particles.

Unless an industry discharges nitrate ions to the activated sludge process, activated sludge processes that denitrify usually nitrify. Industrial discharges that may contain nitrate ions include pretreated leachate, pretreated meat processing wastewater, meat processing wastewater containing flavoring compounds, and steel mill wastewater. The presence of nitrate ions in the sewer system is highly undesired. Here, nitrate ions permit the rapid degradation of soluble cBOD. The degradation of soluble cBOD results in a decrease in the quantity of cBOD in the influent to a wastewater treatment plant. This decrease in cBOD makes it difficult for the operator of an activated sludge process to achieve an 85% removal efficiency for cBOD.

There are four factors that must be satisfied in order for an anoxic condition to occur. First, an abundant and active population of denitrifying bacteria must be present. Second, nitrate ions must be present. Third, free molecular oxygen (O_2) must be absent or an oxygen gradient must present. Fourth, a source of soluble cBOD must be present.

Denitrifying bacteria enter an activated sludge process through fecal waste and inflow and infiltration (I/I) as soil and water organisms. Approximately 80% of the bacteria in the activated sludge process are facultative anaerobes (Table 1). These organisms are present in millions per milliliter of bulk solution and billions per gram of floc particle, and most denitrifying bacteria reproduce every 15–30 min. The most significant genera of bacteria containing denitrifying species are *Alcaligens*, *Bacillus*, and *Pseudomonas*.

Denitrifying bacteria can use either free molecular oxygen or nitrate ions to degrade soluble cBOD. However, the bacteria prefer free molecular oxygen to nitrate ions to degrade soluble cBOD, because the use of free molecular

Table 1. Genera of Activated Sludge Bacteria that Contain Denitrifying Species

Achromobacter	*Hyphomicrobium*
Acinetobacter	*Kingella*
Agrobacterium	*Methanonas*
Alcaligenes	*Moraxella*
Bacillus	*Neisseria*
Chromobacterium	*Paracoccus*
Corynebacterium	*Propionibacterium*
Denitrobacillus	*Pseudomonas*
Enterobacter	*Rhizobium*
Escherichia	*Rhodopseudomonas*
Flavobacterium	*Spirillum*
Gluconobacer	*Thiobacillus*
Halobacterium	*Xanthomonas*

oxygen to degrade soluble cBOD results in the production of more offspring (bacterial cells or sludge) and more useable cellular energy than the use of nitrate ions. For example, the use of free molecular oxygen to degrade 1 lb of sugar results in the production of approximately 0.6 lbs of bacterial cells or sludge. The use of nitrate ions to degrade 1 lb of sugar in the activated sludge process results in the production of approximately 0.4 lbs of bacterial cells or sludge.

Nitrate ions may enter an activated sludge process from an industrial discharge. Typically, the nitrate ions used by denitrifying bacteria are produced in the activated sludge process through nitrification. Nitrate ions produced in the activated sludge process may be discharged to a secondary clarifier, denitrification tank, thickener, and anaerobic digester. Nitrate ions also may be recycled in the wastewater treatment plant to the headworks, primary clarifier, or influent to the activated sludge process. Depending on operation conditions in each treatment unit, the nitrate ions received in these units may undergo denitrification and may contribute to operational problems.

Nitrate ions are used by denitrifying bacteria in the absence of free molecular oxygen or in the presence of an oxygen gradient. An oxygen gradient is established when the dissolved oxygen concentration outside the solids is <1 mg/L and the size of the solids is >100 μm. The oxygen gradient does not permit oxygen to reach the core of the solids. Therefore, bacteria on the perimeter of the floc particle degrade soluble cBOD using free molecular oxygen, while bacteria in the core of the solids use nitrate ions to degrade soluble cBOD. In the presence of an oxygen gradient, measurable oxygen is detected yet denitrification occurs.

The presence of soluble cBOD is the most important factor affecting the occurrence of an anoxic condition. The more soluble cBOD available to the facultative anaerobic bacteria, the more quickly the bacteria exhaust the available oxygen and begin to use nitrate ions. There are several sources of soluble cBOD that can be used by denitrifying bacteria. Chemical compounds that often are used in denitrification tanks include acetate, ethanol, glucose, and methanol. Methanol is the most commonly used source of soluble cBOD for denitrification tanks. Methanol is simplistic in structure, highly soluble, quickly absorbed by bacterial cells, and easily degraded. However, domestic wastewater often is used in an anoxic tank to achieve denitrification and destroy filamentous organisms and strengthen floc particles.

Denitrification proceeds in a step-by-step series of events through the reduction of nitrate ions. Nitrite ions are reduced to nitrite ions (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and finally molecular nitrogen (N_2). When denitrification occurs there are three gases that are produced and released by the denitrifying bacteria. These gases in order of quantity produced are molecular nitrogen, carbon dioxide (CO_2), and nitrous oxide. Many bubbles of these gases escape from the wastewater, while some bubbles become entrapped in solids. The entrapped bubbles render the solids buoyant and result in a loss of settleability and solids from the secondary clarifier.

Denitrification also results in the production of alkalinity (Eq. 1).

$$6\ NO_3^- + 5\ CH_3OH \longrightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^- \qquad (1)$$

Alkalinity is returned in the form of the hydroxyl ion (OH^-) and the production of bicarbonate alkalinity (HCO_3^-) from carbon dioxide. Approximately 50% of the alkalinity lost during nitrification is returned to the activated sludge process through denitrification.

Clumping in the secondary clarifier can be prevented or controlled through several operational measures. Appropriate measures should be selected depending on whether a nitrification requirement exists for the activated sludge process.

If an activated sludge process is not required to nitrify, then nitrification may be terminated. This can be done by reducing solids inventory in the aeration tank, reducing the mean cell residence time (MCRT), reducing the dissolved oxygen level in the aeration tank, and taking an aeration tank off-line. If an aeration tank is taken off-line, then the remaining on-line aeration tanks have reduced hydraulic retention time (HRT) and increased organic loading. Reduced hydraulic retention time and increased organic loading disfavor nitrification.

If an activated sludge process is required to nitrify, then nitrification must be maintained. Clumping in the secondary clarifier can be prevented or controlled by increasing the return activated sludge (RAS) rate or treating secondary clarifier solids with a polymer or coagulant and increasing the RAS rate. Clumping also can be prevented or controlled by using plug flow mode of operation that incorporates an anoxic tank in the first tank (Fig. 1), or periodically terminating aeration for 1–2 h in an aeration tank while maintaining mixing action. Terminating aeration provides for the use of nitrate ions to degrade soluble cBOD in the aeration tank before they can be discharged to the secondary clarifier. However, once aeration is terminated to a tank, the tank can no longer nitrify.

Indicators of denitrification in the secondary clarifier are numerous. Rising bubbles of molecular nitrogen, carbon dioxide, and nitrous oxide are present in the clarifier. The bubbles may be found rising freely in

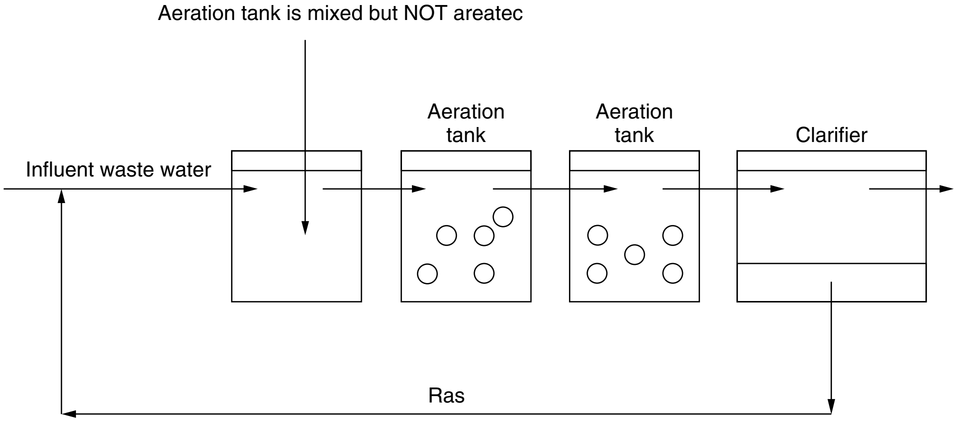

Figure 1. Plug flow mode of operation using an anoxic tank.

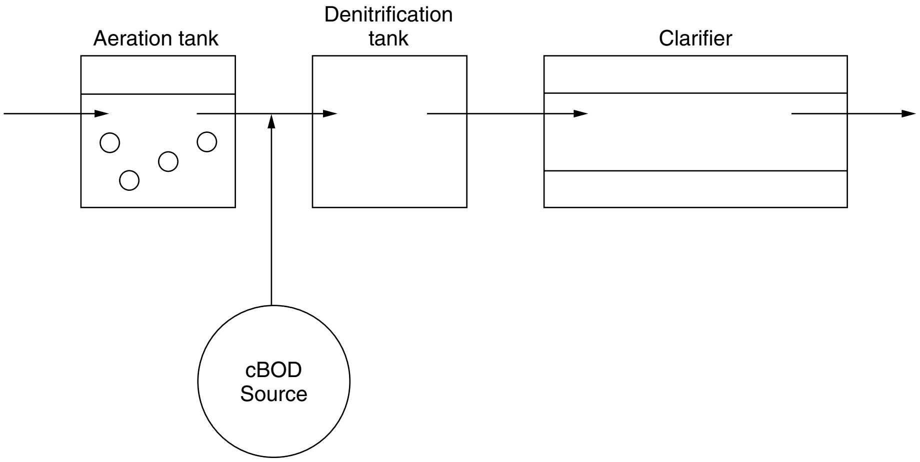

Figure 2. Denitrification tank.

the bulk solution, on the surface of rising solids, or released from the solids when the solids burst upon reaching the surface of the clarifier. The solids rising to the surface usually are dark due to the high MCRT required to grow a large population of nitrifying bacteria. Because nitrate ions are used during denitrification, the influent concentration of nitrate ions to the clarifier is greater than the effluent concentration of nitrate ions. Because denitrification returns alkalinity to the wastewater, the influent concentration of alkalinity to the clarifier is less than the effluent concentration of alkalinity from the clarifier. If sufficient alkalinity is returned to the secondary clarifier, an increase in pH across the clarifier occurs.

A denitrification tank is used to reduce the quantity of nitrogen in the effluent of an activated sludge process as required by permit (Fig. 2). A denitrification tank is located downstream of the activated sludge process. The denitrification tank receives the nitrate ions produced through nitrification in the aeration tank as well as the aeration tank's facultative anaerobic bacteria, residual dissolved oxygen, and residual soluble cBOD. In order to denitrify in the tank, slow subsurface mixing action is used to suspended large numbers of facultative anaerobic bacteria and place them in contact with the residual dissolved oxygen. Because the quantity of soluble cBOD entering the tank from the aeration tank is relatively small, soluble cBOD must be added to the denitrification tank. Approximately 3 mg/L of soluble cBOD are consumed in the denitrification tank for each mg/L of nitrate ion present. The soluble cBOD compound most often used in the denitrification tank is methanol. Retention times in the denitrification tank vary greatly, but most retention times are usually 30–60 min in length.

DETERGENTS

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Detergents are formulations that have cleaning and solubilization properties. Their main fields of application are industry (cleaning products, food, industrial processing), household (laundry, dishwashing), and personal care (soaps, shampoos, cosmetics). Detergents consist of surface-active agents known as surfactants and other subsidiary components that include boosters, builders, and fillers. In 1996, the production of surfactants including soaps was reportedly around 30×10^9 kg per year worldwide (1). Detergents are thus environmentally important because they are used in huge quantities. Historically, potential detergent contamination of the environment followed when the use of soap-based detergents changed to synthetic detergents. Detergents are discharged to the environment typically through wastewater treatment plant effluent and the use of sewage sludge on land. Industrial discharges to surface waters, oil spills, and surfactant-enhanced remediation of contaminated soil can also be other sources. Biological treatment of wastewater typically removes 95% of the detergents and their metabolites (2). However, recent research has generated scientific and regulatory concern because certain detergents and their metabolites appear toxic to aquatic organisms (3–7). These studies also indicate that detergent metabolites are also more toxic than their parent compounds. The complexity of detergent products, it has also been shown, leads to synergistic effects (8).

DETERGENT STRUCTURE AND USE

Detergents consist of surface-active agents, known as surfactants, and other subsidiary components that include boosters, builders, and fillers (9). Surfactants, as defined by Rosen (9), are substances that adsorb onto surfaces or interfaces and alter the surface or interfacial free energies of those surfaces when present at low concentrations in a system. The term interface means a boundary between any two immiscible phases: the term surface implies an interface where one phase is a gas. Surfactants have a characteristic molecular structure consisting of a structural group that is solvent hating (*lyophobic*) and a group that is solvent loving (*lyophilic*). This type of structure is called *amphipathic*. A typical surfactant molecule is shown in Fig. 1.

This nature of the surfactant causes concentration of the surfactant at a surface and the reduction of surface tension and also the orientation of the molecule at the surface: its *lyophilic* group is in the solvent phase, and its *lyophobic* group is oriented away from it. In an aqueous solution, the *lyophobic* term is *hydrophobic*, and the lyophilic term is *hydrophilic*. The hydrophobic group is typically a long-chain hydrocarbon, whereas the hydrophilic group is an ionic or highly polar group. Depending on the nature of the charge of the hydrophilic group, surfactants are classified as anionic (negative charge), cationic (positive charge), nonionic (no charge), and zwitterionic (both charges).

Anionic surfactants are used extensively in toilet soap bars, toothpaste, hair preparations and shampoos, wax strippers, textile lubricants, and degumming silk. Various types of anionic surfactants are listed in Table 1.

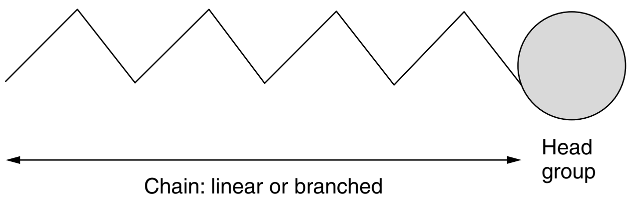


Figure 1. Structure of a surfactant molecule.

Table 1. Types of Anionic Surfactants[a]

Type	Example
1. Carboxylic acid salts	Soap
2. Sulfonic acid salts	LAS—linear alkyl benzenesulfonate in industrial detergents; petroleum sulfonates for oil recovery
3. Sulfuric acid ester salts	Na lauryl sulfate—toothpaste, fabric detergent
4. Phosphoric and polyphosphoric acid esters	Emulsifying agents in pesticides and herbicides
5. Perflourinated anionics	Control of oil and gasoline fires

[a] Reference 9.

Cationic surfactants are compatible with nonionic and zwitterionic surfactants. They carry a positive charge, so they strongly adsorb onto most solid surfaces. These surfactants exhibit poor detergency and are more expensive than other surfactants. Typical types of cationic surfactants and their uses are shown in Table 2.

Nonionic surfactants are widely used because they are compatible with other types of surfactants. They are generally available as 100% active material, free of electrolyte. They have poor foaming properties and are excellent carbon dispersing agents. Typical types of nonionic surfactants and their use are shown in Table 3.

Zwitterionic surfactants are compatible with all other kinds of surfactants. They are used as bactericides, corrosion inhibitors, pigment dispersion aids, cosmetics, fabric softeners, and soap detergent formulations.

Of all the types of surfactants mentioned, LAS (anionic) and APE (nonionic) are the major forms of surfactants found in detergent wastewater. APEs are further classified as OPEs (octylphenolethoxylates) and

Table 2. Types of Cationic Surfactants[a]

Type	Example
1. Long chain amines and their salts	Corrosion inhibitors; anticaking agents for fertilizers; flotation agents for metal ores
2. Di- and polyamines and their salts	Pigment coating; ore flotation
3. Quaternary ammonium salts	Textile softeners; germicides; disinfectants; sanitizers; health products
4. Polyoxyethylenated long-chain amines	Emulsifying agent for herbicides, insecticides, polishes, and wax emulsions
5. Quaternized polyoxyethlenated long-chain amines	Textile antistatic agent; dyeing leveler; corrosion inhibitor;
6. Amine oxides	Foam stabilizer for detergents, shampoos, and dishwashing liquids

[a] Reference 9.

Table 3. Types of Nonionic Surfactants[a]

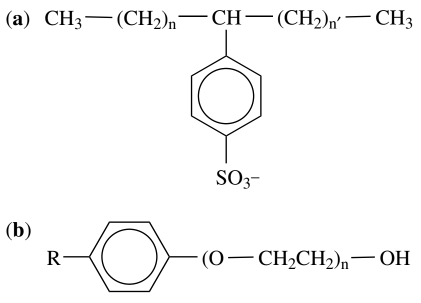
Type	Example
1. Polyoxyethylenated alkylphenols; alkylphenol ethoxylates (APE)	Foam control; paint emulsifier; cosmetic emulsions; liquid detergents; dyeing retarders
2. Alcohol ethoxylates (AE)	Heavy-duty liquid detergents
3. Polyoxyethylenated polyoxypropylene glycols	Dispersants for pigments in latex paints; scale removal in boilers; petroleum deemulsifiers; foam control in laundry detergents
4. Polyoxyethylenated mercaptans	Cleaning and scouring of wool; metal cleaning; shampoos
5. Long-chain carboxylic acid esters	Food and pharmaceutical industries; cosmetics; textile antistats;
6. Alkanolamides	Foam stabilizers; thickeners for shampoos and liquid detergents
7. Tertiary acetylenic glycols	Wetting agents for use in powdered solids and emulsion paints
8. Polyoxyethylenated silicones	Wetting agents for polyester and polyethylene

[a] Reference 9.

NPEs (nonylphenolethoxylates), depending on the number of carbons. The general chemical structures of LAS and APE are presented in Fig. 2.

Analytical Methods

The qualitative and quantitative analysis of surfactants using titrimetric, spectrometric, and chromatographic techniques has been reported (3,4,10). Dissolved surfactant can be separated from dilute aqueous solution using the Wickbold method (11). This method is independent of the type of surfactant and isolates the surfactant as a residue suitable for analysis. The method, however, is lengthy and requires large sample volumes. Therefore, some studies have investigated and reported the use of SPE (solid-phase extraction) columns (12–13). The MBAS method (10) is useful for estimating the anionic surfactant content in water and wastewater samples. The CTAS (10) method is used to estimate the nonionic surfactant content in water if interference from other surfactants such as cationic and anionic can be eliminated. For more accurate and individual oligomers, normal-phase, high-performance liquid chromatography (HPLC) techniques have been reported for both LAS and APE surfactants. Ahel et al. (3,4,7) outlined analytical methods for APEs and their metabolites using normal-phase and reverse-phase HPLC for water, wastewater, and sludge samples. Ethoxylated nonionic surfactants are not volatile; therefore, their analysis is not well suited to gas chromatography. Typically, only lower molecular mass surfactant components can be analyzed by gas chromatography but only at high column temperatures (14). LAS analysis by HPLC has been described in detail by Matthijs and De Henau (15). Major metabolites for APE surfactants such as nonylphenol (NP) and octylphenol (OP) can also be analyzed by HPLC techniques (16–18).



where R: C_9H_{19} n-Nonyl or C_8H_{17} O Octyl and n ~ 1 to 50

Figure 2. General chemical structure of (**a**) LAS and (**b**) APE.

OCCURRENCE OF DETERGENTS IN WASTEWATER AND SEWAGE SLUDGE

PT benzene (propylene tetramer benzene sulphonate) was used as the major surfactant in detergents until 1960. It was found that PT benzene is recalcitrant and causes foaming in rivers. This led to the use of more biodegradable straight-chain alkyl surfactants such as LAS. LASs currently represent 40% of all surfactants used (19). The other commonly used class of surfactants is APEs; the worldwide production is reportedly around 500×10^3 tons pa (19). Therefore, literature has focused more on the environmental impacts of LASs and APEs. Measured concentration of surfactants in municipal sewage effluents reportedly range from 0.008 to 6.2 mg/L and in river waters from 0.0042 to 2.6 mg/L (20–21). Literature indicates that a significant portion of the surfactants in raw sewage adsorbs to particulate matter. Primary sludge removed from primary settling tanks are reportedly rich in LAS, and concentrations vary from 5,000–15,000 mg/L (19). Most surfactants also do not biodegrade under anaerobic conditions. Therefore, sludge treated via anaerobic processes is rich in surfactants. Anaerobically digested sewage sludge reportedly contains 0.3–1.3% LAS (19).

Dentel (22) reported the load of LAS and APE in a typical WWTP and their subsequent fate. His data are presented in Fig. 3. The figure indicates that significant

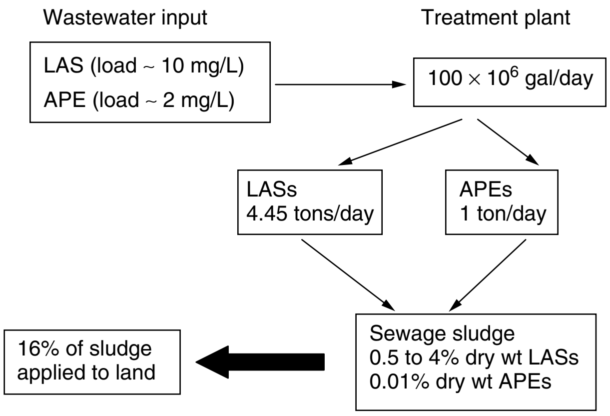


Figure 3. Surfactant transport through a typical WWTP (22).

amounts of surfactants are transported to the environment through WWTP effluent discharge and sludge disposal.

BIODEGRADATION OF DETERGENTS

Biodegradation of surfactants can be classified as primary or ultimate. Primary biodegradation is the loss of detergency, whereas ultimate indicates complete conversion to CO_2, CH_4, water, salts, and biomass. The biodegradation of LASs and APEs is well documented. LASs are highly biodegradable—rates are as high as 97–99% under aerobic conditions. Typically, the process involves breakdown of the straight-chain alkyl chain, then the sulphonate, and finally the benzene ring. There is no evidence for comparable LAS degradation under anaerobic conditions. Biodegradation of LAS, it has been shown, is dependent on dissolved oxygen concentrations, the presence of other organic contaminants and other surfactants, and pH.

In contrast to LASs, APEs are less biodegradable: values of 0–20% have been reported (19). APEs undergo complete primary degradation in aerobic environments, and metabolic products accumulate. APEs consist of NPES and OPEs. Nonylphenol (NP) and octylphenol (OP) have been identified as the major metabolites of these two classes of surfactants. Both are toxic and xenoestrogenic; octyplenol is more toxic than nonylphenol (23). NP is approximately 10 times more toxic than its ethoxylate precursor. Biodegradation is accomplished by stepwise shortening of the ethoxylate chain. This produces a complex mixture of compounds that can be divided into three main groups: short-chain ethoxylates, alkylphenoxy carboxylic acids, and alkylphenols such as NP and OP. As the chain gets shorter, the molecule becomes less soluble. The alkylphenoxy carboxylic acids and longer chain APEs are soluble in water; the shorter chain APEs are insoluble in water, particularly NP and OP. Both compounds have low water solubility and tend to adsorb onto suspended solids or sediments.

The biodegradation of surfactants in sewage sludge poses some problems. Typically a common initial step in WWTP is primary settling of particulates. Sludge from this tank can be rich in surfactants because surfactants tend to adsorb to particulates. Anaerobic sludge treatment at high temperature is typically the norm for WWTPs. Most common surfactants are not biodegradable under anaerobic conditions. Therefore, anaerobically digested sewage sludge is a potential source of surfactants for the soil.

LAS are not biodegradable either by mesophilic or thermophilic anaerobic digestion. Therefore, anaerobically digested sludge can contain 0.3–1.2% LAS and thus be a potential source. Jensen (24) reported that LAS concentrations in sludge are highly dependent on the sludge treatment method employed. LAS in sludge-amended soil, however, was rapidly biodegraded in the aerobic soil. Concentrations of APE are much higher in anaerobically digested sludge (900–1,100 mg/kg) than in aerobically digested sludge (0.3 mg/kg) (19). Marcomini (25) reported that sewage-amended soil in aerobic environments exhibited rapid NP degradation.

Cationic surfactants are considered readily biodegradable under aerobic conditions. These surfactants carry a positive charge, so they have a strong affinity for negatively charged particulate surfaces in sewage sludge. The adsorption of cationic surfactants to particulate matter makes the sludge treatment method employed important. However, there is no evidence of anaerobic biodegradation for this class of surfactants.

Data for soap indicates that it is readily biodegradable in both aerobic and anaerobic environments (26). Fatty acid esters (FES) are also readily biodegradable under aerobic conditions (27) but poorly degradable under anaerobic conditions (28). Steber and Werich (29) found rapid degradation of FES in aerobic soils amended with anaerobically treated sludge.

Fatty alcohol sulphates (FES) are readily biodegradable under both aerobic and anaerobic conditions (30). Research also indicates that alcohol ether sulfates (AES) are readily biodegradable under aerobic and anaerobic conditions. Fatty alcohol ethoxylates (AE) are known to be readily biodegradable and thus maybe a suitable replacement for APEs.

TOXICITY OF DETERGENTS

Toxicity of detergents has received a lot of attention in recent years. Detergents and their metabolites are common constituents of municipal effluents, so they also contribute to the toxicity. Toxicity data for surfactants to various marine species of freshwater and marine life have been documented as early as 1950 (31). In most cases, these data were generated from standard toxicity tests in the laboratory under controlled conditions. Detergent products and their ingredients are relatively toxic to aquatic life. Lewis (35) has provided an extensive review on the toxicities of surfactants to freshwater and marine life. Household washing detergents and softeners, it has been shown, are toxic from 0.07 to 35.4 mg/L (32). Both LAS and NPE exhibit relatively high acute toxicities; 48-h LC_{50} values are typically in the range of 5 to 10 and 0.1 to 2.0 mg/L. There is a large and growing body of literature on the acute and chronic toxicity of NP and NPEs toward aquatic organisms (33–36). Exposure of fathead minnows to 22.7 mg/L of NP in water for 20 days resulted in a bioconcentration factor of 344 (34). Selected values for NP toxicity determined by Naylor (36) are presented in Table 4.

REGULATORY STANDARDS

There are no regulatory restrictions on the use of APEs in the United States. Massive monitoring studies conducted in the United States (36) indicate that NP does not pose a significant risk to aquatic organisms. The USEPA is clarifying the regulatory status of NPEs by issuing water quality guidance (37–38). The draft guidance indicates the following levels for nonylphenol:

Freshwater 6.6 ppb water (4-day average) and 25 ppb (1-hour average)
Saltwater 1.6 ppb (4-day average) and 6.2 ppb (1-hour average)

The APE Research Council supports the draft EPA water quality guidelines for NP.

Table 4. Nonyphenol Aquatic Toxicity[a]

Species	Type	LC_{50} (96 h), ppb	No Observable Effect, ppb	Lowest Observable Effect, ppb	Maximum Acceptable Toxicant, ppb
Mysidopsis bahia	Acute	43			
Marine shrimp	Chronic	Length at 28 days	3.9	6.7	5.1
		Reproduction	6.7	9.1	7.8
		Survival	6.7	9.1	7.8
Pimephales promelas	Acute	300			
		135			
Fathead minnow, freshwater	Chronic	Hatch rate	23	>23	>23
		length, 28 days	23	>23	>23
		Survival, 33 days	7.4	14	10.2
Cyprinodon variegates	Acute	310			
Sheepshead minnow, marine					
Salmo gairdneri	Acute	230			
Trout freshwater		480 (24 h)			
Daphnia magna	Acute	190 (48 h)	77	160	111
Flea freshwater		440 (48 h)			
	Chronic	Reproduction rate	24	39	31
Selanastrum capricornutum	Acute	EC_{50} 410	92	190	132
Freshwater green alga					
Skelatonema costatum	Acute	EC_{50} 27	10	20	14.1
Marine algae					
Rana Catesbiana	Acute 10 day	260 mg/kg			
Tadpole, freshwater	NP in sediment				
Chironomus tentans	Subacute, 14 day NP in sediment				26.1 mg/kg
Midge larva, freshwater					
Mytilus edulis	Acute	2600			
Mussel marine	Chronic	Growth and strength, 32 days		56	

[a] Reference 36.

The Soaps and Detergents Association found that the present use of NPES in detergents and cleaning products poses little or no risk to the environment in the United States. Environmental monitoring studies (39–41) demonstrate that APEs and their metabolite concentrations in rivers and lakes in the United States are below toxic levels. These studies also demonstrate that 92 to 99% of NPEs are effectively removed in wastewater treatment plants in the United States. Based on research conducted in the USA, APEs do not appear to pose a significant ecological risk.

The Canadian Government is currently reviewing the environmental and health characteristics of NP and NPEs under its PSL2 program. European countries, however, have started phasing out the use of APEs in their products. In 1986, Germany instituted voluntary restrictions and Switzerland banned the use of surfactants in laundry detergents (39). A voluntary ban on APE use in household products began in 1995 throughout northern Europe (42). Denmark has introduced an environmental quality standard for NP and NPEs of 1 μg/L. Studies conducted in Japanese wastewater treatment plants (43) indicated widespread pollution by NPEs and their metabolites.

CONCLUSIONS

Literature indicates that the presence of detergents in wastewaters may pose problems, depending on the treatment methodology for the wastewater and sludge. Most detergents are biodegradable under aerobic conditions. However, concerns with degradation products of APEs, particularly nonylphenol, remain. There is also concern over the resistance of all major classes of detergents to biodegradation in anaerobic environments, especially because this is the predominant method of sludge treatment from primary tanks. The amphiphilic nature of surfactants makes them prone to adsorption to the sludge during primary tank settling. Therefore a significant portion of the surfactants in wastewaters may be passed untreated into the sludge. Studies indicate that application of sludge in aerobic soil environments can lead to further biodegradation. However, more studies are required to determine the fate of toxic intermediates in soil.

BIBLIOGRAPHY

1. Schroder, H.Fr. (2001). Tracing of surfactants in the biological wastewater treatment process and the identification of their metabolites. *J. Chromatogr.* **926**: 127–150.
2. Swisher, R.D. (1987). *Surfactant Biodegradation*. Marcel Dekker, New York.
3. Ahel, M., Giger, W., and Koch, M. (1994). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment-I. Occurrence and transformation in sewage treatment. *Water Res.* **28**: 1131–1142.
4. Ahel, M., Giger, W., and Koch, M. (1994). Behaviour of alkylphenol polyethoxylate surfactants in the aquatic

environment-II. Occurrence and transformation in rivers. *Water Res.* **28**: 1143–1152.

5. Banat, F., Prechtl, S., and Biscof, F. (2000). Aerobic thermophilic treatment of sewage sludge contaminated with 4-nonylphenol. *Chemosphere* **41**: 297–302.
6. Bennett, E.R. and Metcalfe, C.D. (1999). Distribution of degradation products of alkylphenol ethoxylates near sewage treatment plants in the lower great lakes, North America. *Environ. Toxicol. Chem.* **19**(4): 784–792.
7. Brunner, P.H., Capri, S., Marcomini, A., and Giger, W. (1988). Occurrence and behaviour of linear alkylbenzenesulphonates, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment. *Water Res.* **22**: 1465–1472.
8. Lewis, M.A. (1992). The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Res.* **28**(8): 1013–1023.
9. Rosen, M.J. (1989). *Surfactants and interfacial phenomena*, 2nd Edn. John Wiley & Sons, New York.
10. AWWA, APHA, and WEF. (1995). *Standard Methods for the Evaluation of Waste Water*. Washington, DC.
11. Wickbold, R. (1972). On the determination of nonionic surfactants in river and wastewater. *Ten. Surf. Deterg.* **9**: 173–177.
12. Riu, J. et al. (2000). Determination of LAS in WWTPs and coastal waters by automated solid phase extraction followed by capillary electrophoresis. *J. Chromatogr.* **889**: 221–229.
13. Stephanou, E. and Giger, W. (1982). Persistent organic chemicals in sewage effluents: quantitative determinations of NP and NPEs by glass capillary gas chromatography. *Environ. Sci. Technol.* **16**: 800–805.
14. McEvoy, J. and Giger, W. (1986). Determination of LAS in sewage sludge by high resolution gas chromatography/mass spectrometry. *Environ. Sci. Technol.* **20**: 376–383.
15. Matthijs, E. and De Hanau, H. (1987). Determination of LAS in aqueous samples, sediments, sludges and soils using HPLC. *Tens. Surf. Deterg.* **24**: 193–199.
16. Giger, W., Brunner, P.H., and Schaffner, C. (1984). 4-nonylphenol in sewage sludge: accumulation of toxic metabolites from nonionic surfactants. *Science* **225**: 623–625.
17. Field, J.A. and Reed, R.L. (1996). NPEC metabolites of nonionic surfactants in US paper mill effluents. *Environ. Sci. Technol.* **30**: 3544–3550.
18. Lee, H.-B. and Peart, T.E. (1995). Determination of 4-nonylphenol in effluent and sludge from sewage treatment plants. *Anal. Chem.* **67**: 1976–1980.
19. Scott, M.J. and Jones, M.N. (2000). The biodegradation of surfactants in the environment. *Biochim. Biophys Acta* **1508**: 235–251.
20. Dorn, P., Salanitro, J., Evans, H., and Kravetz, L. (1992) Assessing the aquatic hazard of some branched and linear non-ionic surfactants by biodegradation and toxicity. *Environ. Toxicol. Chem.* **12**: 1751–1762.
21. Hennes-Morgan, E.C. and Oude, N.T. (1993). Detergents In: *Handbook of Ecotoxicology*. P. Calow (Ed.). Blackwell Scientific, Oxford, UK, pp. 130–154.
22. Dentel, S.K., Allen, H.E., Srinivasarao, C., and Divincenzo, J. (2002). *Third Year Completion Report Project No. 6, Water Resources Center*. University of Delaware, Newark, DE. Available: http://bluehen.ags.udel.edu/dewre/surfact.htm.
23. Johnson, A.C., White, C., Bhardwaj, L., and Jurgens, M.D. (2000). Potential for octylphenol to biodegrade in some english rivers. *Environ. Toxicol. Chem.* **19**(10): 2486–2492.
24. Jensen, J. (1999). Fate and effects of LAS in the terrestrial environment. *Sci. Total Environ.* **226**: 93–111.
25. Marcomini, A., Capel, P.D., Goger, W., and Hani, H. (1988). Residues of detergent derived organic pollutants and PCBs in sludge amended soil. *Naturwissenschaften* **75**: 460–462.
26. Birch, R.R., Gledhill, W.E., Larson, R.J., and Nielsen, A.M. (1992). Role of Anaerobic Biodegradability in the Environmental Acceptability of Detergent Materials, *Proc. 3rd CESIO*. London, Int. Surf. Congr. Exhib., 26, pp. 26–33.
27. Gode, P., Guhl, W., and Steber, J. (1987). Environmental compatibility of fatty acid, alpha-sulfomethyl esters. *Fat. Sci. Technol.* **89**: 548–552.
28. Maurer, E.W., Weil, J.K., and Linfield, W.M. (1965). The biodegradation of esters of α-sulfo fatty acids. *J. Am. Oil Chem. Soc.* **54**: 582–584.
29. Steber, J. and Weirich, P. (1987). The anaerobic degradation of detergent range fatty alcohol ethoxylates-studies with ^{14}C labeled surfactants. *Water Res.* **21**: 661–667.
30. Thomas, O.R.T. and White, G.F. (1989). Metabolic pathway for the biodegradation of sodium dodecyl sulphate by *pseudomonas* sp-c12b. *Biotechnol. Appl. Biochem.* **11**: 318–327.
31. Holt, M.S., Mitchell, G.C., and Watkinsson, R.J. (1992). The environmental chemistry, fate and effects of nonionic surfactants. In: *Anthropogenic Compounds*. Vol. 3, Part F, Handbook of Experimental Chemistry, O. Hutzinger (Ed.). Springer, Berlin, pp. 89–144.
32. Ankley, G.T. and Burkhard, P. (1992). Identification of surfactants as toxicants in a primary effluent. *Environ. Toxicol. Chem.* **11**: 1235–1248.
33. Argese, E. et al. (1994). Submitochondrial particle response to LAS, nonylphenol polyethoxylates and their biodegradation derivative. *Environ. Toxicol. Chem.* **13**(5): 737–742.
34. Staples, C.A. (1998). An evaluation of the aquatic toxicity and bioaccumulation of C8- abd C9- alkylphenol ethoxylates. *Environ. Toxicol. Chem.* **17**: 2470–2480.
35. Lewis, M.A. (1992). The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Res.* **26**(8): 1013–1023.
36. Naylor, C.G. (1998). *Environmental Fate and Safety of Nonylphenol Ethoxylates*. The Alkylphenols and Alkylphenol Ethoxylates Review, APE Research Council, Washington, DC.
37. Renner, R. (1997). European bans on surfactants trigger transatlantic debate. *Environ. Sci. Technol.* **31**: 316A–320A.
38. VandenHenvel, C. (2000). A more certain future for nonylphenol ethoxylates. *Chem. Times Trends* **Spring**: 38–39.
39. Hale, R.C. et al. (2000). Nonylphenols in sediments and effluents associated with diverse wastewater outfalls. *Environ. Toxicol. Chem.* **19**(4): 946–952.
40. Bennett, E.R. and Metcalfe, C.D. (2000). Distribution of degradation products of APEs near sewage treatment plants in the lower great lakes, north america. *Environ. Toxicol. Chem.* **19**(4): 784–792.
41. Naylor, C.G., Williams, J.B., Varineau, P.T., and Webb, D.A. (1998). Nonylphenol ethoxylates in an industrial river. *Alkylphenols Alkylphenol Ethoxylates Rev.*: 44–53.
42. Warhurst, A.A. (1985). *Environmental and Human Safety of Major Surfactants*. Friends of the Earth Scotland, Edinburgh, Scotland.
43. Fujita, M. et al. (2000). Behavior of nonylphenol ethoxylates in sewage treatment plants in Japan—biotransformation and ecotoxicity. *Water Sci. Technol.* **42**: 23–30.

ECOLOGICAL WASTEWATER MANAGEMENT

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Conventional sanitation concepts are neither an ecological nor an economical solution for rural areas in both industrialized and developing countries. Ecological sanitation (EcoSan) represents a holistic approach toward ecologically and economically sound sanitation. The underlying aim is to close nutrient and water cycles with as small an expenditure on material and energy as possible to contribute to sustainable development. EcoSan is a systemic approach and an attitude. Single technologies are only a means to an end. Therefore, EcoSan-technologies may range from nearly natural wastewater treatment techniques to compost toilets, simple household installations, and to complex, mainly decentralized systems. These technologies are not ecological per se but only in relation to the observed environment. Promotion of EcoSan concepts, therefore, is the strategy for achieving the goal—closing the loop in wastewater management and sanitation.

DEFINITION OF ECOLOGICAL SANITATION

A sanitation system that provides ecological sanitation (EcoSan) is a cycle—a sustainable, closed-loop system (Fig. 1). The EcoSan approach is resource minded, not waste minded. Human excreta are treated as a resource and are usually processed on-site and then, if necessary, processed further off-site until they are completely free of disease organisms. The nutrients contained in excreta are then recycled by using them, for example, in agriculture.

The basic motivation behind the need to reshape the management of nutrients and streams of organic residuals in society may be found in the so-called "basic system conditions for sustainable development" for water and sanitation management, formulated in Agenda 21 (1):

1. The withdrawal of finite natural resources should be minimized.
2. The release of nonbiodegradable substances to the environment must be stopped.
3. Physical conditions for circular flows of matter should be maintained.
4. The withdrawal of renewable resources should not exceed the pace of regenerating them.

If a sanitation system shall contribute toward the goals of ecological sanitation, it has to meet or at least to be on the way toward meeting the following criteria, as given by Esrey et al. (2):

1. *Prevent disease*: A sanitation system must be capable of destroying or isolating pathogens.
2. *Affordable*: A sanitation system must be accessible to the world's poorest people.
3. *Protect the environment*: A sanitation system must prevent pollution, return nutrients to the soil, and conserve valuable water resources.
4. *Acceptable*: A sanitation system must be aesthetically inoffensive and consistent with cultural and social values.
5. *Simple*: A sanitation system must be robust enough to be easily maintained within the limitations of

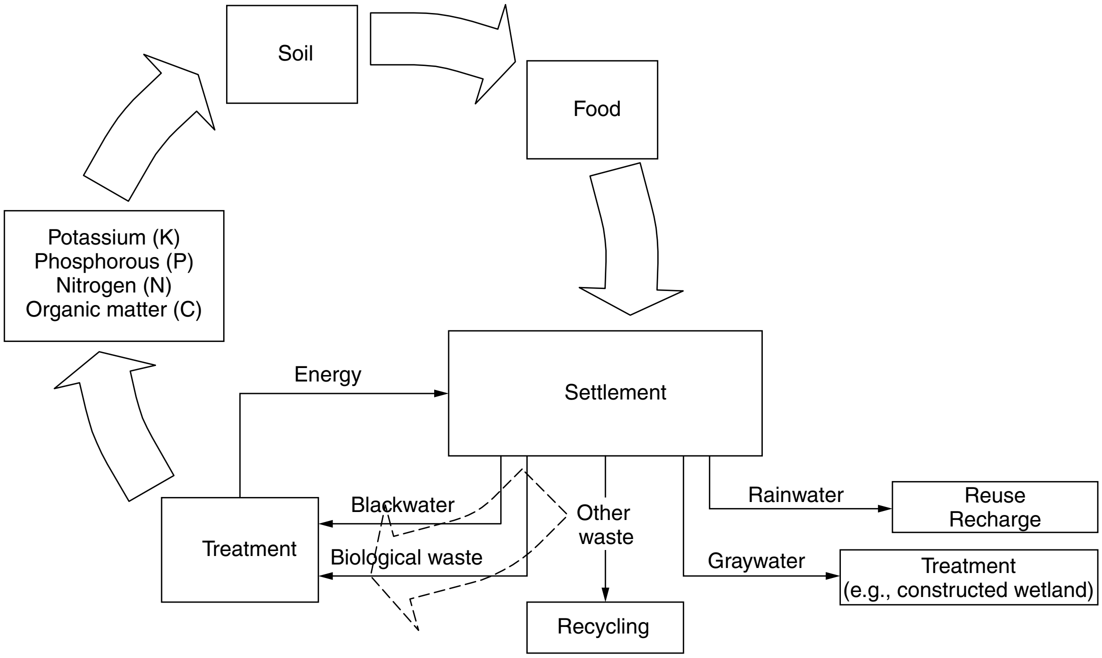

Figure 1. An ecological sanitation system.

the local technical capacity, institutional framework, and economic resources.

6. *Comfortable*: A sanitation system must be nearly as comfortable as a flush toilet. That means it has to be indoors or accessible under the same roof of the house.

Successful implementation of sanitation systems requires understanding all components of the system. The components have to be considered together when designing and making sanitation systems work. Following are the main components (Fig. 2):

- *Nature*: The most relevant natural variables are climate (humidity, temperature), water (amount available, groundwater level), and soil (stability, permeability).
- *Society*: The factors that describe the society include the settlement pattern (concentrated/dispersed, low/high rise), attitude (fecophobic/fecophilic), habits, beliefs and taboos related to human excreta, and the economic status of the community.
- *Process*: Physical, chemical, and biological processes turn human excreta into a nondangerous, inoffensive, useful product. Dehydration and decomposition are the principal processes.

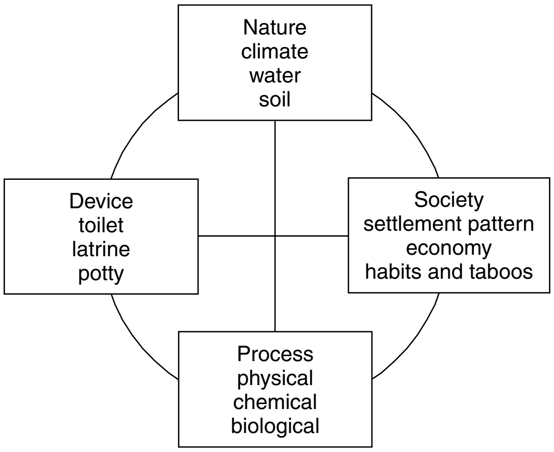

Figure 2. Main components of the "sanitation" system.

- *Device*: The device is the on-site structure specifically built for defecation and urination.

It is essential to sanitize human excreta before they are recovered and reused. Figure 3 shows the different approaches for handling human excreta:

- *Mix and drain*: In conventional sanitation systems, urine and feces are mixed and flushed away with water.
- *Mix and evaporate*: Excreta are mixed; however, they are not flushed away but treated on-site, for example, composted.
- *"Don't mix" and dehydrate*: Urine and feces are collected and treated separately.

The principles underlying EcoSan are not novel. Sanitation systems based on ecological principles have been used in different cultures, for hundreds of years. EcoSan systems are still widely used in parts of East and Southeast Asia. In Western countries, this option was largely abandoned, as flush-and-discharge became the norm, but in recent years, there has been a revival of interest in EcoSan (2).

WASTEWATER IS A RESOURCE

Wastewater from households contains urine (yellowwater), feces (brownwater), and graywater. Graywater is the part of the wastewater which is not mixed with excreta (from kitchens, bathrooms, and laundries). If urine and feces are mixed, the resulting mixture is called blackwater.

For a long time, wastewater has been regarded as a problem because wastewater involves hygienic hazards and contains eutrophying substances in the form of organic matter, nitrogen, and phosphorus. These substances cause problems in seas, lakes, and streams, but, on the other hand, they would be valuable to farmers. Nitrogen (N), phosphorus (P), and potassium (K) in wastewater can be used instead of artificial fertilizer, and the organic material increases the humus content. Recirculating nutrients from wastewater as fertilizer reduces the need for industrially produced fertilizer and also reduces

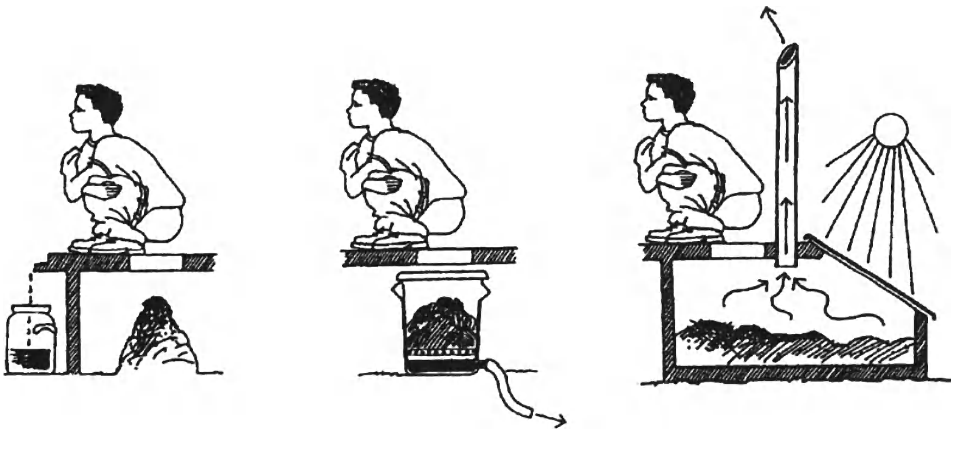

Figure 3. Different approaches for handling excreta: "Don't mix" and dehydrate (left); mix and drain (middle); mix and evaporate (right).

discharges of nutrient-rich water from treatment plants into watercourses.

Wastewater Characteristics

One person produces about 500 liters of urine and 50 liters of feces per year. The same person, additionally, produces a range of 25,000 to more than 100,000 liters of graywater. Blackwater and graywater have very different characteristics (Table 1). Most of the nutrients essential in agriculture (N, P, K) occur in urine. Feces contain smaller amounts of nutrients, and the quantities in graywater are insignificant. If blackwater is collected separately at low dilution, it can be converted, for example, to a safe natural fertilizer that replaces synthetic products and prevents the spread of pathogens and other pollutants to receiving waters.

Sources of Hygienic Hazards

Watersheds may be affected directly by excreta that contain large amounts of pathogens from humans and animals, or indirectly through wastewater outlets, from large-scale wastewater treatment plants and from smaller units of wastewater or graywater on-site sanitation. Stormwater and runoff from agricultural lands may also carry large amounts of pathogens to watersheds emanating directly from excreta, or pathogens occurring in sludge, excreta, and manure applied to land. Stormwater and runoff water may also carry pathogens from domestic and wild animals and birds that may affect humans. Organic waste from human settlements and activities may also be a source of pathogenic organisms.

- *Human fecal excreta* may be harmless but can contain large amounts of pathogenic organisms. The risk depends on the frequency of infected persons and symptomless carriers in the population. Anyway, human fecal excreta are responsible for the major part of hygienic hazards.
- *Human urine* does not normally contain pathogenic organisms that will transmit enteric disease to other individuals. Fecal material is thus the main source of infectious organisms. Only in special cases, for example, a systemic infection with fever, will pathogenic organisms be present in urine.
- All microorganisms in *wastewater* originating from human excreta occur in amounts reflecting their occurrence in infected persons or carriers connected to the system. Their concentrations also depend on the dilution of the water. Untreated wastewater should always be regarded as a potential carrier of pathogenic organisms.
- *Graywater* normally contains small amounts of pathogenic organisms. However, due to a relatively high load of easily degradable organic substances, regrowth of indicator organisms of fecal pollution may occur.
- *Stormwater* may have high loads of fecal contamination. This is of special concern in areas of the world where open-air defecation is practiced, because high loads of pathogens, as in wastewater, may occur. Stormwater may also contain high loads of zoonotic pathogens originating from animal or bird feces.

Table 1. Typical Characteristics of the Main Components of Household Wastewater[a]

		Graywater	Urine	Feces
Volume ($l.p^{-1}.yr^{-1}$)		25,000–100,000	~500	~5
Yearly loads ($kg.p^{-1}.yr^{-1}$)				
N	~4–5	~3%	~87%	~10%
P	~0.75	~10% (P-free detergents)	~50%	~40%
K	~1.8	~34%	~54%	~12%
COD	~30	~41%	~12%	~47%

[a] Reference 3.

Resource Wastewater?

Summarizing the characteristics of wastewater and the sources of hygienic hazards, the following conclusions can be drawn:

- Most of the soluble nutrients are found in urine. If urine is segregated and converted to agricultural usage, the biggest step toward nutrient reuse and highly efficient water protection will have been taken.
- The hygienic hazards of wastewater originate mainly from fecal matter. Segregation opens the way to sanitation and finally to an excellent end product.
- Wastewater that is not mixed with feces and urine is a great resource for high quality reuse of water.
- Source control should include evaluating all products that end up in the water. High quality reuse will be far easier when household chemicals are not only degradable (original substance disappears, even if metabolites do not degrade) but can be mineralized by the available technology. Additionally, pipes for drinking water should not emit pollutants (e.g., copper or zinc).
- To reduce stormwater runoff, local infiltration and/or trenches to surface waters for relatively unpolluted rainwater can be used. Prevention of pollution includes avoiding copper or zinc gutters and roof materials that can cause heavy metal pollution of rainwater runoff.

TREATMENT SYSTEMS

Limitations of Conventional Sanitation

In conventional sanitation systems, human excreta are mixed with water and flushed away by conventional flush toilets. The wastewater is then collected and transported in sewers and treated in a centralized plant.

This results in high water demand, the spread of potentially dangerous pathogens and micropollutants (e.g., residues of pharmaceuticals) in a large volume of water and also the loss of the option to reuse graywater and to produce fertilizer. The initially small amount of feces could be hygienized easily by cheap methods.

For the strange mixture called "municipal wastewater," hygienization is an expensive further treatment step. Hormones and medical residues reveal another weakness of sanitation systems. These substances reach receiving waters easily especially because of their polarity and usually very low degradation rates in treatment plants.

Sewerage systems have a couple of severe disadvantages. In general, they are a very costly part of the infrastructure (if sufficient rehabilitation is done) and drain large amounts of water from the region. Combined systems emit raw wastewater into receiving waters with overflows. Storage tanks are very expensive if the number of overflows is low. Separate systems often have a large number of wrong connections (4).

Centralized Versus Decentralized Wastewater Treatment

Sanitation systems can be classified as follows:

- *Decentralized or 'on-plot' systems* in which safe disposal of excreta takes place on or near a single household or a small settlement.
- *Centralized or 'off-plot' systems* in which excreta are collected from individual houses and carried away from the plot to be treated off-site.

The selection of the most appropriate sanitation system is influenced by ecological, technical, social, cultural, financial, and institutional factors.

Proper decisions on where to connect houses to a sewerage system and where to build on-site facilities or small decentralized plants are the key issue for the economics of the whole wastewater infrastructure. Good regional planning can avoid the deadlock of very expensive sewerage systems that use all the money which could serve the environment in highly efficient decentralized treatment and collection systems.

There are cost calculation procedures that include long-term development to balance operating- and investment costs and products (reuse water, fertilizer, soil improver). The price of secondary products can be very relevant in economically weak and water-scarce countries where water and industrial fertilizers are no longer subsidized. Reuse-oriented sanitation can easily exceed the performance of the most advanced high-tech end-of-the-pipe plant often at much lower costs (4). Water and sanitation projects and programs will fail to be sustainable if they are not planned and designed to meet the needs of the end user (5).

Decentralized Wastewater Treatment Systems

The use of decentralized wastewater treatment systems offers these advantages (6). They save money, protect the homeowner's investment, promote better watershed management, offer an appropriate solution for low density communities, provide a suitable alternative for varying site conditions, and furnish effective solutions for ecologically sensitive areas.

Decentralized systems prevent unnecessary costs by focusing on preventive measures (assessment of community conditions/needs and maintenance of existing systems), instead of reacting to crises. They further maximize the potential for homeowners, who have existing septic systems, to continue to benefit from their original investment and avoid the potentially large transfers of water from one watershed to another that can occur in centralized systems. In small communities of low population density, decentralized systems are the most cost-effective option. These systems are variable, can be designed for various sites that have, for example, shallow water tables, shallow bedrock, low-permeability soils, and small property lot size. Additionally, decentralized systems can provide cost-effective solutions for areas that require advanced treatment, such as nutrient removal and/or disinfection, while recharging local aquifers and providing reuse opportunities close to points of wastewater generation.

Technology Options

Decentralized wastewater treatment alternatives for small communities can be broadly placed in the following categories that represent the basic approaches to wastewater conveyance, treatment, and/or disposal (6, revised):

- *Natural systems* use soil as a treatment and/or disposal medium, including land application, constructed wetlands, and subsurface infiltration. Some sludge and septage handling systems, such as sand drying beds, land spreading, and lagoons, are included.
- *Conventional treatment systems* use a combination of biological, physical, and chemical processes and employ tanks, pumps, blowers, rotating mechanisms, and/or mechanical components as part of the overall system. These include suspended growth, fixed growth, and combinations of the two. This category also includes some sludge and septage management alternatives, such as digestion, dewatering and composting systems, and appropriate disposal.
- *Alternative collecting systems* that use lightweight plastic pipe buried at shallow depths, have fewer pipe joints and less complex access structures than conventional gravity sewers. These include pressure, vacuum, and small-diameter gravity sewer systems.
- *Alternative treatment systems* use source control and separating systems. An example of an alternative treatment system for ecological sanitation is given later.

None of the described systems is a priori or not an EcoSan system. A number of criteria as given above have to be met for a sanitation system to be called an EcoSan system.

Low Water Consumption and Water-Free Toilets and Urinals. A major part of alternative treatment systems are devices suitable for reducing water consumption and/or for separating feces and urine. Therefore, the available systems of low water consumption and water-free toilets and urinals are described:

1. *Conventional water-flush toilet* (listed as the reference system): The conventional water-flush toilet is

standard in most industrialized countries. A precondition to the effective disposal of excrements in this manner is sufficient availability of flushing water (about 6–8 liters per flush) as well as a corresponding disposal system (sewer system and wastewater treatment plant or other disposal). At the high dilution of human excretions (approximately 100 to 250 g feces and 1 to 1.5 liters urine), the use of a conventional flush toilet requires about 40 liters of water per day, and the wastewater produced contains both nutrients and pathogens.

2. *Water-conserving toilet*: The water-conserving toilet reduces the required consumption of water to 1.0 to 4.5 liters per flush. Together with a reduction in water costs and an increase in the available capacity of the existing wastewater collection system (e.g., collection pits), water-conserving toilets produce a more concentrated wastewater that can be used further more easily (e.g., biogas extraction, solid waste separation). Due to the smaller volume of flushing water, blockages in the pipes must be prevented by a flushing device, and certain structural requirements must be observed (e.g., minimum gradient in the downstream pipe).
3. *Water-conserving toilet with waste segregation*: In addition to the reduction in water consumption, the water-conserving toilet with waste segregation allows the division of feces and urine. Therefore, urine can be used for, for example, agricultural purposes, and costs can be reduced by avoiding removal of nutirents in sewage treatment. The installation of a waste-segregation toilet is only possible in combination with a corresponding collection system (urine collection tank in the house, regular emptying of the tanks, agricultural application). Feces and urine are divided in a user-friendly manner by an adapted effluent vent in the toilet bowl.
4. *Vacuum toilets*: Vacuum toilet systems dispose of flushing water and excrement by using a pipeline network under vacuum (approximately 0.5 bar) connected to a collection tank. Water is required only to rinse the toilet bowl, not for facilitating transport (approximately 0.7 to 1.0 liter per flush). Until now, the vacuum system has been used mostly in ships, trains, and aircraft (limited flush and wastewater capacities). The wastewater is very concentrated, so it is suitable for energy generation in a biogas plant. Drawbacks to the system are the technical requirements (operation and maintenance of the vacuum unit) and the associated financial costs (with susceptibility to breakdown, for example, blockages).
5. *Toilet systems without water (dry toilets)*:
   - *Compost toilets*: The compost in this system is formed from an aerated mixture of excrements and composting earth held in a container. For proper function, a minimum air temperature of 10 °C is required as well as regular checks (approximately once/month) of the structural composition and equipment. Regular extraction of the humus is necessary.
   - *Dehydration toilets* are based on drying excrements, which are odorless and almost sterile in dehydrated form and can be used as a soil conditioner. It is therefore important to segregate urine and feces. Urine can then be collected for agricultural applications, drained away, or evaporated. The dehydration process can be accelerated by using moisture-absorbing material or heat, such as exposure to the sun. Dehydration toilets are ideal for dry and arid climates.
   - *Water-free urinals* are made of ceramics or plastics, that must be regularly impregnated with an antibacterial agent. Odor is contained by an insert with a special sealant that has a lower specific mass than urine and is buoyed upward or by using a float. As crystalline precipitation occurs only on contact of urine with water, such deposits cannot occur in the down pipe. A further advantage of the water-free urinal is the low installation and maintenance costs (no connection to a water supply and no mechanical or electrical flushing fixtures).

It has been clearly demonstrated that urine sorting toilets are feasible (e.g., Sweden has more than 3000 installations; Ref. 7). Drawbacks have been observed from too small diameters of urine pipes that clog from scaling. For waterless separating toilets, one major problem remains: Men are often reluctant to sit down to urinate. This would cause a loss of urine and mix urine with feces. A luxury solution for this problem would be a private waterless urinal.

Dry toilets will fail if those who plan/design do not understand the basics, wrong materials are used, or there is poor workmanship, and users are not involved and sufficiently instructed. “Fail” usually means that the content of the processing chambers turns wet, resulting in odors, fly breeding, and incomplete sanitation.

Example of an Alternative Treatment System

Figure 4 shows an alternative treatment system that is suitable for single houses and rural settlements and is based on sorting toilets (6). The example presented is more suitable for developed countries due to the number of technical systems used.

Urine from separating toilets and waterless urinals flows into a storage tank where it stays until it is used mainly for agricultural purposes. The storage period should be at least half a year because this is an appropriate time for collection and part of the eventual medical residues can be destroyed during this period.

Feces are flushed by an appropriate amount of water (e.g., 4 or 6 liters) and discharged into one chamber of a two-chamber composting tank (with filter floor or filter bag) where the solids are precomposted. After a 1-year collecting, dewatering, and composting period, the flow is directed to the second chamber; the first one is not fed for 1 year. This allows further dewatering and precomposting and makes removal from the tank safer (although the matter is not sanitized then).

The products removed from the composting tank are brought further to full composting. They could be

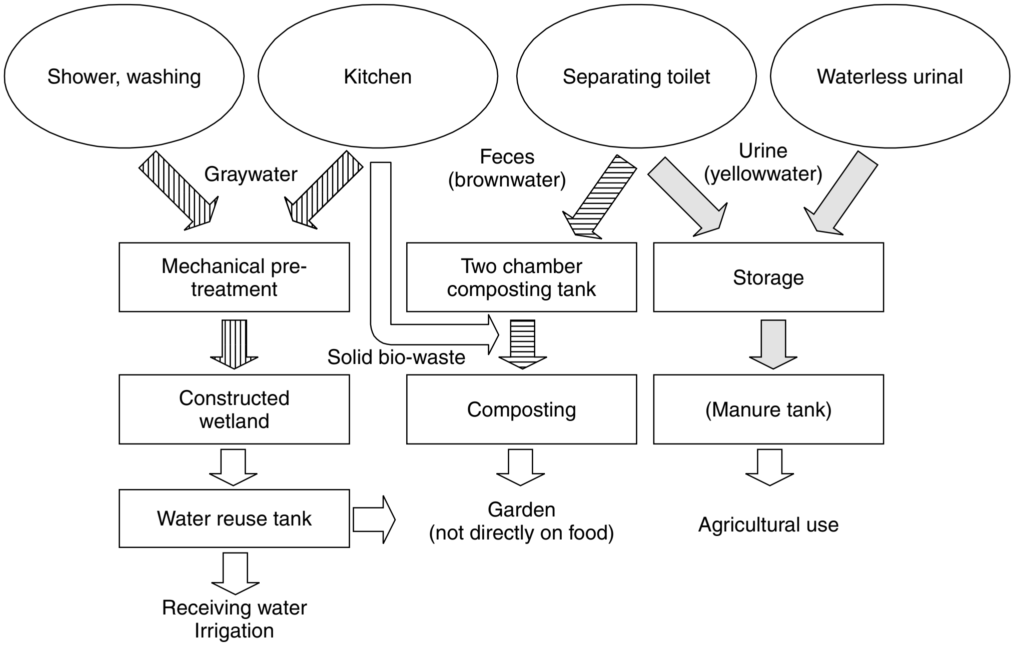

Figure 4. Concept for an alternative treatment system.

mixed with solid kitchen and garden waste to decompose completely and allow further sanitizing. The filtrate from the composting tank is low in nutrients due to the previous separation of urine. Therefore, the filtrate can be treated together with the graywater unless high-quality reuse is planned.

Graywater is pre-treated mechanically and afterward treated by a vertical-flow constructed wetland, intermittently loaded. The treated graywater is either stored and used in the garden and for irrigation or is discharged.

SUMMARY

The underlying aim of ecological sanitation (EcoSan) is to close nutrient and water cycles to contribute to sustainable development. Single technologies are only a means to an end to reach EcoSan goals. EcoSan-technologies, therefore, may range from nearly natural wastewater treatment techniques to separating toilets, simple household installations, and to complex, mainly decentralized systems. Technologies are not ecological per se but only in relation to the observed environment.

The main objectives of sanitation systems are that they have to minimize health risks and protect the environment. Ecological sanitation systems, additionally, have to return nutrients to the soil and conserve valuable water resources. They have to be affordable and therefore accessible to the world's poorest people, acceptable, aesthetically inoffensive, and consistent with cultural and social values, simple and robust in design and operation, and as comfortable as conventional systems.

A sanitation system consists of the following components: nature (climate, water, and soil as main factors), society (including settlement pattern, attitudes, beliefs and taboos related to human excreta, and the economic status of the community), the processes occurring (that convert human excreta into a nondangerous, inoffensive, useful product), and the device (the on-site structure specifically built for defecation and urination). These components have to be considered together when designing sanitation systems and making them work.

EcoSan systems have a number of advantages that can be summarized as follows:

- *Advantages to the environment*: If EcoSan systems could be adopted on a large scale, it would protect groundwater, streams, lakes, and the sea from fecal contamination. Less water would be consumed. Farmers would require smaller amounts of commercial fertilizers, much of which today washes out of the soil into water, thereby contributing to environmental degradation.
- *Advantages to households and neighborhoods*: Urine separating systems, if properly managed and maintained, do not smell or produce flies and other insects. This is a great advantage over ordinary pit toilets. Urine and feces do not come into contact and produce odor. Moisture levels are too low for fly breeding. Over half the population of the developing world has no sanitary system for excreta disposal. The market for appropriate sanitation devices is enormous, and there is a big demand. The majority of separation toilets do not require expensive or high-tech equipment. Jobs could be created for builders and for collectors of urine and sanitized feces. These products can be sold to farmers or used in the garden.
- *Advantages to municipalities*: Municipalities all over the world are experiencing greater and greater difficulty in supplying water to households and neighborhoods. EcoSan systems do not use these scarce water resources and may create therefore,

a more equitable allocation of water to rich and poor households.

A wastewater infrastructure is usually built for extremely long service. The lifetimes of existing house installations, sewerage systems, and treatment facilities have to be considered. A change to EcoSan systems is easier for newly constructed settlements or rehabilitation of complete houses. The lifetime of a house installation is far shorter than that of sewerage systems. Components of source control sanitation could be installed in each renovated flat and be connected to conventional systems first. This can be economical based on the water saving from the beginning; later, after conversion of a group of houses, separate treatment can be implemented.

Acknowledgments
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BIBLIOGRAPHY

1. Agenda 21. (1992). *The United Nations Program of Action from Rio*. United Nations, New York.
2. Esrey, S., Gough, J., Rapaport, D., Sawyer, R., Simpson-Hèbert, M., Vargas, J., and Winblad, U. (1998). *Ecological Sanitation*. SIDA, Stockholm, Sweden.
3. Lange, J. and Otterpohl, R. (2000). *Abwasser—Handbuch zu einer zukunftsfähigen Wasserwirtschaft (Wastewater—Manual for sustainable water management)*, 2nd Edn. MALLBETON-Verlag, Donaueschingen-Pfohren, Germany [*in German*].
4. Otterpohl, R. (2002). Resource efficient wastewater concepts—technical options and initial experience. *Proceedings IFAT 2002*. Munich, Germany.
5. Parry-Jones, S. (1999). *Optimising the Selection of Demand Assessment Techniques for Water Supply and Sanitation Projects*. Final Report Project/Task No: 207. Water and Environmental Health at London and Loughborough (WELL), UK.
6. Lens, P., Zeeman, G., and Lettinga, G. (Eds.). (2001). *Decentralized Sanitation and Reuse—Concepts, Systems and Implementation*. IWA Publishing, London, UK.
7. Johansson, M., Jönsson, H., Höglund, C., Richert, S. A., and Rodhe, L. (2001). *Urine Separation—Closing the Nutrient Cycle*. Report, Stockholm Water Company, Stockholm, Sweden.

WASTE TREATMENT IN FISH FARMS

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WASTE TREATMENT: GENERAL ASPECTS

With increasing aquacultural production, there is a greater need to reduce the amount of waste in fish farm effluents. These days, simple dilution is no longer considered an appropriate treatment (1). Generally, waste in fish farms is treated for two reasons: (1) in recirculating systems, it can negatively affect the fish and (2) in open systems, it can negatively affect the environment. Pollution control in general and in fish farming in particular should aim first at prevention rather than a cure, which can be achieved by using the best available technology (BAT) and best management practices (BMP). These have been reviewed and critically discussed in a recent comprehensive workshop (2). The use of highly digestible diets and stress-free husbandry have greatly reduced waste production per quantity of produced fish; for example, salmonid farms have achieved a reduction of about 80% in the last twenty years (3). However, despite BAT and BMP, the effluent often still needs to be treated and aquacultural waste management still relies heavily on end-of-pipe solutions. For treatment to be economically sustainable in terms of capital costs, running costs, and space requirements, some specific features of aquacultural waste loading must be taken into account.

The waste loads in aquacultural facilities have some properties that make treatment difficult. These include very low but strongly fluctuating concentrations of solids and nutrients and high flow. Table 1 compares some important effluent load parameters in salmonid farms with those in municipal waste waters. (Fig. 1). The average effluent load from a land-based flow-through fish farm is normally much lower than that in the treated water leaving a sewage plant. However, the flow from fish farms can be very high—greater than 500 $L\cdot s^{-1}$—and the total solid load can vary by two orders of magnitude in the course of a single day. Aquaculture treatment devices have to meet these diverse challenges but without the benefit of many of the technologies applied in sewage plants such as flocculation chemicals or biological treatments, which are often too expensive or otherwise impracticable under fish farm conditions.

With respect to effluent treatment, it is important to differentiate between four types of fish culture systems: (1) flow-through fish farms, (2) recirculating aquaculture systems (RAS), (3) open net cages, and (4) pond or integrated aquaculture.

In flow-through fish farms, the water quality for the fish is ensured by the steady discharge of wastes with the bulk flow. The relative loading is usually low, but due to the high flow rates, the total load in the recipient water body may become elevated, thus causing environmental problems. Waste treatment in flow-through systems is almost exclusively restricted to mechanical techniques. In RAS, where only compensatory water is added, wastes accumulate and remain within the system. The accumulated wastes must be removed to maintain physiologically adequate conditions in the culture water. In this case, waste control usually involves mechanical separation for the removal of particulate matter and the use of some kind of biofilter to remove dissolved compounds. In open net cages, waste control is very difficult as the waste can pass freely in nearly all directions. Particle traps provide the only means of collecting settled uneaten feed or fecal pellets. New

Table 1. Waste Loads of Flow-Through Fish Farms (Range of Values from Germany) Compared With Municipal Waste Loadings (11)

Source	Total Suspended Solids, mg·L^{-1}	Total Phosphorus, mg·L^{-1}	Total Nitrogen, mg·L^{-1}	BOD$_5$^{a}, mg·L^{-1}
Salmonid farms	0.5–10	<0.1	<1.4	0.5–5
Municipal wastes				
Low strength	350	4	20	110
Medium strength	720	7	40	190
High strength	1230	12	70	350

^{a}BOD$_5$, biological oxygen demand in 5 days.

advanced waste control measures use adjacent cultures of seaweeds, filtering organisms like mussels, or sediment feeders to transform the wastes near the net cages into valuable products. In pond or integrated aquaculture, the waste from one species is beneficial to other species and treatment is generally not desired. Some pond systems employed in Asian countries raise ducks or chickens on platforms from which manure falls directly into ponds stocked with filtering and omnivorous fish. The overflow may be used to irrigate paddy fields.

The principal wastes that can reasonably be expected to be removed from fish farm effluents comprise solids, biodegradable organics, and phosphorus and nitrogen compounds, including toxic ammonia and nitrite. Particles can be removed in a comparatively easy and effective manner; but the removal of the soluble components of effluents requires more sophisticated methods that must often be designed specifically for the culture system in use, taking account of the individual circumstances. Table 2 gives an overview of different waste handling systems and their capacities and restrictions. Irradiation and ozonation to control pathogens are special cases and will not be considered further here.

SOLID REMOVAL

Solids can be removed using settling basins, microscreen filters, granular media filters, and flotation (by air or foam fractionation as well as by ozonation). The two latter techniques are rarely applied in fish farming practice. The effectiveness of mechanical treatment depends on the particle size distribution and the ratio of bound particles to dissolved wastes. Results of empirical studies show considerable variations in the size distribution of suspended solids and in the efficiency of mechanical treatments (4).

Settling basins are the most traditional and widespread method for removing solids. They are simple to operate and have moderate costs; but as they are dependent on flow and sinking velocity of the particles, they require large

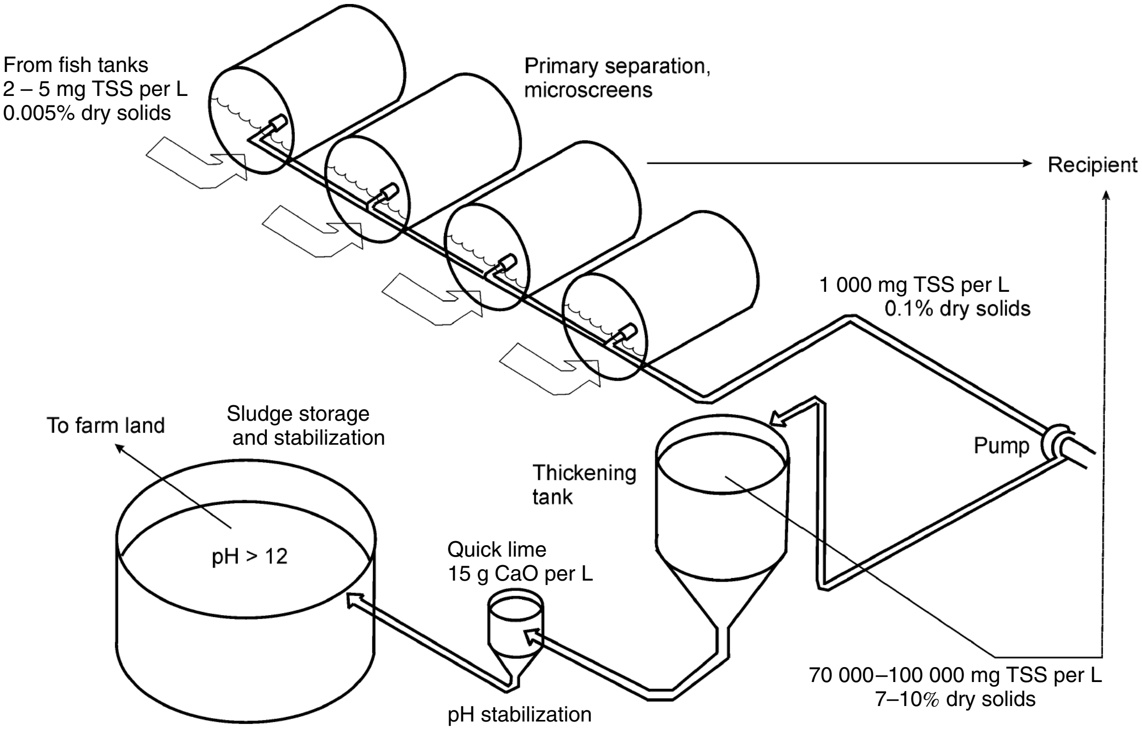

Figure 1. Diagram of an integrated effluent treatment and sludge processing system (2).

Table 2. Different Separation Processes for Aquacultural Facilities, Removal Potential, Advantages, and Disadvantages

Waste System	Treatment Types	Effective Removals	Advantages	Disadvantages
Sedimentation	Settling basin, swirl settler	Solids larger than 100 μm	Robust, easy to handle, cheap	High space requirements, re-release of wastes from settled solids, efficiency depends on TSS concentration
Microscreen	Drum filter, disk filter, Triangel filter	Solids larger than 30 μm	Low space requirements, easy to handle, tolerating high hydraulic loads, little TSS dependency	High capital and energy costs
Granular media filter	—	Solids larger than 15 μm, dissolved matter	Dual system removing particles and dissolved matter, low space requirements	Large amount of backwash water, suboptimal removal of solids and dissolved matter, high energy costs
Flotation	Dissolved air systems, dispersed air systems	Solids smaller than 30 μm	Capable of removing very small solids, low space requirements	Insufficient removal of large solids, high energy costs, dependent on bubble sizes and foam stability
Ozonation	—	Organic solids and dissolved matter, disinfections	Combines waste removal and control of pathogens	Toxic substance, system must be built with inert materials to avoid corrosion, high costs, underflow only
Biofilter	Submerged filter, trickling filter, rotating biological contactors, pressurized-bead filters, fluidized-bed biofilters	Solids and dissolved matter	Able to treat total wastes including toxic ammonia and nitrite	Costs sensitive to pH fluctuations, temperature, growth phase etc., low hydraulic loading capacity
Constructed wetlands	No standards available	Solids and dissolved matter	Very high removals (more than 90% of most compounds), can be integrated into the environment	High capital costs, each constructed wetland has to be developed for the individual situation, no long-term data available, dependent on climatic conditions

spaces. Solids settle as a result of their density. As the density of solids in aquaculture is typically close to that of water with values of 1.005–1.2, very small solids settle very slowly. Effective removal therefore requires very long hydraulic residence time. As a result, settling basins are often unable to effectively treat total suspended solid (TSS) loads lower than 10 $\text{mg}\cdot\text{L}^{-1}$ (dry weight) or solids smaller than 100 μm, and they do not attain solid effluent concentrations of less than 6 $\text{mg}\cdot\text{L}^{-1}$ (dry weight) (5,6).

Microscreen filters act as sieves that strain suspended particles larger than the mesh size. The collected particles are cleared from the screen with a dispersed hydraulic jet, thereby generating a backwash volume of 0.2–2% of the bulk flow. According to Cripps (7), mesh sizes below 60 μm give little advantage in solid removal but superproportionally decrease hydraulic capacity and increase backwash water. TSS removal in flow-through farms averages 68–80% compared with 22–70% in RAS. In practice, there are three main varieties of microscreen, namely, drum filters, Triangel filters, and disk filters.

Swirl settlers or hydroclones utilize the "tea-cup effect" generated by water injected at the outer radius of a conical tank. This effect improves settlement of the particles and forces them to the center of the tank, where they are removed from the flow. This process has a distinct advantage over classical sedimentation, and in fish farming, swirl settlers are used in small underflows comprising just 5–10% of total flow.

In recirculating aquaculture systems—in contrast to the other systems mentioned above—small solids (less than 50 μm) constitute most of the solid mass. Small solids are difficult to remove by the methods described above, but flotation is an efficient measure. In a flotation chamber, bubbles from the bottom float upward against the bulk flow, "collecting" surface-active particles, which become attached to the bubbles. The particles are carried to the surface where the bubbles break and form a foam layer. The small solids are released into the foam, which can be separated from the bulk flow by a weir. Another method sometimes used in recirculating systems employs granular media filters, which function as both mechanical and biological filters (8). Buoyant, inert beads up to 5 mm in diameter are carried through by the water stream and small particles are strained out or precipitated on the bead surface. The effects of microbial settlement on the beads are described in the next section. To clear the filter, the flow is stopped and the beads are washed forcibly backward. The backwash volume is 1–5% of the bulk flow. The dual function of this kind of filter brings considerable advantages but does not allow optimal removal of both solids and dissolved or colloid compounds.

Settling basins, flotation, and granular media filters provide opportunities for significant microbial degradation, leaching processes, and resuspension of settled waste, all of which lead to re-release of wastes back into the bulk flow. Only microscreen filters and swirl settlers ensure steady and permanent separation of solid-bound wastes from the flow that is treated.

DISSOLVED AND COLLOID COMPOUNDS REMOVAL

Ammonia and dissolved organic compounds are accessible for degradation by microorganisms attached to submerged or wetted surfaces. Ammonia is oxidized by autotrophic bacteria in a two-step process called nitrification. Biodegradable organic compounds are oxidized by heterotrophic bacteria, protozoa, and micrometazoa. When applied in aquacultural situations, this natural process is called biofiltration. The capacity of a biofilter depends on the surface area available for biological growth and on the oxygen supply. The efficiency of the biofilter depends on the accessibility of the media surface and the rate of mass transfer into the biofilm. It also varies with the growth phases of the filter (lag, log, stationary, or death phase). The voids ratio is critical for the hydraulic performance. A large variety of biofilters are available and the appropriate one must be chosen according to the individual fish farm. An overview is given by Summerfelt (6).

INTEGRATED TREATMENT SYSTEMS

Recently, there has been an increasing effort to use artificially or naturally constructed wetlands of different types for the removal of waste loads from fish farm effluents. This kind of treatment is very effective for both solids and dissolved or colloidal compounds. A current study by Michael (9) showed that an abatement pond coupled with a constructed wetland was able to remove more than 98% of solids, over 90% of biodegradable organics and phosphorus, and more than 84% of ammonia. However, further studies and monitoring are needed to assess the long-term effectiveness and economic viability of such treatments.

REUSE AND DISPOSAL OF SLUDGE

For each separation technique leading to an accumulation of sludge, it is crucial that the sludge is thickened to minimize its volume. Figure 1 gives a diagram of integrated effluent treatment combined with sludge processing. On average, the solid concentrations are increased from 2 to 5 $\text{mg}\cdot\text{L}^{-1}$ in the effluent entering the microscreens to 7–10% dry solids in the thickened sludge, an increase of more than 20,000 times. Beneficial reuse of aquacultural sludge includes four possibilities: agricultural application, composting, vermiculture, and reed drying bed. Sludge from fish farms is rich in organic nitrogen (3–9% of dry matter) and phosphorus (1–4% of dry matter) but poor in potassium (less than 0.3% of dry matter) (10). Decomposition processes are necessary to make the nutrients accessible for plants. Heavy metal concentrations are usually below regulatory limits.

This brief review gives an insight into the tasks, challenges, and possibilities for treating aquacultural wastes. In reality, effective waste removal is often based on a combination of different waste treatment systems (11). Standard proceedings can seldom be recommended unmodified. Thus, the consultation of experts for the individual situation is often necessary.

BIBLIOGRAPHY

1. Davenport, J., Black, K., Burnell, G., Cross, T., Culloty, S., Ekaratne, S. et al. (2003). *Aquaculture: the Ecological Issues*. Blackwell Science Ltd., London.
2. Boyd, C.E. (2003). Guidelines for aquaculture effluent management at the farm-level. *Aquaculture* **226**(1–4): 101–112.
3. Bergheim, A. and Brinker, A. (2003). Effluent treatment for flow through systems and European environmental regulations. *Aquacultural Eng.* **27**: 61–77.
4. Kelly, L.A., Bergheim, A., and Stellwagen, J. (1997). Particle size distribution of wastes from freshwater fish farms. *Aquaculture Int.* **5**: 65–78.
5. Henderson, J.P. and Bromage, N.R. (1988). Optimising the removal of suspended solids from aquacultural effluents in settlement lakes. *Aquacultural Eng.* **7**: 167–181.
6. Summerfelt, S.T. (1999). Waste-handling systems. In: *CIGR Handbook of Agricultural Engineering*, Vol. II *Aquaculture Engineering*. F.W. Wheaton (Ed.). American Society of Agricultural Engineers, Baltimore, MD, pp. 309–350.
7. Cripps, S.J. and Bergheim, A. (2000). Solids management and removal for intensive land-based aquaculture productions systems. *Aquacultural Eng.* **22**: 33–56.
8. Chen, S., Timmons, M.B., and Malone, R.F. (1993). Production, characteristics, and modeling of aquaculture sludge from a recirculating aquaculture system using a granular media biofilter. In: *Techniques for Modern Aquaculture*. J-K. Wang (Ed.). American Society of Agricultural Engineers, pp. 16–25.
9. Michael, J.H.J. (2004). Nutrients in salmon hatchery wastewater and its removal through the use of a wetland constructed to treat off-line settling pond effluent. *Aquaculture* **226**: 213–225.
10. Bergheim, A., Cripps, S.J., and Liltved, H. (1998). A system for the treatment of sludge from land-based fish-farms. *Aquat. Living Resour.* **11**(4): 279–287.
11. Tchobanoglous, G., Franklin, B.L., and Stensel, D.H. (2003). *Wastewater Engineering—Treatment and Reuse*, 4th Edn. McGraw-Hill, New York.

FLOTATION AS A SEPARATION PROCESS

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The importance of the flotation process to the economy of the whole industrial world is considered enormous.

Without this process, many familiar metals and inorganic raw materials would be exceedingly scarce and costly because the high-grade ores that could be processed by simple physical and mechanical methods have long since been used up (1). Flotation initially originated from the field of mineral processing, usually termed froth flotation. For many years, various particulate solids besides minerals have been extracted from water by using this effective gravity separation method that is based on the idea of applying rising gas bubbles as the transport medium; the attachment of bubbles to particles transfers the solids from the body of water to the surface. As opposed to settling, flotation is a solid–liquid separation technique that is applied to particles whose density is lower or has been made lower than the liquid they are in. These flotation applications include mainly the treatment of water and wastewater (2,3); in the former paper, a useful discussion forum was placed on the Internet by the conference secretariat, Mr. Eero Teerikangas. Today, for example, applications of flotation exist in paper manufacturing for deinking and waste paper recycling (4), emulsified oil from various industrial wastewaters (5,6), and the separation of used plastics (7).

The typical classification of flotation processes is based on the method used to generate bubbles; so, two broad categories exist:

1. dispersed-air flotation (including electroflotation), and
2. dissolved-air flotation (DAF).

These are essentially two different techniques for bubble size, flow conditions, separation aim, and economics. Very few comparison studies, in similar experimental conditions, of these techniques are in the literature (8).

Dispersed-air flotation uses aeration, a well-known step in wastewater treatment as also is its design (guides are given by various companies, for example, Sanitaire). Fine bubble aeration is a subsurface form of diffusion, in which air is introduced in the form of very small bubbles; fine pore diffusers are usually made from ceramic, plastic, or flexible perforated membranes. Several papers have been published on bubble size and distribution, such as (9,10).

Dissolved-air flotation (see Fig. 1) is the dominant flotation technique in water and wastewater treatment. It is based on the theory of a recycle chemical reactor for its operation and on Henry's law for the dissolution of air in water as a function of pressure (1,11).

Computational fluid dynamics (CFD) codes have been also used to study the flow characteristics of this system. Multiphase flow equations for the conservation of mass, momentum, and turbulence quantities must be solved using an Eulerian–Eulerian approach in which the phases

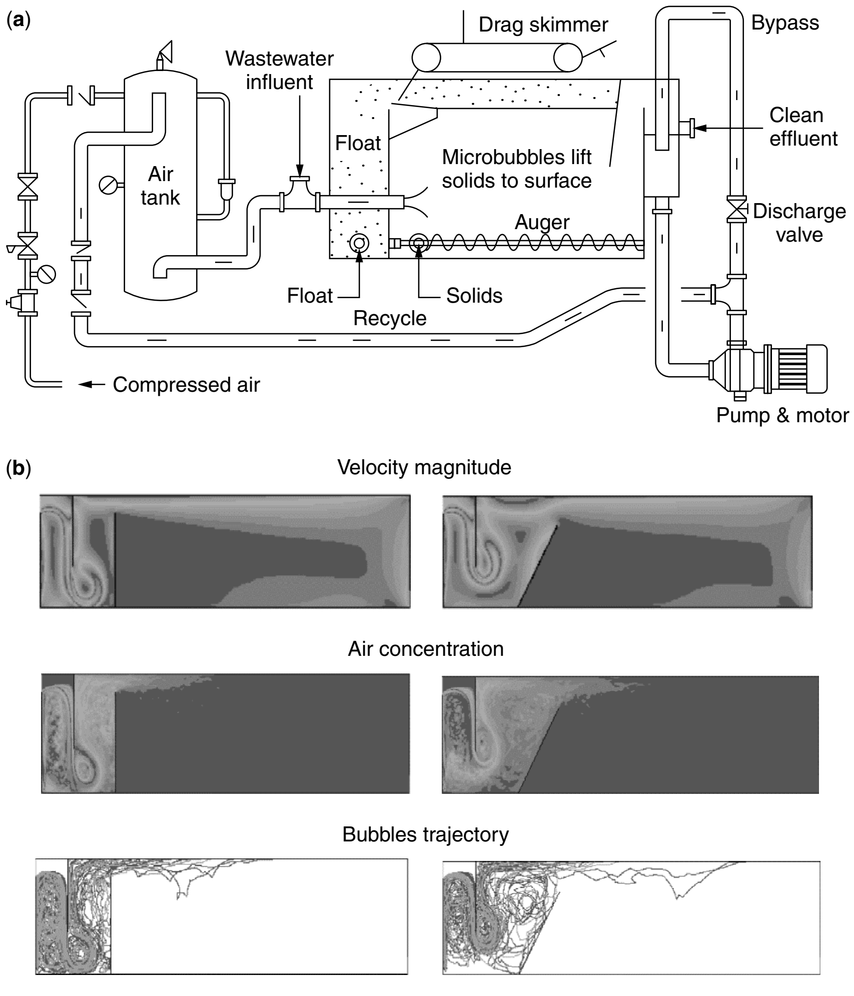

Figure 1. (**a**) The dissolved-air flotation technique (Courtesy Ecologix Environmental Systems) (top). (**b**) Impact of inclined internal baffle on the separation process obtained by CFD simulation—(unpublished results of EU METASEP project) (bottom).

are treated as interpenetrating continua. A four-phase model has been used for water, air bubbles, solid particles, and the aggregate of bubbles with particles (Fig. 1b).

Generally, low air volumes are available for dissolved-air flotation; this is not a parameter easily changed, and the reason is that the pressure in the saturation tank is raised up to 5–6 atm. For this reason, effective flocculation is a prerequisite mainly for dissolved-air flotation (12).

The trend in the development of DAF technology for potable water is to very thick microbubble beds with high flow rates, advertised as 3rd generation technology (2). A flow rate of more than 60 m/h was given, where flotation operation approaches turbulent flow. A compact (downstream filtration in the same basin) so-called re-flotation plant with hydraulic flocculation was built, for instance, for the Tampere, Finland, water and sewerage works in 1997 by the company OY Rictor AB. One of the advantages of flotation is its speed, hence its ability to operate inside a factory (Fig. 2).

Sorption combined with flotation has been investigated (8). The combination of processes is a necessity because of high existing standards and media pressure, not to mention the scarcity of water in many places. The process examined (often termed sorptive flotation) involves abstracting metal ions onto sorbents, in a fine or ultrafine size range, followed by flotation to separate metal-loaded particles. The sorbents used in the first stage were also industrial by-products (1,3). In this way, treated clear water is produced as an underflow and a foam concentrate, from which recovery of metals is possible, leading to clean technology.

A comparison between dispersed-air and dissolved-air flotation, applied to metal-loaded goethite, is presented in Fig. 3a. The recycle was the main parameter studied (at least 20% was necessary) for dissolved-air flotation (8). A flocculant was also required, particularly for DAF. Generally both flotation techniques gave good flotation recoveries; nevertheless, dispersed-air flotation looks preferable. Metal removals were near 100%.

Many industrial wastewater streams with large flow contain toxic metals, which have to be removed prior to water recycling, indirect discharge into a sewage system, or direct discharge into surface waters. Metal compounds such as copper, zinc, manganese, lead, and arsenic dominate the list of greatest releases. Mines and processing plants are often situated in water catchment areas (mountain slopes), and so environmental action plans are required to limit acid drainage and prevent pollution.

Copper recovery was investigated with a wastewater from the Assarel mine (in Bulgaria) composed of Cu(II) 240, Mn(II) 40, Fe(III) 8, Pb(II) 0.2, SO_4^{2-} 4200, Ca(II) 270, and Mg(II) 260 mg/L as the main constituents (13). Almost complete copper removal was obvious for all cases (Fig. 3b), even though the requisite xanthate dose was doubled for real effluents; the quantity needed was around 1 g/L for synthetic wastewater and around 2 g/L for real effluents. In all cases, the residual copper concentration was lower than 0.11 mg/L; the limit in Europe for indirect discharge of chemical industry effluents is 0.5 mg/L copper.

Xanthates are known to exhibit a high level of chemical reactivity for heavy metals. Precipitate flotation is the mechanism that involves first the immobilization of ions as precipitates, for example, raising the respective concentrations may lead to precipitation of the ions as a surfactant floatable product before air is injected (1). This means that it is not a solution any longer but rather a dispersion. In Reference 13, economic considerations of the various processes were also given, including microfiltration downstream.

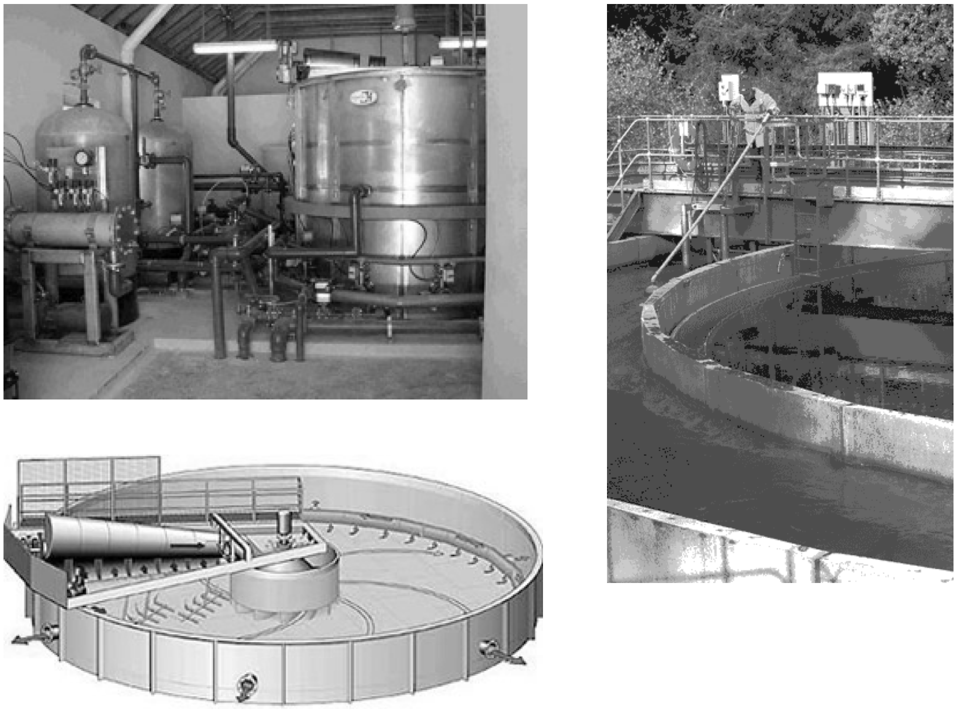

Figure 2. Possibility for the flotation process to operate in a closed factory (top) or open air. Gratitude is given to the companies Krofta (Sandfloat design), Meri Technologies (Deltapurge clarifier), and Purac Ltd. (bottom right).

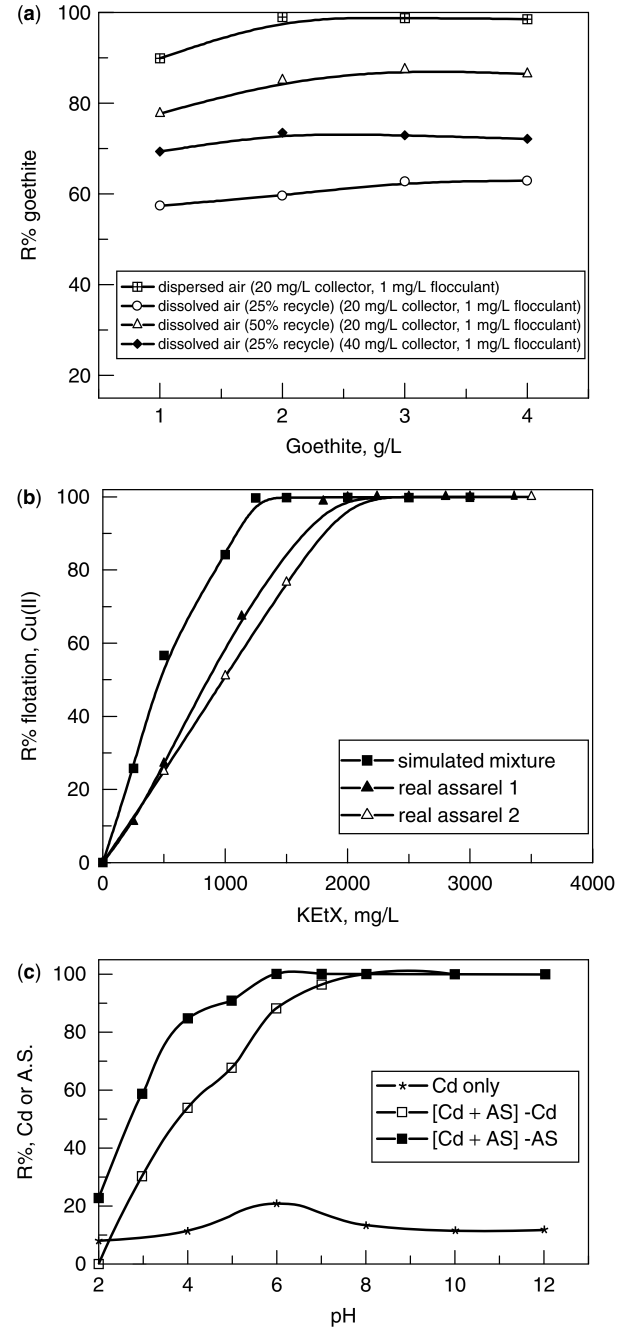

Figure 3. (**a**) Comparison of dispersed-air with dissolved-air flotation for Cr(VI) removal, applying dodecylamine as the flotation collector. Copyright Technical Faculty and Copper Institute, Bor Yugoslavia (top). (**b**) Copper ion flotation applied to a mine effluent: influence of xanthate collector concentration on copper removal. Reprinted from the periodical Hydrometallurgy, Ref. 13, copyright (2004) with permission from Elsevier. (**c**) Biosorptive electroflotation of cadmium on anaerobically digested activated-sludge biomass (denoted as AS): effect of solution pH. Reprinted from Ref. 2.

To the various abnormal reasons for serious contamination of water and soil by toxic heavy metals, one has to add ecological accidents. Like those at Aznalcóllar, Spain, in 1998, an accident in an area close to the Doñana Natural Park in South Andalusia released 2 million m^3 of tailings and 4 million m^3 of water contaminated by heavy metals into the Guadiamar River and that at Baia Mare, Romania, in 2000 where a tailings pond burst releasing approximately 100,000 m^3 of waste water containing up to 120 tonnes of cyanide and heavy metals into the Lapus River; this then traveled downstream into the Somes and Tisa Rivers into Hungary before entering the Danube.

Electrolytic flotation or electroflotation constitutes an unconventional technique in which the bubbles necessary for the flotation are produced by electrolysis of the medium. Electrodes are usually mounted horizontally and receive a low voltage current (6,14). A large amount of very small bubbles is formed with minimum turbulence. Clarification can be effected with effluents that previously would not have been considered suitable for treatment by flotation. The electric field gradient between the electrodes aids flocculation of suspended matter. Gas production, residence time, and the other operating conditions can be checked quickly and are easily controlled. No high-pressure pumps, pressurized vessels, or other complex machinery are needed, and moving parts are minimal.

When aluminum alloy electrodes were used (Fig. 3c), the results were improved; biomass recovery was possible from pH 7 approximately. Results were not highly affected by shorter process duration (10 min) and even lower current density (65 A/m^2). The two curves (of cadmium removal on biomass and of floated Cd-loaded biomass almost coincide with pH variation. Attention should be paid to metals aqueous speciation.

Since the discovery that the activated sludge treatment process can also remove metals from wastewaters, much progress in research has been made. Nowadays, it is known that biosorption, using appropriate usually nonliving biomass, is one of the innovative methods for removing toxic metals from effluent; the more conventional methods are precipitation, adsorption, and ion exchange. The process is based on several mechanisms; the most important are physical adsorption, ion exchange, surface complexation, and surface precipitation. The source of biosorbents can be an industrial waste material, as in the application of biomass from large-scale fermentation processes such as filamentous fungi and bacteria from pharmaceutical production (8).

The cost of an electroflotation device plus a sand filter compared favorably with a conventional treatment system using cyanide oxidation/alkaline precipitation/polymer-aided clarification (15). By the former system, a saving of approximately 43% was found when cyanide is present in the groundwater.

If required, the sorbents may be recycled after metal desorption, which is also no problem. A two-stage countercurrent scheme was selected based on extensive studies, with one parallel of elution; flotation was included following each respective biosorption stage (16). This scheme is similar to a conventional activated-carbon system for separating liquids. The partially loaded biomass was guided from the polishing to the leading biosorption stage, where the wastewater feed was introduced.

Concluding, flotation applications (apart from mineral processing) include mainly the treatment of water and wastewater, but also bacteria, coal, clays, corn, resins, protein, fats, rubber, dyes, glass, fruit juices, and cane sugar. Flotation is beneficial for a large variety of dissolved chemical species (e.g., ions and molecules), which can either be concentrated from the solution/dispersion or may be selectively separated from one another, leading to sustainability. Sustainable water and wastewater treatment plant is a combination of technology and practice that meets the multiple and changing requirements of the society in optimal economical and ecological ways during the life cycle of a treatment plant. The flotation techniques applied are often based on the differences in surface activity of the various substances. They have been called, according to the removal mechanism followed, ion flotation or sorptive flotation. Usually, the separation action is aided or induced by introducing appropriate chemical reagents.

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BIBLIOGRAPHY

1. Matis, K.A. and Zouboulis, A.I. (1995). An overview of the process. In: *Flotation Science and Engineering*. K.A. Matis (Ed.). Marcel Dekker, New York, p. 1.
2. IWA. (2000). *Proc. 4th Intl. Conf. Flotation in Water and Waste Water Treatment*. Finnish Water and Wastewater Works Assoc., Helsinki, Finland.
3. Rubio, J., Souza, M.L., and Smith, R.W. (2002). Overview of flotation as a wastewater treatment technique. *Miner. Eng.* **15**: 139.
4. Finch, J.A. and Hardie, C.A. (1999). An example of innovation from the waste management industry: Deinking flotation cells. *Miner. Eng.* **12**: 467.
5. Zouboulis, A.I. and Avranas, A. (2000). Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation. *Coll. Surf. A.* **172**: 153.
6. Backhurst, J.R. and Matis, K.A. (1981). Electrolytic flotation in effluent treatment. *J. Chem. Tech. Biotechnol.* **31**: 431.
7. Frenay, J. (1998). Recycling of plastics: Application of flotation. In: *Mineral Processing and the Environment*. G.P. Gallios and K.A. Matis (Eds.). Kluwer Academic, Dordrecht, The Netherlands, p. 295.
8. Matis, K.A. and Lazaridis, N.K. (2002). Flotation techniques in water technology for metals recovery: Dispersed-air vs. dissolved-air flotation. *J. Min. Metall. A* **38**: 1.
9. Burns, S.E., Yiakoumi, S., and Tsouris, C. (1997). Microbubble generation for environmental and industrial separations. *Sep. Purific. Tech.* **11**: 221.
10. Filippov, L.O., Joussemet, R., and Houot, R. (2000). Bubble spargers in column flotation: adaptation to precipitate flotation. *Miner. Eng.* **13**: 37.
11. Zabel, T.F. (1992). Flotation in water treatment. In: *Innovations in Flotation Technology*. P. Mavros and K.A. Matis (Eds.). Kluwer Academic, Dordrecht, The Netherlands, p. 431.
12. Valade, M.T., Edzwald, J.K., Tobiason, J.E., Dahlquist, J., Hedberg, T., and Amato, T. (1996). Pretreatment effects on particle removal by flotation and filtration. *JAWWA* **88**(12): 35.
13. Lazaridis, N.K., Peleka, E.N., Karapantsios, Th.D., and Matis, K.A. (2004). Copper recovery from effluents by various separation techniques. *Hydrometallurgy*. **74**: 149.
14. Matis, K.A. and Zouboulis, A.I. (2001). *Metals loading on sorbents and their separation. ESF Workshop In-Situ Reactive Barriers versus Pump-and-Treat Methods for Groundwater Remediation*. BAM, Berlin.
15. Poon, C.P.C. (1997). Electroflotation for groundwater decontamination. *J. Hazardous Mater.* **55**: 159.
16. Matis, K.A., Zouboulis, A.I., and Lazaridis, N.K. (2003). Heavy metals removal by biosorption and flotation. *Water Air Soil Pollut. Focus* **3**: 143.

DEGRADATION OF CHLORO-ORGANICS AND HYDROCARBONS

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Chloro-organics include chlorinated aromatic and aliphatic compounds. The chemical characteristics of chlorinated aromatic compounds cover a range of compounds that include chlorophenols, chlorobenzenes, chloroanilines, polychlorinated biphenyls, and many pesticides. Chlorinated aliphatic compounds make up a major portion of the Environmental Protection Agency (EPA) Hazardous Substances List of halogenated volatile constituents.

Typical chlorinated aliphatics include trichloroethylene, tetrachloroethylene, 1,1-dichloroethylene, 1,2-dichloroethylene, carbon tetrachloride, chloroform, 1,1,1-trichloroethane, and chloroethylene. Hydrocarbons are petroleum-based compounds that contain carbon and hydrogen. Hydrocarbons can be separated into aliphatic, alicyclic, and aromatic hydrocarbon groups. Aliphatic hydrocarbons are straight or branched-chain hydrocarbons of differing length. These hydrocarbons are divided into alkane, alkene, alkyne, and unsaturated alkyl groups. Alicyclic hydrocarbons include the components of petroleum oils and complex substituted compounds. These hydrocarbons can be grouped into cycloalkanes and cycloalkenes. Aromatic hydrocarbons are comprised of benzene and its derivatives and polynuclear aromatic hydrocarbons. The potential and extent of substance degradation of each of these compound groups differs with the complexity of the compound and the nature of the aquatic environment. The principal focus of this discussion is that of microbial degradation in water and wastewater.

DEGRADATION OF CHLORINATED AROMATIC COMPOUNDS

Chlorinated aromatic compounds are typically produced for direct commercial use and as chemical intermediates during chemical synthesis. They are used in industrial operations to produce dyes, pharmaceuticals, pesticides, synthetic rubbers, solvents, cleaners, deodorants, pigments, and related formulations.

Microbial Transformations

Chlorinated aromatic compounds include chlorophenols, chlorobenzenes, chloroanilines, polychlorinated biphenyls, and many pesticides. Bacteria can remove chlorine from aromatic compounds by several different mechanisms. In aerobic systems, a hydroxyl group prior to ring cleavage can replace the chlorine atom. However, the more usual route involves removing the chlorine after ring cleavage through bacterial metabolism by a modified ortho pathway. Opening of the aromatic ring under aerobic conditions requires the presence of two hydroxyl groups. The hydroxyl groups derived from molecular oxygen can be added to the ring in reactions catalyzed by either monooxygenase or dioxygenase enzymes. Generally, the enzymes involved in the biodegradation of chlorinated aromatic compounds have broad substrate specificity that allows them to degrade or detoxify a number of other compounds (e.g., benzene, toluene, ethylbenzene, phenol) that also support growth (1).

Monochlorophenols are readily biodegradable compounds; degradation proceeds rapidly when they are exposed to acclimated cultures of activated sludges in conventional biological wastewater treatment processes. Dichlorophenols are also readily biodegradable, but degradation proceeds at a lower rate than that of monochlorophenols. Pentachlorophenol (PCP) is also biodegradable, but its degradation is very slow, and bacteria must be acclimated for prolonged time periods before effective biological treatment can be achieved. The biodegradation of chlorophenols is characterized by an increasing period of acclimation and a decreasing degradation rate in the following order (2):

Acclimation period for

$$\begin{aligned}&\text{Phenol} < \text{monochlorophenol} < \text{dichlorophenol}\\&\quad < \text{trichlorophenol} < \text{tetrachlorophenol}\\&\quad < \text{pentachlorophenol}\end{aligned}$$

Rate of biodegradation for

$$\begin{aligned}&\text{Phenol} > \text{monochlorophenol} > \text{dichlorophenol}\\&\quad > \text{trichlorophenol} > \text{tetrachlorophenol}\\&\quad > \text{pentachlorophenol}\end{aligned}$$

The rate of biodegradation is inversely proportional to the number of chlorine atoms in the molecule for most chlorinated aromatic compounds. This is demonstrated by chlorobenzoic acids. Monochlorobenzoic acids are readily biodegradable, but most dichloro derivatives and trichlorobenzoic acids are much more stable. For polychlorinated biphenyl (PCB), there is also a relationship between the rate of biodegradation and the number and position of chlorine atoms in the molecule. The resistance of PCB in the environment is directly proportional to the number of chlorine atoms in the molecule. Chloro-substituted diphenylmethanes behave similarly. The rate of chlorinated aromatic compound biodegradation in the activated sludge process usually decreases in the order of mono-, di-, tri-, tetra-, and pentachloro derivatives, depending on the position of the chlorine in the molecule (3).

Chloroanilines are biodegraded more slowly than chlorophenols because of the presence of both Cl and NH_2 groups that retard the biodegradability of the compound. As for chlorophenols, an increased number of chlorine atoms in the chloroaniline molecule results in increased resistance to biological treatment by the activated sludge process. There is also a retardant effect due to the number, type, and position of substituents on the aromatic ring. In addition to the halogens, the substituents that retard biodegradation are NH_2, NO_2, and SO_3H. These substituents retard the rate of biodegradation by decreasing the electron density on the aromatic ring (3). Alternatively, substituents that facilitate biodegradation by increasing electron density on the aromatic ring are OH, COOH, CHO, and CH_3. Consequently, the susceptibility of chloroaniline to biodegradation depends on whether the NH_2 group is readily transformed to OH by oxidative deamination. In certain compounds, a substituent (e.g., halogens) is not eliminated before the bacterium cleaves the aromatic ring. Chloroanilines are biodegraded most slowly when the Cl–NH_2 group is meta-substituted, whereas para-substituted derivatives are degraded rapidly (4).

The enzyme toluene dioxygenase catalyzes the hydroxylation of chloro-substituted benzenes (e.g., chlorobenzenes) as well as methyl- and chloro-substituted phenols. The dioxygenase system for initial attack, combined with the chlorocatechol degradation pathway, allows complete degradation of a range of industrial chemicals (1). Because of the nonspecific nature of the enzymes that transform benzoate to catechol, many aerobic bacteria can cometabolize chlorinated aromatic compounds. However, this biodegradation is not complete because chlorinated benzoates and catechols are the final end product of the oxidative biodegradation (5). The complete aerobic mineralization of chlorinated aromatic compounds is not typically seen, and the persistence of these compounds in the environment illustrates the ineffectiveness of bacteria for these degradations.

It is known that bacteria can mediate the anaerobic dehalogenation of chlorobenzoate compounds. Reductive dehalogenation has been confirmed for a number of chlorinated aromatic acids, chlorobenzenes, chlorophenols, chlorophenoxyacetate, herbicides, and PCBs (6). During reductive dechlorination, the chlorinated aromatic compound serves as the electron acceptor. Theoretical calculations of the Gibbs free energy available from dehalogenation indicates that bacteria can benefit from the use of chlorinated aromatic compounds as electron acceptors under anaerobic conditions (7). Nevertheless, most anaerobic dehalogenation is probably the result of cometabolism.

Methanogenic metabolism has been used successfully to dehalogenate a number of chlorinated aromatic compounds, including 2,4,5-trichlorophenoxyacetate, 3-chlorobenzoate, 2,4-dichlorophenol, 4-chlorophenol, 2,3,6-trichlorobenzoate, and 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dichlorobenzoates (6,8). Haggblom et al. (9) found that methanogenic bacteria preferentially remove ortho-substituted chlorine and that the meta- and para-substituted chlorine atoms are removed at much slower rates. Methanogenic metabolism does not result in the final mineralization of chlorinated aromatic compounds. To achieve mineralization, a balanced microbial consortium is required to perform the sequential biodegradations so that the transformation products are not more toxic than the parent compound.

Anaerobic dechlorination of aromatic compounds can be stimulated by adding electron donors. The addition of volatile fatty acids (i.e., acetate, butyrate, propionate) and ethanol increases the rate of dechlorination and the extent of biodegradation of many chlorinated aromatic compounds (8). Haggblom et al. (9) found that the addition of *p*-cresol and propionate enhances the methanogenic degradation of 2,4-dichlorophenol.

The presence of electron acceptors also influences the extent of anaerobic dechlorination in the environment. Certain electron acceptors may block the desired reduction reactions through competitive inhibition of methanogenic metabolism. However, Haggblom et al. (9) report that sulfate-reducing conditions actually enhance the apparent rates of biodegradation of 4-chlorophenol, 3-chlorophenol, 2-chlorophenol, and 2,4-dichlorophenol. Chlorophenols act as a source of carbon and energy and are degraded under sulfidogenic conditions by sulfate-reducing bacteria. In groundwater environments that contain sulfate-reducing bacteria, sulfate may be the preferred electron acceptor, and methanogens and sulfate reducers probably compete for suitable electron donors.

DEGRADATION OF CHLORINATED ALIPHATIC COMPOUNDS

Chlorinated aliphatic compounds are typically used as solvents for cleaning and reagents for chemical synthesis. The uses include paint and ink formulations, dry cleaning, synthetic rubber production, fumigants, paint and varnish removers, degreasers, pesticide solvents, adhesives, photographic supplies, pharmaceutical products, and household and office supplies.

Microbial Transformations

Microbial degradation of chlorinated aliphatic compounds can use one of several metabolic processes. These include oxidation of chlorinated alkanes for an energy source, cometabolism under aerobic conditions, and reductive dechlorination under anaerobic conditions. The response of different chlorinated aliphatic compounds to these metabolic processes differs, depending on the nature of the contamination, the redox condition, and the available electron acceptors.

When molecular oxygen is the electron acceptor, one- and three-atom substituted chlorinated aliphatic compounds are transformed by three types of enzymes: oxygenases, dehalogenases, and hydrolytic dehalogenases (10). The transformation products of oxygenases are alcohols, aldehydes, or epoxides. Dehalogenase transformation products are an aldehyde and glutathione. The glutathione is required as a cofactor for nucleophilic substitution by the dehalogenase enzyme. Hydrolytic dehalogenases hydrolyze the aliphatic compound and yield alcohols as a transformation product. Higher chlorinated compounds, particularly when all available valences on carbon are substituted (e.g., tetrachloride or tetrachloroethylene), have not been transformed under aerobic conditions. They must be transformed by reductive dechlorination.

Chlorinated aliphatic compounds may be either oxidized or reduced, depending on their structure and the redox potential of the aqueous environment where they are found. Reduction is possible because of their electron negative character. Consequently, polychlorinated aliphatic compounds often behave as an electron acceptor or the oxidant in a redox reaction. The more chlorinated a compound, the higher its oxidation state, and the more susceptible it is to reduction. This explains why the rate of dechlorination decreases under anaerobic metabolic conditions as, for example, tetrachloroethylene is dechlorinated to vinyl chloride. The reaction proceeds as follows:

tetrachloroethylene >>>> trichloroethylene >>>
1,2-dichloroethylene >> vinyl chloride > ethylene

Vinyl chloride (monochloroethylene) is more reduced, so the thermodynamic equilibrium tends to stabilize vinyl chloride as the typical end product of trichloroethylene degradation in aquifers that have negative redox potentials (i.e., an anaerobic environment).

Aerobic Processes

Biotransformation of some chlorinated aliphatic compounds has been demonstrated under aerobic conditions (11). Under aerobic conditions, many soil microorganisms can oxidize vinyl chloride. Most chlorinated aliphatic compounds are eventually mineralized to carbon dioxide. The aerobic degradation capabilities of these microorganisms for chlorinated aliphatic compounds have provided successful treatment processes in seeded (i.e., cultured) activated sludge reactors.

Some chlorinated aliphatic compounds are degraded by cometabolism under conditions that support aerobic metabolism. These aerobic microbes generate oxygenase enzymes of broad-substrate specificity that oxidize chlorinated aliphatic compounds. These include microorganisms that belong to the genera *Alcaligenes, Mycobacterium, Pseudomonas, Nitrosomonas, Xanthobacter*, and *Ancylobacter* (12). For example, *Nitrosomonas europaea* catalyzes the aerobic transformation of vinyl chloride, *cis-* and *trans*-dichloroethylene, *cis*-dibromoethylene, and trichloroethylene (13).

During the cometabolism of chlorinated alkenes, other microorganisms derive their energy from organic compounds such as methane, propane, phenol, and toluene. Several toluene-using microorganisms can degrade trichloroethylene by cometabolism. Even under varied pH and temperature, significant rates of microbial degradation are measured (14). Trichloroethylene degradation decreased by 30% at 4 °C compared with that at 30 °C (14). Phenol-oxidizing bacteria have a much higher capacity to degrade trichloroethylene than methane-oxidizing microorganisms (i.e., methanotrophs). Trichloroethylene degradation by phenol-oxidizing bacteria reportedly removed greater than 90% of TCE after phenol injection (15). *In situ* studies of trichloroethylene degradation have demonstrated that phenol-using microorganisms can be readily stimulated in the environment. Phenol addition is a good primary substrate; it achieves degradation of *cis*- and *trans*-dichloroethylene and trichloroethylene *in situ*. The apparent rate of chlorinated alkene transformation increases as phenol concentrations increase.

Many investigators have confirmed the biotransformation of trichloroethylene by methanotrophic bacteria using methane as a primary substrate. These methanotrophs have the monooxygenase enzyme that will incorporate one oxygen atom from molecular oxygen into methane to produce methanol. The monooxygenase enzyme can hydroxylate many alkanes and aromatic compounds and form epoxides from chlorinated alkenes because it is not compound-specific (10). The products of these reactions are not further oxidized by methanotrophs, so a diverse community of microorganisms is needed to achieve complete mineralization of a given constituent. Trichloroethylene has been successfully degraded aerobically to carbon dioxide with methane in air, although the rate of transformation was less than that for dichloroethylenes (16). However, there are toxicity problems because some trichloroethylene oxidation products are toxic to many methanotrophic bacteria. It also appears that trichloroethylene concentrations greater than 50 mg/L inhibit methane use by methanotrophs (10).

Another serious limitation of methane-oxidizing bacteria is that they cannot transform tetrachloroethylene (i.e., perchloroethylene) or higher chlorinated aliphatic compounds. The less chlorinated the compound, the greater the rate and extent of the transformation under aerobic conditions, as expected from thermodynamics. The lower the oxidation state of the compound, the less difficult it is to oxidize. Trichloroethylene is more oxidized than vinyl chloride, so it is more difficult to oxidize this compound further. As noted previously, the opposite is true when reducing an oxidized compound. The higher the degree of oxidation, the easier it is to reduce that compound.

Anaerobic Processes

Many chlorinated aliphatic compounds are transformed under anaerobic conditions. These compounds are mineralized in the presence of a diverse community of microorganisms. One of the predominant mechanisms for transforming chlorinated aliphatic compounds is reductive dechlorination. Reductive reactions result in replacing the chlorine atom by dihaloelimination. The reductive process usually occurs through cometabolism.

Chlorinated aliphatic compounds are transformed by reductive dechlorination even at low concentrations of less than 200 parts per billion (ppb). During reductive dechlorination, the chlorinated organic compound serves as an electron acceptor. The rate of dechlorination under anaerobic conditions is linked to the rate of primary substrate oxidation. Electrons from the oxidation of a primary substrate carry out the dechlorination. The control of these reactions for bioremediation requires an understanding of the redox conditions and the influence and availability of specific electron acceptors and donors on the overall metabolic condition of the bacteria that perform the reduction.

The availability of electron acceptors in anaerobic systems affects reductive dechlorination by competing with the chlorinated compounds for reducing potential. For example, nitrate and sulfate can inhibit the dechlorination of some chlorinated alkenes. It has been reported that the addition of nitrate to natural soil microcosms completely blocked the dechlorination of tetrachloroethylene (17).

According to thermodynamic principles, microorganisms couple half reactions that yield the greatest free energy. As redox conditions become more reducing, more chlorinated compounds undergo transformation. Thus more compounds are transformed under methanogenic conditions than under other anaerobic respirations (e.g., sulfate or nitrate). Additionally, several biologically active donors (e.g., acetate and H_2) and the ferrous ion have lower reduction potentials than most chlorinated aliphatic compounds. As a result, they can be involved in chlorine removal by reduction.

Sulfate also influences these reactions. Using sulfate as the electron acceptor (e.g., sulfate reduction by *Desulfovibrio sp.*), the dechlorination of tetrachloroethylene proceeds at a slower rate than if carbon dioxide is the electron acceptor (e.g., methanogenesis). Sulfate may also block the dechlorination of trichloroethylene (18). The specific influence of sulfate and other electron acceptors cannot be generalized. Different microbial systems and different aquifer and groundwater chemical conditions shift the thermodynamic equilibrium. Therefore, treatability studies are always required to assess the particular situation.

Chlorinated aromatic hydrocarbons can serve as both the electron acceptor and the electron donor in a reductive dechlorination reaction (7). However, chlorinated alkenes need an additional electron donor to support anaerobic dechlorination. Typical electron donors are the following: methanol, ethanol, glucose, sucrose, benzoate, lactate, formate, acetate, and butyrate. Volatile fatty acids produced under methanogenic conditions are generally considered the most effective electron donors for enhancing dechlorination. Because some methanogens consume hydrogen as an electron donor, microbial fermentations involve the reoxidation of a reduced electron carrier, such as nicotinamide adenine dinucleotide (NAD)H_2, as part of the metabolic reaction. This means that $NADH_2$ is oxidized to NAD and H_2 in the presence of methanogens. Usually, nonmethanogenic bacteria provide the hydrogen for methanogenesis (19).

Abiotic Transformations

Chlorinated aliphatic compounds include trichloroethylene, tetrachloroethylene, 1,1-dichloroethylene, 1, 2-dichloroethylene, carbon tetrachloride, chloroform, 1,1,1-trichloroethane, and chloroethylene (vinyl chloride). In addition to biological transformations, these compounds undergo abiotic transformations in the environment. The important abiotic transformations include substitution, dehydrohalogenation, and reduction in water (20). A typical substitution is the addition of water resulting in hydrolysis. The nucleophiles of OH^- and H_2O are the principal species responsible for abiotic dehydrohalogenation

Table 1. Ions Capable of Abiotic Displacement of Halogen[a]

Oxygenated Waters	Anaerobic Waters
H_2O	SO_3^{2-}
OH^-	$S_2O_3^{2-}$
Cl^-	NH_3
Br^-	NO_2^-
SO_4^{2-}	S_n^{2-}
HCO_3^-	$R–C_6H_{13}S^-$
—	$C_6H_5S^-$

[a] Reference 20.

of chlorinated aliphatic compounds in water. However, a variety of other species can displace the chlorine. These are presented in Table 1. Under anaerobic conditions, the sulfur nucleophiles are generally the most powerful. Sulfides react with chlorinated aliphatic compounds via substitution to produce mercaptans.

These reactions proceed slowly in the absence of biological activity. The half-lives for the monochloroalkanes are approximately a month at 25 °C (20). Polychlorinated species can have half-lives as long as 40 years. Stronger nucleophiles such as HS^- can reduce the half-lives of the abiotic degradation of chlorinated aliphatic hydrocarbons. Microbial enzymes also catalyze these reactions and reduce half-lives significantly.

A variety of transition metals, including nickel, iron, chromium, and cobalt, can reduce chlorinated aliphatic compounds. As a result of this oxidation–reduction (redox) reaction, the metals are oxidized. Vogel et al. (11) defined the reduction products and metals that mediate such reactions. The transition metal reduces a chlorinated compound, removing the chlorine and creating an alkyl radical that readily picks up a hydrogen atom from water, resulting in the formation of an alkane. The reduction of polychlorinated alkanes can result in both alkanes and alkenes.

DEGRADATION OF PETROLEUM HYDROCARBONS

Petroleum hydrocarbons include the common components of petroleum oils and products. They are found in wastewaters from petroleum refineries, petrochemical facilities, fuel storage and transportation facilities, and industrial organic chemical production facilities. Benzene and other single-ring aromatic hydrocarbons are used as solvents in industrial processes. Substituted forms of single-ring aromatic compounds are used in many industrial processes for preparing dyes, resins, antioxidants, polyurethane foams, fungicides, stabilizers, coatings, insulation materials, fabrics, and plastics. Polynuclear aromatic hydrocarbons (PAHs) are associated with petroleum refining and coal tar distillation. PAHs are also associated with waste by-products from coal gasification and coke production.

Microbial Transformations

Petroleum hydrocarbons can be classified into aliphatic, alicyclic, and aromatic hydrocarbon groups. Aliphatic hydrocarbons are divided into alkane, alkene, alkyne, and unsaturated alkyl groups. Alicyclic hydrocarbons can be grouped into cycloalkanes and cycloalkenes. Aromatic hydrocarbons are comprised of benzene and its derivatives and polynuclear aromatic hydrocarbons.

The presence of molecular oxygen as a terminal electron acceptor is required for successful microbial degradation of petroleum hydrocarbons. Nitrate and sulfate also serve as alternative electron acceptors during anaerobic respiration of hydrocarbons. Generally, the biodegradation rate decreases with decreasing redox potential. Only negligible biodegradation is observed under strictly anaerobic (i.e., fermentative) conditions. Consequently, hydrocarbons remain for a relatively long period of time in bottom sediments and other anaerobic portions of the aquatic environment.

Petroleum hydrocarbons are generally hydrophobic compounds. Bacteria and fungi frequently attach to oil droplets because intimate contact between a microorganism and the surface of the petroleum hydrocarbon is necessary for biodegradation. Consequently, dispersing the petroleum oil in water makes it more susceptible to microbial attack. Bacteria often produce extracellular surfactants that aid in solubilizing petroleum hydrocarbons. These bacterial surfactants are complex mixtures of proteins, lipids (e.g., rhamnolipids, phospholipids), and carbohydrates (21).

Aliphatic and Alicyclic Hydrocarbons

The biodegradation potential of alkanes is a function of carbon chain length. Short carbon chains of less than 10 carbons are more difficult to biodegrade than longer chains. Because of their higher solubility, short-chain hydrocarbons also exhibit a high degree of toxicity in the aquatic environment (22). Longer chain aliphatic hydrocarbons are more easily biodegraded than the short-chain variety. A large number of facultative anaerobic bacteria are prevalent in the aquatic environment that can use aliphatic hydrocarbons as a source of carbon and energy. These bacteria include the genera *Acinetobacter, Alcaligenes, Arthrobacter, Flavobacterium, Methylococcus, Mycobacterium, Nocardia*, and *Pseudomonas* (21). Numerous fungi and yeast also biodegrade aliphatic hydrocarbons. Although fungi are more versatile than yeast in biodegrading short-chain hydrocarbons, both are effective in using long-chain alkanes.

Aerobic biodegradation of a long-chain aliphatic hydrocarbon requires incorporating molecular oxygen into the compound. Oxygenase enzymes (i.e., monooxygenases and dioxygenases) mediate this degradation reaction (23). The pathway of alkane biodegradation is oxidation at the terminal methyl group of an alcohol and then of the corresponding fatty acid. The terminal oxidation proceeds by successive removal of two carbon units, termed the beta-oxidation sequence.

Alkene biodegradation is more varied because bacteria attack at either the methyl group or the double bond. Unsaturated straight-chain hydrocarbons are usually biodegraded less easily than saturated compounds. Consequently, bacterial metabolism results in forming intermediates that consist of unsaturated alcohols and fatty acids, primary or secondary alcohols, methyl ketones, epoxides, and diols (21). The methyl group oxidation is the more likely biodegradation pathway.

Petroleum hydrocarbons that have branch chains are less susceptible to biodegradation. Quaternary carbon and β-alkyl-branched compounds are generally considered recalcitrant and accumulate in the environment. However, combining chemical oxidative processes with biodegradation is effective for treating recalcitrant hydrocarbons.

The biodegradation of cycloalkanes is usually by oxidation of the terminal methyl group and yields a primary alcohol. Hydroxylation must occur to initiate the biodegradation of cycloalkanes. The bacteria that can oxidize noncyclic alkanes can also hydroxylate cycloalkanes. Several alternate metabolic pathways exist for microbial attack on alicyclic hydrocarbons, and numerous intermediate compounds have been identified during their degradation. Substituted cycloalkyl compounds vary in their capacity for biodegradation, but those that contain carboxylic acid groups are readily biodegraded. Bacteria capable of degrading cycloalkyl carboxylic acids are numerous in the environment (24).

Aromatic Hydrocarbons

The nature and extent of the biodegradation of aromatic hydrocarbons depends on the number of rings in the structure, the number of substitutions, the type and position of the substituted groups, and the nature of the atoms in heterocyclic compounds. The solubility of the aromatic hydrocarbon greatly affects its potential for biodegradation under either aerobic or anaerobic conditions. Mixtures of aromatic compounds can also influence the rate of biodegradation.

Aerobic microbial attack on single-, double-, and triple-ring aromatic compounds involves the foundation of a dihydrodiol compound. Oxidative attack on the dihydrodiol compound results in forming an alkyl catechol, a common intermediate formed during the oxidation of many aromatic hydrocarbons. Additional metabolic oxidation results in ring fission, forming either an aldehyde or an acid. This step results in the destruction of the aromatic ring leaving an oxidized aliphatic hydrocarbon, which is easily biodegraded, releasing hydrogen (25). Bacteria of the genus *Nocardia* can oxidize substituted aromatic hydrocarbons, such as *p*- and *m*-xylene, and use these compounds as a sole source of carbon and energy (4).

A second metabolic pathway for degrading aromatic hydrocarbons involves oxidation of alkyl substitutes, which results in forming aromatic carboxylic acids that are then oxidized to dihydroxylated ring fission products (i.e., aldehydes and acids). The aldehydes and acids are then readily biodegraded by the beta-ketoadipic and meta fission pathways (26). In general, alkyl-substituted aromatic hydrocarbons are less biodegradable, the longer the chain length, or the more numerous the alkyl groups.

Single-ring aromatic hydrocarbons can be transformed anaerobically by denitrifying, sulfate-reducing, iron-reducing, and methanogenic bacteria (27). These are all anaerobic respirations where the nitrate, sulfate, ferric, and carbonate ions act as terminal electron acceptors (TEA) for energy metabolism. The use of these compounds as electron acceptors in microbial energy metabolism is called dissimilative metabolism. During dissimilative metabolism, a comparatively large amount of the TEA is reduced, and the reduced product is excreted into the aquatic environment. The possible end products of these reductions are HS^-, N_2, $NO_2{}^-$, N_2O, Fe^{2+}, and CH_4.

The presence or absence of oxygen in the structure of an aromatic compound impacts both the degradation mechanism and the rate of biodegradation. The initial step in the degradation of aromatic hydrocarbons is conversion of the compound to an oxygenated form. Under anaerobic metabolic conditions, oxygen is incorporated from water into the aromatic structure by hydroxylation (28). The microbial fermentation of benzene and toluene is characterized by end products that are both partly oxidized and partly reduced. The oxidation might include both methyl group oxidation and ring oxidation. The reduction generally results in forming saturated cyclic rings (3).

Grbic-Galic (29) observed that the biodegradation of benzene is initiated by ring oxidation, resulting in the formation of phenol. Three pathways are possible for toluene, starting with ring oxidation to *p*-cresol or *o*-cresol and methyl group oxidation to benzyl alcohol. Thereafter, the biodegradations proceed along pathways that are similar to the anaerobic transformations of oxygenated aromatic compounds (30).

The biodegradation of multiring aromatic hydrocarbons (PAHs) is a function of the complexity of the chemical structure of the compound. In general, PAHs that contain four or more aromatic rings are much less biodegradable than compounds that contain only two to three rings (3). Several of the higher ring number PAHs and the intermediate products of their biodegradation are either toxic or carcinogenic. They are also strongly hydrophobic, which predicts that their concentration in the aqueous phase is always relatively low. Therefore, significant portions of the PAHs are found adsorbed on particles and possibly trapped in the micropores of these particles. Consequently, the rate of biodegradation is controlled by the sorption–desorption kinetics of the strongly sorbed PAH compounds. Enhancing solubilization by introducing bacteria that produce extracellular surfactants improves the *in situ* biodegradation of PAHs in groundwater.

Biodegradation of the unsubstituted di- and tri-ring PAHs in marine and freshwater is well documented in the literature (25,31,32). The bacterial degradation rates for phenanthrene and anthracene appear to be related to the water solubilities of these compounds. As for benzene and its derivatives, the oxidation of di- and tri-ring PAHs involves the formation of dihydrodiol intermediates. Catechol is the principal intermediate product of these microbial degradations (25). Bacteria that can degrade anthracene and phenanthrene include the genera *Aeromonas, Beijerinckia, Flavobacterium, Nocardia*, and *Pseudomonas* (31).

Biodegradation of unsubstituted PAHs that contain four or more aromatic rings (e.g., fluorene, pyrene, benzo(a)pyrene, benzo(a)anthracene, dibenzo(a)anthracene) has been documented in the literature (33–35). The bacteria that can degrade the higher molecular weight PAHs were also identified in this literature; they include the genera *Alcaligenes, Beijerinckia, Mycobacterium*, and

Pseudomonas. These research studies have indicated that cometabolism coupled with analog substrate enrichment may be necessary to treat PAHs that contain four or more aromatic rings. Cometabolism appears to be the principal mechanism for biodegrading benzo(a)anthracene (35). The presence of biphenyl, *m*-xylene, and salicylate were necessary to induce oxidation of benzo(a)anthracene to carbon dioxide and a mixture of *o*-hydroxy polyaromatic compounds. Because the high molecular weight PAHs do not induce enzyme production in many bacteria, the addition of naphthalene as an analog substrate was necessary to biodegrade benzo(a)anthracene in this study.

BIBLIOGRAPHY

1. Spain, J.C., Haigler, B.E., and Nishino, S. (1989). Development of bacteria for biodegradation of chloroaromatic compounds. In: *Biotechnology Applications in Hazardous Waste Treatment*. G. Lewandowski, P. Armenante, and B. Baltzis (Eds.). Engineering Foundation, New York, pp. 129–147.
2. Compeau, G.C., Mahaffey, W.D., and Patras, L. (1991). Full-scale bioremediation of contaminated soil and water. In: *Environmental Biotechnology for Waste Treatment*. G.S. Sayler, R. Fox, and J.W. Blackburn (Eds.). Plenum Press, New York, pp. 91–109.
3. Pitter, P. and Chudoba, J. (1990). *Biodegradability of Organic Substances in the Aquatic Environment*. CRC Press, Boca Raton, FL.
4. Gibson, D.T. (1989). Recent advances in the microbial degradation of aromatic hydrocarbons. In: *Biotechnology Applications in Hazardous Waste Treatment*. G. Lewandowski, P. Armenante, and B. Baltzis (Eds.). Engineering Foundation, New York, pp. 149–165.
5. Reineke, W. (1984). Microbial degradation of halogenated aromatic compounds. In: *Microbial Degradation of Organic Compounds*. D.T. Gibson (Ed.). Marcel Dekker, New York, pp. 319–360.
6. Young, L.Y. (1984). Anaerobic degradation of aromatic compounds. In: *Microbial Degradation of Organic Compounds*. D.T. Gibson (Ed.). Marcel Dekker, New York, pp. 487–523.
7. Dolfing, J. (1992). Gibbs free energy of formation of halogenated aromatic compounds and their potential role as electron acceptors in anaerobic environments. *Environ. Sci. Technol.* **26**: 2213–2218.
8. Gibson, S.A. and Suflita, J.M. (1990). Anaerobic biodegradation of 2,4,5-Trichlorophenoxyacetic acid in samples from a methanogenic aquifer: stimulated by short chain organic acids and alcohols. *Appl. Environ. Microbiol.* **56**: 1825–1832.
9. Haggblom, M.M., Rivera, M.D., and Young, L.Y. (1991). Anaerobic degradation of chloroaromatic compounds under different reducing conditions. *EPA Symposium on Bioremediation of Hazardous Wastes*. Falls Church, VA.
10. Semprini, L., Grbic-Galic, D., McCarty, P.L., and Roberts, P.V. (1992). Methodologies for evaluating in-situ bioremediation of chlorinated solvents. U.S. Environmental Protection Agency, EPA/600/R-92/042.
11. Vogel, T.N., Criddle, G.S., and McCarty, P.L. (1987). Transformation of halogenated aliphatic compounds. *Environ. Sci. Technol.* **21**(8): 722–736.
12. Rainwater, K. and Scholze, R.J. (1991). In-situ biodegradation for treatment of contaminated soil and groundwater. In: *Biological Processes-Innovative Hazardous Waste Treatment Technology Series*. Vol. 3, H.M. Freeman and P.R. Sferra (Eds.). Technomic, Lancaster, PA, pp. 107–122.
13. Vanelli, T., Logan, M., Arciero, D.M., and Hooper, A.B. (1990). Degradation of halogenated aliphatic compounds by the ammonia-oxidizing bacterium *nitrosomonas europaea*. *Appl. Environ. Microbiol.* **56**(4): 1169–1171.
14. Shields, M. (1991). Treatment of TCE and degradation products using *Pseudomonas cepacia*. *Symposium on Bioremediation of Hazardous Wastes: EPA's Biosystems Technology Development Program*, Abstracts, Falls Church, VA., April 16–18.
15. Hopkins, G.D., Semprini, L., and McCarty, P.L. (1993). Microcosm and in-situ field studies of enhanced biotransformation of trichloroethylene by phenol-utilizing microorganisms. *Appl. Environ. Microbiol.* **59**: 2277–2285.
16. Tsien, H.C., Bousseau, A., Hanson, R.S., and Wackett, L.P. (1989). Biodegradation of trichloroethylene by *Methylosinus trichosporium*. *Appl. Environ. Microbiol.* **55**: 3155–3161.
17. Sewell, G.W., Gibson, S.A., and Russell, H.H. (1990). Anaerobic in-situ treatment of chlorinated ethenes. *Workshop on In-Situ Bioremediation of Groundwater and Contaminated Soils*. Water Pollution Control Federation Hazardous Wastes Committee, WPCF, Annual Conference, October 7–11, Washington, DC, pp. 68–79.
18. Bouwer, E.J. and Wright, J.P. (1988). Transformations of trace halogenated aliphatics in anoxic biofilm columns. *J. Contam. Hydrol.* **2**: 155–169.
19. Baek, N.H. and Jaffe, P.R. (1988). Anaerobic mineralization of trichloroethylene, presented at the *International Conference on Physicochemical and Biological Detoxification of Hazardous Wastes*. Vol. II. X.C. Wu (Eds.). Technomic, Lancaster, PA, pp. 772–782.
20. Reinhard, M., Barbash, J.E., and Kunzle, J.M. (1988). Abiotic dehalogenation reactions of haloaliphatic compounds in aqueous solution, presented at the *International Conference on Physicochemical and Biological Detoxification of Hazardous Wastes*, Vol. II, X.C. Wu (Ed.). Technomic, Lancaster, PA, pp. 722–741.
21. Britton, L.N. (1984). Microbial degradation of aliphatic hydrocarbons. In: *Microbial Degradation of Organic Compounds*. D.T. Gibson (Ed.). Marcel Dekker, New York, pp. 89–130.
22. Bitton, G. and Gerba, C.P. (1984). *Groundwater Pollution Microbiology*. John Wiley & Sons, New York, pp. 23–24.
23. Wackett, L.P., Brusseau, G.A., Householder, S.R., and Hansen, R.S. (1989). Survey of microbial oxygenases: trichloroethylene degradation by propane-oxidizing bacteria. *Appl. Environ. Microbiol.* **55**: 2960–2964.
24. Trudgill, P.W. (1984). Microbial degradation of the alicyclic ring: structural relationships and metabolic pathways. In: *Microbial Degradation of Organic Compounds*. D.T. Gibson (Ed.). Marcel Dekker, New York, pp. 131–180.
25. Gibson, D.T. and Subramanian, V. (1984). Microbial degradation of aromatic hydrocarbons. In: *Microbial Degradation of Organic Compounds*. D.T. Gibson (Ed.). Marcel Dekker, New York, pp. 181–252.
26. Arvin, E., Jensen, B., Godsy, E.M., and Grbic-Galic, D. (1988). Microbial degradation of oil and creosote related aromatic compounds under aerobic and anaerobic conditions, presented at the *International Conference on Physicochemical and Biological Detoxification of Hazardous Wastes*. Vol. II, X.C. Wu (Ed.). Technomic, Lancaster, PA, pp. 828–847.
27. Huling, S.G., Pivetz, B., and Stransky, R. (2002). Terminal electron acceptor mass balance: light nonaqueous phase liquids and natural attenuation. *J. Environ. Eng.* **128**: 246–252.

28. Vogel, T.N. and Grbic-Galic, D. (1986). Incorporation of oxygen from water into toluene and benzene during anaerobic fermentative transformation. *Appl. Environ. Microbiol.* **52**: 200–202.
29. Grbic-Galic, D. (1990). *Microbial Degradation of Homocyclic and Heterocyclic Aromatic Hydrocarbons under Anaerobic Conditions*. Department of Civil Engineering, Environmental Engineering and Science, Stanford University, Stanford, CA.
30. Grbic-Galic, D. and Vogel, T.M. (1987). Transformation of toluene and benzene by mixed methanogenic cultures. *Appl. Environ. Microbiol.* **53**: 254–260.
31. Hogan, J.A., Toffoli, G.R., Miller, F.C., Hunter, J.V., and Finstein, M.S. (1988). Composting physical model demonstration: mass balance of hydrocarbons and PCBs, presented at the *International Conference on Physicochemical and Biological Detoxification of Hazardous Wastes*. Vol. II, X.C. Wu (Ed.). Technomic, Lancaster, PA, pp. 742–758.
32. Mahaffey, W.R., Compeau, G., Nelson, M., and Kinsella, J. (1990). *Development of Strategies for Bioremediation of PAHs and TCE*. *In-Situ Bioremediation of Groundwater and Contaminated Soils*. WPCF Annual Conference, Washington, DC, pp. 3–47.
33. Environmental Protection Agency. (1993). *Pilot-Scale Demonstration of a Slurry-Phase Biological Reactor for Creosote-Contaminated Soil—Applications Analysis Report*. EPA/540/A5-91/009.
34. Grifoll, M., Casellas, M., Bayona, J.M., and Solanas, A.M. (1992). Isolation and characterization of a fluorene-degrading bacterium: identification of ring oxidation and ring fission products. *Appl. Environ. Microbiol.* **58**: 2910–2917.
35. Mahaffey, W.R., Gibson, D.T., and Cerniglia, C.E. (1988). Bacterial oxidation of chemical carcinogens: formation of polycyclic aromatic acids from benzo(a)anthracene. *Appl. Environ. Microbiol.* **54**: 2415–2423.

LANDFILL

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INTRODUCTION

All countries rely to a greater or lesser degree on landfilling to dispose of the huge quantities of municipal solid waste (MSW) generated. For example, the United Kingdom has traditionally relied very heavily on landfilling of MSW as it has a relatively poor recycling infrastructure compared with some other European countries. The United Kingdom produces roughly 28 million tons of MSW per annum, of which about 80% is landfilled. Only some 12% is recycled and about 8% incinerated with energy recovery. Moreover, the amount of waste being generated is growing some 3–4% per annum.

Globally, landfilling has had a checkered history, and poor practice in design and operation of landfills has led to serious environmental problems. With regard to the threats to water bodies, the production of landfill leachate is by far the most significant. Liquid leachate develops at a site when its water holding capacity is exceeded. If the site is unlined, the leachate makes its way off-site to groundwater or to a surface water body and can cause drastic water pollution.

The Landfill Directive of the EU (1) has the overall aim "to prevent or reduce as far as possible negative effects on the environment, in particular the *pollution of surface water, groundwater* (authors' italics), soil and air, and on the global environment, including the greenhouse effect, as well as any resulting risk to human health, from the landfilling of waste, during the whole life-cycle of the landfill." This succinctly crystallizes the objectives of modern landfill design, and the Directive has far-reaching consequences for the way we handle and dispose of MSW. There are various stringent requirements of the Directive, the most important of which for preventing water pollution are:

- Higher engineering and operating standards are to be followed.
- Biodegradable waste has to be progressively diverted away from landfill. By 2020, the amount going to landfill will be 35% of that of 1995.
- Banning of disposal of liquid wastes to landfill sites, along with certain hazardous and other wastes, will be implemented.

THE MICROBIOLOGY OF REFUSE DECOMPOSITION

One view of a landfill is as an enormous, solid-state fermenter in which naturally selecting microbial populations, usually bacteria, anaerobically decompose refuse components, ultimately to their mineral constituents. The process of anaerobic decomposition is microbiologically complicated, and a great many details remain to be elucidated. However, the overall process can be summarized as in Fig. 1. Although this image seems to separate the various processes, it should be kept in mind that all happen contemporaneously. As the landfill is microbiologically active over long periods, often decades, only the anaerobic processes (those in blue in Fig. 1) concern us here: hydrolysis and fermentation, acetogenesis, and methanogenesis. One of the reasons that these processes occur over decades is that

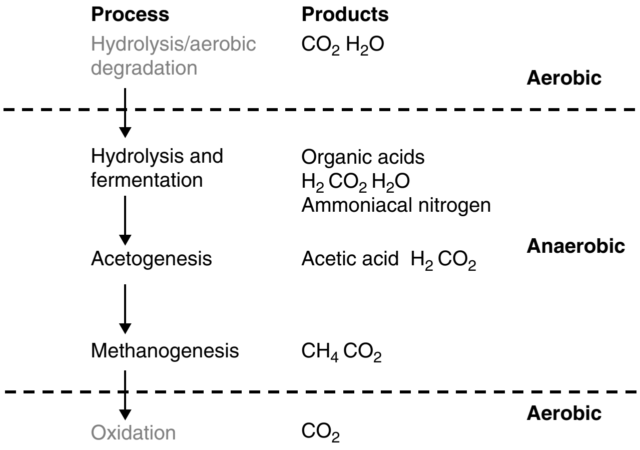

Figure 1. The various microbiological processes in a landfill.

the energy available from anaerobic processes is much lower than that from aerobic processes. For example, the aerobic mineralization of glucose to CO_2 and H_2O liberates more than seven times as much energy as the anaerobic mineralization of glucose to CO_2 and methane (CH_4).

Hydrolysis and Fermentation

Long-chain, insoluble carbohydrates, lipids, and proteins are not in a form in which they are readily metabolized by microorganisms. Hydrolytic reactions break down these long-chain molecules to smaller, more water-soluble molecules that can then be metabolized. Fermentation reactions produce soluble fermentation end products such as short-chain volatile fatty acids (VFA) and gaseous products of variable water solubility such as CO_2 and hydrogen.

Acetogenesis

The soluble acids from fermentation are converted to acetic acid, CO_2, and hydrogen by acetogenic bacteria. Other bacteria, acidogenic bacteria, convert carbohydrates, CO_2, and hydrogen to acetic acid. An important point is that the conversion of fermentation products to acetic acid occurs only at low concentrations of hydrogen. Hydrogen is produced at several stages, so it must be removed to prevent the inhibition of acidogenesis. If the partial pressure of hydrogen is too high, reduced organic acids, such as propionic, lactic, butyric, valeric, and caproic, start to accumulate, producing smells. Either from lowering the pH, mobilizing toxic metals, or inhibition due to the presence of high concentrations of these acids, there would be subsequent inhibition of methanogenesis.

Methanogenesis

Hydrogen concentration is kept low as a result of consumption by strictly anaerobic sulfate-reducing bacteria and methanogenic (methane-producing) bacteria. The methanogenic pathways of all species have the conversion of a methyl group to methane in common; however, the origin of the methyl group is variable. Although most isolated species can reduce CO_2, the majority of biological methanogenesis (about 70%) originates from conversion of the methyl group of acetate to methane, although in most cases acetate is not used as an energy source. Others acquire the methyl group directly from substrates such as methanol or methylamines.

Syntrophism

The low-energy yields involved in the anaerobic conversion of refuse to methane forces these different organisms into very efficient cooperation. Such cooperations are known as syntrophic relations. Syntrophism is a special case of symbiosis between two metabolically different types of bacteria, which depend on each other for degradation of a certain substrate, usually for reasons of energetics.

There is a classic example in landfill microbiology. Metabolism of low molecular weight fatty acids, such as propionate by *Syntrophobacter* and caproate and valerate by *Syntrophomonas*, produce acetate, hydrogen, and carbon dioxide, which are used by methanogens. The result is the overall conversion of fatty acids to methane. The conversion of fatty acids to acetate is energetically unfavorable, and the reaction depends on the removal of hydrogen by methanogens. Likewise, the methanogens need hydrogen for their metabolism.

Landfill Microbiology Is Mass Transfer Limited

Very often mass balance calculations of methane generation at landfills suggest that the overall process is not working nearly as efficiently as it might, even considering that several steps along the way have poor thermodynamics, which leads to very protracted timescales for return of the site to stability, and the consequent need is for long-term monitoring. If the bottleneck is not in thermodynamics, then where is it? The answer lies in a very common observation; that newspaper, although very rich in calories, can still be read after excavation from a landfill site decades after its disposal there.

Cellulose, the most abundant polymer on the planet, represents about 50% of the organic material going to landfills. The rate limitation in a landfill is much more likely to be associated with solid substrates, such as paper. Here the limitation is not thermodynamic, but mass transfer. The substrate has to be converted from the solid form into an aqueous form before other metabolic associations can continue the degradation. The enzymatic hydrolysis of polymers to monomers has long been known as the rate-limiting step in the conversion of cellulose to methane and in the digestion of refuse.

ENVIRONMENTAL IMPACTS OF LANDFILLS

Landfilling domestic refuse creates a whole host of negative environmental impacts, summarized in Fig. 2. These impacts have variable magnitudes and can be categorized as *localized* (odor, noise, litter, transport risks, public health risks created by birds and vermin, explosive gas migration), *diffuse* (groundwater, surface water, drinking water contamination), and *global* (greenhouse gas generation). In the present context, the effects on water pollution are the primary concern. And the water pollution problems are a direct result of leachate generation and its off-site migration.

Leachate Composition

Leachate is the result of water infiltration to the site that exceeds the water holding capacity of the waste and other site materials. The water balance of a landfill site can be summarized as

$$LC = PR + SRT - SRO - EP - ST$$

where LC = leachate
PR = precipitation
SRO = surface run-off
SRT = surface run-to (zero on a well designed site)
EP = evapotranspiration
ST = change in water storage

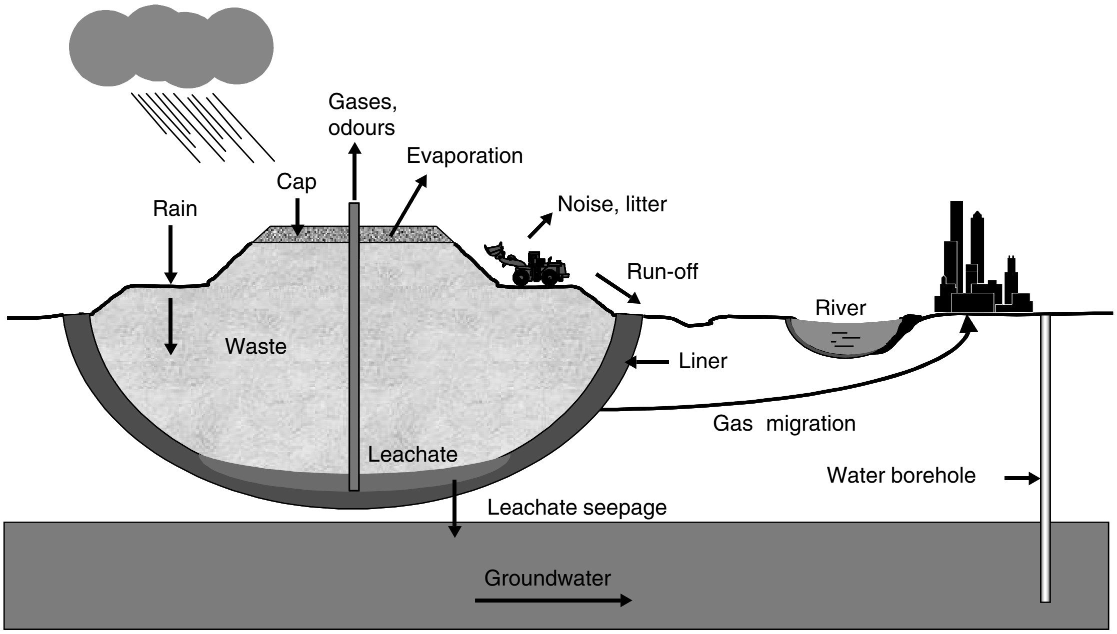

Figure 2. Environmental impacts of landfill practice.

Leachates vary in composition from site to site and also according to the age of the leachate. Leachates generated during the early stages of anaerobic decomposition are characterized by high concentrations of VFA, acidic pH, high BOD:COD ratio, and high levels of ammoniacal nitrogen and organic nitrogen. Ammonia is largely produced from the degradation of proteins. The low redox potential of such leachates facilitates the production of soluble, reduced-state metals, including chromium, iron, and manganese. These “young” leachates are much more environmentally damaging than mature leachates produced during the stable methanogenic phase.

By the time that methanogenesis is occurring at a high rate, many of the fatty acids have been converted ultimately to methane and CO_2. Methanogenic leachates are more likely to have a higher pH (resulting in lower heavy metal concentrations due to precipitation), lower levels of ammoniacal nitrogen, and a lower BOD:COD ratio (from the biodegradation of fatty acids).

LANDFILL DESIGN AND CONSTRUCTION IN RELATION TO ENVIRONMENTAL MITIGATION

It is not an objective to discuss detailed engineering design. Rather, in modern landfills, several design and construction measures can be taken to minimize the environmental effects of the site; and it is these that are summarized here. For example, a critical element of any landfill design is capacity, which is influenced by factors such as waste density, amount of daily cover, and the thickness of the final cap. However, for this discourse, capacity has little relevance to environmental effects.

Phasing and Cell Construction

A phase is a subsection of the total landfill to be filled; generally, it has an operational period of 12 to 18 months. Longer than 18 months results in excessive leachate production in wet areas. Cells are subsections of phases, which vary in size according to operational exigencies. Cell sizes are minimized according to the surface area required for maneuvering large machinery on the site. It may also be possible to size each cell in which the rate of vertical filling exceeds the rainfall plus water holding capacity to minimize leachate generation.

The practice of phasing (Fig. 3) has the objective of progressive excavation and filling of the site. As a result, at any one time, part of the site may be restored, part may be in the process of being capped, part is being prepared to receive waste, and only a relatively small part is being actively filled. When properly done, there will also be sufficient space for storage and protection of materials for subsequent restoration, and also coordination of haul roads and access routes. The environmental benefits of the phase/cell strategy are:

- reduction of leachate generation;
- progressive installation of leachate and gas control systems;
- segregation of clean surface water run-off within and outside the site;
- protection of local amenity.

Phases are generally filled from base to cap in a continuous operation, then capped and restored, leaving a temporary unrestored face sloping to the landfill base (Fig. 3). In deep landfills, such as those constructed in old quarries or opencast mining sites, the phases are vertically tiered so that, overall, the site is a three-dimensional honeycomb of cells.

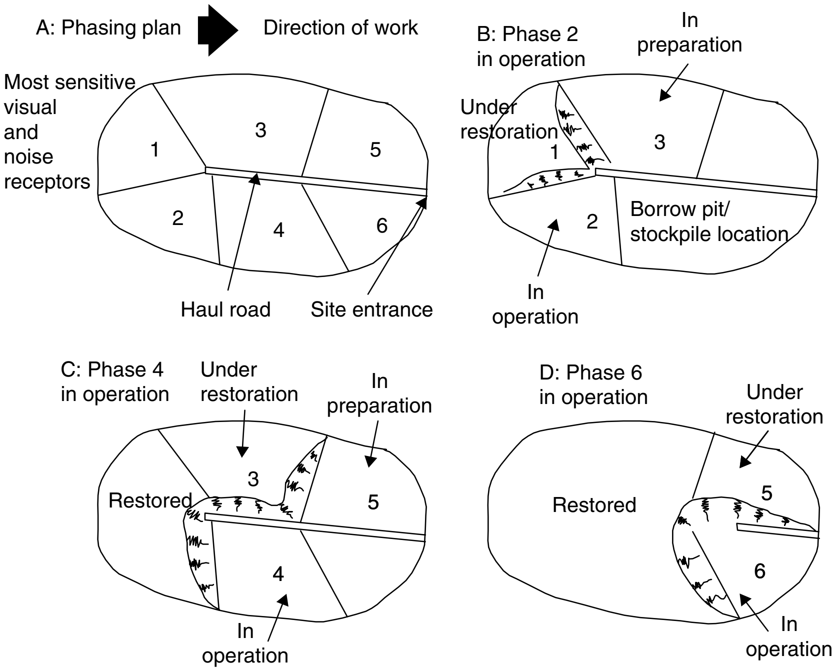

Figure 3. The phased approach to site management (adapted from Ref. 2).

Daily Cover

This practice involves covering refuse to a certain minimum depth daily with the following environmental benefits:

- prevention of wind-blown litter;
- suppression of odor;
- deterrence to vermin and birds;
- improvement of the site appearance.

From the point of view of water (and therefore leachate) and gas management, the material used for daily cover should be sufficiently permeable that it does not impede water or gas flow. Impermeable material creates perched conditions and makes it difficult to extract leachate. Ideally, the material of daily cover is soil excavated from within the boundaries of the landfill to prevent net consumption of void.

Liners

A key design parameter for MSW is to attain an impermeability of 10^{-9} m/s and so prevent leachate breakthrough to the unsaturated zone. The objective should be to select a new site on soil with a hydraulic conductivity lower than this. If this is not possible, then a variety of materials can be used to line the new site, either as single or multiple layers.

Clay liners varying in thickness from about 0.5 m (for imported clay) to 2 m (for *in situ* clay) are natural liners of high ion exchange capacity to retard the movement of toxic metals. Bentonite, the typical clay, is extremely absorbent. The hydraulic conductivity of dry, unconfined bentonite is 10^{-9} m/s. When saturated, however, it drops to less than 10^{-12} m/s^{-1}.

Synthetic liners, normally made of high-density (HDPE) or low-density (LDPE) polyethylene, are available in thicknesses of 0.5 to 2.0 mm. Although of very low permeability, their installation requires great care to prevent tearing.

Geosynthetic clay liners (GCL) (Fig. 4) are relatively new products gaining acceptance as barrier systems in municipal waste landfills. These offer some advantages over traditional bottom liners and covers and retain low hydraulic conductivity. Advantages include

- fast and easy to install;
- self healing of rips and tears due to the swelling property of bentonite;
- cost-effective in regions where clay is not readily available;
- their thin cross-section compared to a clay liner maximizes the capacity of a landfill and still protects groundwater.

Tests show that holes up to 75 mm diameter will self-heal when the clay hydrates and swells. Stitch-bonding or needle-punching creates small holes in the geotextile that heal due to swelling of the bentonite. The geotextile is often a blend of HDPE and very low-density polyethylene (VLDPE).

Drainage and Leachate Collection/Recirculation/Treatment

Leachate collected by the liner system must be removed to accelerate stabilization of the site and prevent liner damage, which is accomplished by drainage to collection sumps at low points via a granular layer containing perforated pipes of sufficient slope to allow gravity drainage. Leachate is then removed from the sumps, either by pumping in vertical wells or by gravity drains in a valley

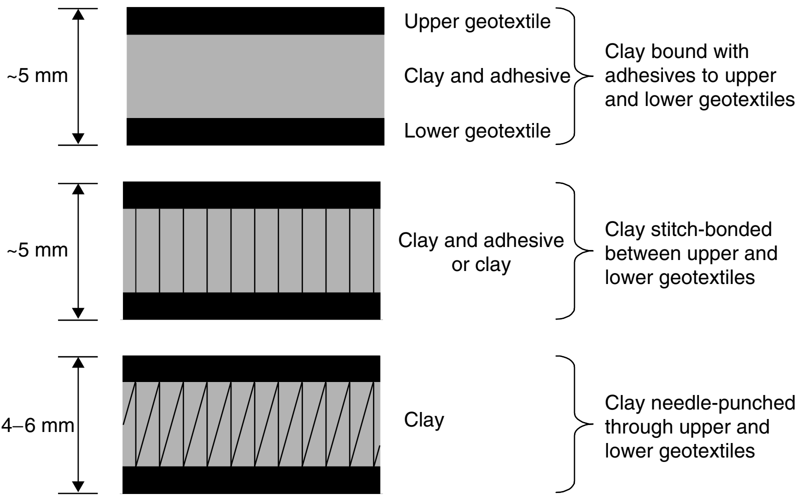

Figure 4. Geosynthetic landfill liner types.

site, where the leachate can either be treated on-site by a dedicated wastewater treatment plant or transported off-site for treatment.

Using a proper leachate collection system, it is possible to spray leachate back onto emplaced waste, which effectively uses the landfill site as a flushing anaerobic bioreactor and can improve landfill gas generation by uniformly wetting the waste.

Gas Abstraction and Use

This is mentioned here for completeness, although methane is highly insoluble in water and therefore contributes very little to the water-related environmental problems of landfills. During the stable methanogenic phase of a landfill, by far the longest phase, landfill gas, consists mainly of methane and carbon dioxide, both of which are greenhouse gases; the former is highly explosive; the latter is relatively water-soluble and corrosive. Most of the landfill gas management systems for landfills are designed with the characteristics of methane in mind. By appropriate siting of vertical or horizontal gas abstraction wells, it is possible to collect the gas, flare it, or, if economically viable, burn it for energy generation.

BIBLIOGRAPHY

1. Council Directive 1999/31/EC on the Landfill of Waste. (1999).
2. Department of the Environment. (1995). Landfill design, construction and operational practice. *Waste Management Paper 26B*. HMSO, London.

READING LIST

Kiely, G. (1996). *Environmental Engineering*. McGraw-Hill, London.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., and Christensen, T.H. (2002). Present and long-term composition of MSW landfill leachate: A review. *Crit. Rev. Environ. Sci. Technol.* **32**: 297–236.

Qian, X., Koerner, R.M., and Gray, D.H. (2002). *Geotechnical Aspects of Landfill Design and Construction*. Pearson Education, Harlow.

Senior, E. (1995). *Microbiology of Landfill Sites*, 2nd Edn. Lewis, Boca Raton, FL.

LANDFILL LEACHATES, PART I: ORIGIN AND CHARACTERIZATION

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INTRODUCTION

Sanitary landfilling is the most widely used method for disposing of urban solid wastes around the world. The extensive use and the public awareness of this disposal method have raised concerns, over the negative environmental impacts and the pollution potential that this practice creates, as well as by the by-products of landfills (e.g., leachates, biogas, odors, etc.). Among them, leachates are considered the most important environmental burden. Depending on the composition and extent of decomposition of the disposal of refuse, as well as on the hydrological parameters existing in the landfill site, leachates may become highly contaminated wastewaters.

Landfill leachate, as defined in the U.S. Environmental Protection Agency Code of Federal Regulations (CFR) Title 40, Part 258.2, is the liquid that has passed through, or emerged from the disposal of solid wastes and contains soluble, suspended, or miscible materials from these wastes. Over time, the seepage of water through the landfill mainly from precipitation increases the mobility of pollutants and the potential for transferring them into the surrounding environment. As water passes through the layers of disposed solid wastes, it may "leach" pollutants from them, moving them deeper into the soil. The mobility of pollutants may present a potential hazard to public health, as well as to the environment, causing significant pollution problems in the groundwater aquifer and in adjacent surface waters. As a result, understanding and predicting leachate generation routes, as well as containing it and the subsequent appropriate treatment are required for environmentally proper handling of these heavily polluted wastewaters.

A simple measure to prevent the movement of toxic and hazardous waste constituents from a landfill is a liner operated in conjunction with a leachate collection system. Leachates are typically collected from a collection system placed at the bottom of the landfill. Leachates may also be collected by using slurry walls, trenches, or other containment systems. The leachate generated may vary from landfill site to site, based on a number of factors, which include the types of waste accepted for disposal, the operating practices (such as shredding, daily cover with soil, or capping), the depth of fill, the applied compaction of wastes, the annual precipitation at the landfill site, and the landfill operational age.

LEACHATE GENERATION

Leachates are the combined wastewater, containing organic and inorganic constituents, produced when water and/or other liquids seep through solid wastes, deposited in urban or hazardous solid waste landfills. The quantity of leachates is influenced by several interacting factors, such as annual precipitation, runoff, infiltration, evaporation, transpiration, mean ambient temperature, waste composition, waste density, initial moisture content, and underlying soil conditions (depth) (1). A number of techniques have been reported, using the water budget analysis through a landfill site, to estimate the amount of leachate generated (2). The various components of moisture used in the water budget are shown in Fig. 1. According to this analysis, the primary source of moisture is precipitation over the landfill site. A part of this moisture results in surface runoff, another part is returned to the atmosphere in the form of evapotranspiration from the soil and the surfaces of plants, and the remainder is added to soil moisture storage.

The maximum moisture that can be retained, without continuous downward percolation by gravity, is known as field capacity. Whenever the moisture content exceeds the field capacity of the soil, water percolates down into (through) the solid waste. The addition of moisture to solid waste over a period of time saturates the solid waste to its field capacity, resulting thereafter in leachate generation. The various moisture components, which constitute the processes taking place in a landfill that produce leachate, are affected by several parameters, such as (3):

1. Precipitation, which varies geographically and seasonally.
2. Surface runoff and infiltration, which depend on the intensity and duration of storms, surface slope, permeability of soil cover, and amount and type of vegetation.
3. Evapotranspiration at a landfill site, which is affected by the type of the soil and vegetation.
4. Soil moisture storage capacity, which is continually changing; it increases due to infiltration and decreases due to evapotranspiration.

Several methods used water balance calculations of these components to assess leachates generation rates. In general, following are the characteristics of the leachates produced (4):

1. A higher leachate generation rate is expected in humid than in dry areas.
2. Leachate generation follows a pattern similar to that of precipitation (rain), then remains at constant flow for a time period.
3. Production of leachates may be minimized by proper and efficient covering operations, careful drainage design, selection of vegetative cover, etc.
4. The quantity of leachate generated and its qualitative characteristics are significant for designing and constructing the most appropriate collection and treatment devices.

In general, leachates are generated over a long time period, unless percolation is prevented by the closure procedures and the final land use (5). In this case, leachate generation will cease shortly after the completion and closure of the landfill. However, for the proper design of

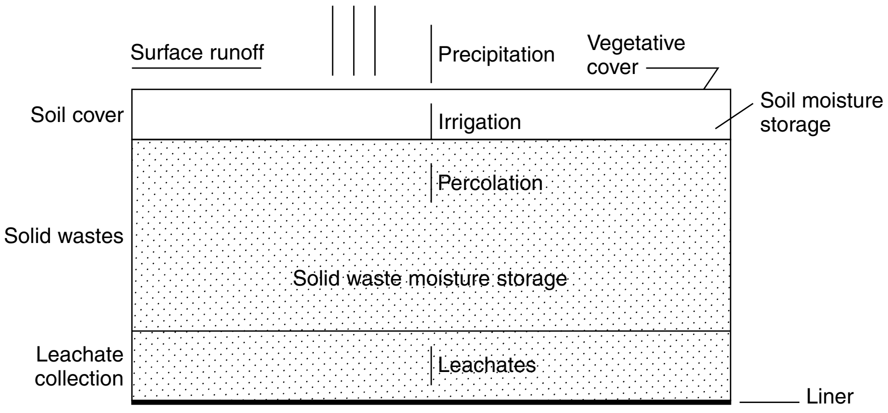

Figure 1. The various moisture components in a sanitary landfill.

a leachate treatment system, the characteristics of the leachate are necessary in addition to quantitative data.

LEACHATE CHARACTERISTICS

As leachates pass through or emerge from deposited solid wastes, they may contain soluble, suspended, or miscible materials from the wastes. Several factors may affect leachate quality, such as (6)

- specific types of solid waste accepted/deposited
- operating practices (shredding, cover, or capping)
- amount of infiltration
- depth of fill
- compaction
- age

The specific waste types received for disposal are the most representative characteristic of a landfill and, therefore, of the respective wastewater generated because the main contaminants in this wastewater are derived from the materials deposited in the site. The amount of infiltration and the age of a landfill are the primary factors that affect the concentration of contaminants in the leachate produced. The remaining factors influence mainly the rate of infiltration.

The highest concentrations of contaminants are typically present in leachates of new or very young landfills (7). However, the overall loads (i.e., the mass) of pollutants are generally not very large because new landfills typically generate low volumes of leachate. As the volume of waste approaches the capacity of the landfill and the production of leachate increases, both the pollutant loadings (i.e., flow × concentration) and the concentrations of certain contaminants, which are mainly organic pollutants, tend to increase. The increase of pollutant concentration is attributed to the onset of decomposition within the landfill and to the leachates that traverse the entire depth of the refuse. Therefore, large pollutant loadings from a typical landfill occur during the period of high leachate production and contain high levels of contaminants. The periods of varying leachate production cannot be quantified readily because they are site specific and depend on each of the aforementioned variables.

Over a period of time (as the landfill ages and leaching continues), the concentration of contaminants in the leachate decreases. The landfill may continue to generate substantial quantities of leachate; however, gradually the load of pollutants become lower because of the lower concentrations of soluble, suspended, or miscible contaminants that remain in the landfill. As the decomposition process within the landfill continues, the landfill attains a stabilized state of equilibrium, where further leaching produces leachates with a pollutant load lower, than during the period of peak leachate production. This stabilized state is presumably the result of decomposition of landfill waste by indigenous microorganisms that remove (biodegrade) many of the organic contaminants usually susceptible to further leaching.

Leachate characteristics change over time because there is a shift from the initial relatively short period of aerobic decomposition toward a longer period of anaerobic decomposition that has two distinct subphases (6, 8). The biological decomposition of landfilled municipal refuse is often based on the anaerobic breakdown of organic wastes. The biological activity occurs in a landfill shortly after the deposition of urban wastes, containing a large percentage of organic materials. Initially, the solid wastes, which contain high moisture content, can be decomposed rapidly under aerobic conditions, creating large amounts of heat. As oxygen is depleted, the intermediate anaerobic stage of decomposition begins. This change from aerobic to anaerobic conditions occurs unevenly through the landfill and depends upon the rate of oxygen diffusion into the fill layers.

In the first stage of anaerobic decomposition, the so-called "acidic phase," extra-cellular enzymes convert complex organic wastes, including carbohydrates, proteins, and fats, to more soluble organic molecules. Once the organic wastes are solubilized, their conversion to simpler organic molecules, such as acetic, propionic, butyric, isobutyric, valeric, isovaleric and hexanoic acids takes place; acetic acid is the main catabolic product of anaerobic fermentation. As a group, the low molecular weight, but highly polar, organic acids are termed volatile fatty acids (VFA). These soluble organic acids enter the leachate percolating through a landfill, resulting in a decreased pH of the leachate and increased oxygen demand. VFA impart to the leachate from this phase their characteristic "barnyard" odor and comprise the majority of its organic load. Anaerobic activity in the landfill can also lower the oxidation–reduction (redox) potential of the wastes, which under low pH conditions, can cause an increase in the concentration of dissolved inorganic contaminants.

Eventually, in the second or "methanogenic" phase of anaerobic decomposition, methane gas-forming bacteria within the landfill begin to convert the organic acids to methane and carbon dioxide, reducing the organic strength. The fraction of organic carbon, remaining after this degradation process, tends to be more oxidized, but has a higher molecular weight, higher than 500 amu. The absence of organic acids in the landfill increases the pH of the leachate, toward neutral or alkaline, which can subsequently decrease the solubility of inorganic contaminants and lower their concentrations in the resulting leachate.

The age or degree of decomposition of a landfill may be ascertained by observing the concentration of various leachate "gross" parameters, such as BOD_5, COD, TDS, or the organic nitrogen (N_{org}) concentration (9). The values of these leachate parameters can vary over the decomposition life of a landfill, depending on the specific phase. Typically, leachates from the early, acidic phase of anaerobic decomposition may be up to 35 times stronger than domestic wastewater and can have a COD content of more than 20,000 mg/L, BOD_5 greater than 12,000 mg/L, high volatile fatty acids concentration of about 6000 mg/L, and high content of inorganic compounds, such as 1300 mg/L chloride, but low phosphorous concentration (less than 1 mg/L) (10). Leachates from the older landfills have lower values of BOD_5 and COD, as well as of most organic pollutants, indicating the presence of smaller amounts of degradable compounds, derived from the aged stabilized waste.

The COD of leachates from the "methanogenic" phase tend to be lower, between 1500 and 4000 mg/L, and the significant decrease in the VFA concentration results in an increase in the pH to 7, or even higher. In addition, aged leachates can contain high levels of compounds existing in reduced form, such as ammonia (greater than 1000 mg/L), as well as a high concentration of chlorides because of the anaerobic environment of the landfill. Furthermore, certain metals such as iron, lead, and zinc tend to form stable complexes with the high molecular weight organic compounds (i.e., higher than 50,000), increasing their respective concentrations in the leachate (6).

However, using only these parameters, other refuse-filling variables, such as the processing of wastes prior to disposal or the fill depth, would not be taken into consideration. To compensate for these additional variables, several researchers have proposed examining certain ratios of leachate parameters over time (7). The most important (and widely used) such ratio is BOD_5:COD. Leachates from younger landfills typically exhibit BOD_5:COD ratios of approximately 0.8, whereas older landfills exhibit lower ratios (in many cases as low as 0.1). The decline in the BOD_5:COD ratio with age is due primarily to readily biodegradable material (e.g., phenols, alcohols, VFA) that degrade faster than the more recalcitrant compounds (such as the heavy molecular weight organic compounds, including humic and fulvic acids), which are much more difficult to treat biologically. As a result, as the landfill ages, the BOD_5 of the leachate decreases faster than the COD. Other ratios that decrease over time include the volatile solids to fixed (inorganic) solids (VS:FS), volatile fatty acids to total organic carbon (VFA:TOC), and sulfate to chloride (SO_4:Cl), which is inversely related to the redox potential (ORP).

As a result of the variation in leachate strength, leachates are commonly distinguished as young, acid-phase leachates and old, methanogenic ones, as well as medium- and low-strength leachates (11). For "young" leachates, a typical ratio of BOD_5/COD around 0.7 has been suggested; the corresponding values for mature leachates are 0.5, for aging 0.3, and for "old" 0.1. A typical time period for the transition from young to older leachate types is between 3 to 10 years from the landfill start-up, but may be as short as, 2 years in specific cases.

In summary, the following conclusions can be drawn regarding landfill leachate quality and their treatability (3):

- Leachate characteristics are highly variable.
- The quality of leachates changes with age, and therefore, the treatment facility should be flexible enough to handle/treat appropriately the changing leachate quality.
- A reliable estimate of the chemical quality of leachates should include analytical experimental data measured under the particular conditions prevailing in the landfill area.

The characteristics of leachates are usually very different from those of domestic wastewaters and similar to heavily loaded industrial wastewaters, indicating the need to use advanced treatment methods for the effective removal of pollutants before leachates are discharged.

BIBLIOGRAPHY

1. Leckie, J.O., Pacey, J.C., and Halvadakis, C. (1979). Landfill management with moisture control. *J. Environ. Eng. Div., ASCE* **110**(4): 780–796.
2. Tchobanoglous, G., Theisen, H., and Vigil, S. (1993). *Integrated Solid Waste Management: Engineering Principles Management Issues*. McGraw-Hill, New York.
3. Qasim, S.R. and Chiang, W. (1994). *Sanitary Landfill Leachate: Generation, Control and Treatment*. Technomics, Lancaster, PA.
4. Tatsi, A. and Zouboulis, A.I. (2002). A field investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece). *Adv. Environ. Res.* **6**(3): 207–219.
5. Barlaz, M.A. et al. (2002). A critical evaluation of factors required to terminate the post-closure monitoring period at solid waste landfills. *Environ. Sci. Technol.* **36**(16): 3457–3464.
6. Forgie, D.J.L. (1988). Selection of the most appropriate leachate treatment methods. Part 1. A review of potential biological leachate treatment methods. *Water Pollut. Res. J. Can.* **20**(2): 308–328.
7. Environmental Protection Agency. (2000). *Development Document for Final Effluent Limitations Guidelines and Standards for the Landfills Point Source Category*. EPA-821-R-99-019, Washington, DC.
8. Kjeldsen, P.K. et al. (2003). Present and long term composition of MSW landfill leachate—a review. *Crit. Rev. Environ. Sci. Technol.* **32**(4): 297–336.
9. Al-Yaqout, F. and Hamoda, M.F. (2003). Evaluation of landfill leachate in arid climate—a case study. *Environ. Int.* **29**(5): 593–600.
10. Harrington, D.W. and Maris, P.J. (1986). The treatment of leachate: A UK perspective. *Water Pollut. Control* **85**(1): 45–56.
11. Henry, J.G., Prasad, D., and Young, H. (1987). Removal of organics from leachates by anaerobic filter. *Water Res.* **21**(11): 1395–1399.

LANDFILL LEACHATES: PART 2: TREATMENT

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INTRODUCTION

The characteristics (composition) of sanitary landfill leachates are very different from domestic wastewaters, and their quality varies from landfill to landfill, as well as with the particular landfill age. Hence, their treatment is based largely on industrial wastewater treatment processes. However, no single treatment method is considered efficient enough to achieve the high removal rates of pollutants, usually required; therefore, several treatment trains are currently used, including combinations of aerobic/anaerobic processes and several modes of physical–chemical treatment systems. The selection and design of leachate treatment facilities requires knowledge of several parameters, such as leachate quantity and quality, degree of necessary treatment, disposal methods, and effluents guidelines. These are the main problems that have to be considered:

- Specific treatment schemes applied in a particular landfill may not be transferable to other sites.
- Leachate quantity and quality vary seasonally, depending on climatic and hydrologic factors.
- The composition of disposed of solid wastes greatly affects the composition of leachates.

During plant design, the fluctuations in the leachate generation rate and its composition should be considered. Furthermore, the treatment system should also be flexible enough to treat the "young" leachates during the preliminary stages of landfill operation, as well as the "older" leachates produced during landfill aging.

During the early development of appropriate methods for leachates, the main efforts were focused on the application of treatment processes commonly used for municipal wastewaters; they were based mainly on biological processes. Physical and chemical systems used were later complementary, aimed at the development of more efficient overall techniques (1).

BIOLOGICAL PROCESSES FOR TREATING LEACHATES

Both aerobic and anaerobic biological units have been used to treat landfill leachates. The number of landfill facilities that use variations of biological treatment as part of landfill wastewater treatment systems in the United States has been reviewed by the EPA (2), and it is shown in Table 1. According to this table, most of the biological treatment systems use aerobic processes, including suspended growth processes (i.e., activated sludge, sequencing batch reactors, lagoons, etc.), as well as fixed-film processes (i.e., trickling filters or rotating biological contactors). However, the use of anaerobic systems is rather limited; these systems are most effective for treating high strength leachates (i.e., whose COD values are over 4000 mg/L) and for wastewaters containing refractory (not easily biodegradable) contaminants because of the effectiveness of methanotropic microorganisms in metabolizing these compounds. An important disadvantage of anaerobic treatment systems is the sensitivity of the applied methanotropic microorganisms to certain toxic substances, commonly found in many leachates.

The design of aerobic systems is based mainly on the requirements for removing organic loading in terms of BOD_5 and COD or on requirements for nitrogen removal. The selection of the design estimates depends on the effluents guidelines that have to be met and the problems anticipated from the existing high ammonia concentrations. A rule of thumb proposed for selecting the most appropriate design criteria is the ratio of BOD_5/N-content: when this ratio is less than 1, leachates are characterized by very high nitrogen (mainly ammonia) concentrations, and then nitrification criteria prevail; when this ratio is greater than 1, then the organic removal criteria dominate (3).

Table 1. Biological Treatment Facilities for Leachates in U.S. Landfills[a]

Type of Biological Treatment	% of Nonhazardous Facilities	% of Hazardous Facilities
Activated sludge	9	33
Aerobic lagoon systems	10	—
Facultative lagoons	7	—
Trickling filters	0	—
Anaerobic systems	2	—
Powdered activated carbon treatment (PACT)[b]	1	—
Nitrification systems	2	—
Rotating biological contactors (RBC)	0	—
Sequencing batch reactors (SBR)	1	33
Denitrification systems	1	—
Other biological treatment systems	13	—

[a] Reference 2.

[b] In combination with activated sludge.

Suspended growth biological treatment systems usually include mechanically based aerators to provide the required oxygen to the microbial population and for mixing the liquor components. The ranges of typical design and performance parameters of activated sludge systems are as follows (4):

- hydraulic retention time: 1–10 days.
- solids retention time between 1 and 10 days.
- food to microorganism (F/M) ratio from 0.02–0.4 kg BOD_5/kg MLVSS/day.
- average nutrient requirement ratio BOD_5: N:P = 100:3.2:0.5.
- Removal efficiencies in terms of BOD_5 and COD from 90–99%, depending on experimental conditions and the properties of raw leachates.

Several measurements of operational parameters have indicated that a large part of the organic compounds in raw leachates are usually not readily biodegradable and require prolonged reaction times and extensive biological activity to oxidize them. Efforts to determine the removal rates of various compounds in an aerobic reactor resulted in discriminating four distinct and successive steps of substrate use by microorganisms, in order of gradually increased degree of difficulty: carbohydrates, fatty acids, amino acids, and humic substances of high molecular weight (4). Residual organics consist mainly of fulvic-like materials with molecular weights in the range 500–10,000, which are not readily biodegradable.

Introducing an anoxic stage may enhance the removal of nitrogen from leachates, achieving more than 70% total nitrogen removal. However, the highest removal rates may be achieved by adding an organic carbon source, such as methanol. High metal removal rates (up to 99%) have also been observed in activated sludge treatment systems of leachates; this was attributed to the oxidation of metals, forming insoluble compounds, and the incorporation of the respective precipitates into bacterial flocs (2). However, when metal content is high (e.g., 80 mg/L iron and 10 mg/L manganese), a pretreatment step may be necessary for their efficient reduction to prevent the resulting low MLVSS/MLSS ratios and certain mixing problems.

Stabilization ponds and aerated lagoons have also been used as pretreatment steps for leachates, prior to disposal in municipal sewers or recycling into the landfill. Although extended aeration and lagoon-type systems are favored for treating leachates because of low manpower requirements and operational simplicity, however, this application has a primary drawback, the extended land required. Additional problems connected with suspended growth systems include the intense foaming of leachates, high power consumption, potential inhibition of biological activity by increased concentrations of metals, high sludge production rate, filamentous bulking of sludge, and decreased biological activity due to deficiency in certain nutrients (usually phosphorous) (5).

Fixed-film aerobic systems provide an appropriate substrate for attaching and growing aerobic and facultative (anaerobic) bacteria. However, their use is currently limited for treating leachates. Typical loading rates for such systems are detention time about 10 h and loading rates from 2 to 5 g of NH_3-N/m^2/day. The systems achieve high removal efficiencies and result in effluents whose ammonia content is lower than 1 mg/L and BOD_5 lower than 20 mg/L (2).

Anaerobic biological systems used for treating leachates are often based on fixed-film type reactors using inert media, as well as on suspended growth systems, such as the upflow anaerobic sludge blanket (UASB) reactor. Detention times reported for these systems range from 1–15 days for anaerobic filters and from 1–6 days for UASB units; for the latter systems, removal capacities greater than 80% have been observed, and for anaerobic filters, the corresponding values range from 70–99% COD removal efficiency. The determination of BOD_5/COD and COD/TOC ratios in effluents from anaerobic treatment units showed that the composition of these effluents compared with those of leachates created from landfills of intermediate age. It may be concluded that a substantial part of biodegradable organics can be removed by the landfill itself, acting as an anaerobic bioreactor, and thus, the subsequent application of biological treatment methods and in particular of anaerobic processes are only moderately effective for the removing the remaining organic matter from “older” leachates (1).

In general, aerobic biological treatment of leachates is possible for “young” leachates that have high BOD_5/COD ratios, higher than 0.4, as well as low ammonia content. Activated sludge systems are the most common treatment techniques, and fixed-film systems are best used for nitrification of “older” leachates rich in ammonia. In this case, phosphorous addition may be necessary to provide the proper nutrient balance for sufficient cell growth. Anaerobic treatment systems may also be successful for treating leachates because of the advantages of relatively simple design; low capital, operating, and maintenance costs; and the ability to treat leachates with high BOD_5/COD ratios. However, anaerobic systems also present certain drawbacks that limit their application: slow biomass establishment, requirement for higher (at least mesophilic) temperatures (i.e., difficult use in cold climates); and poor solids separation (2,5).

Combined treatment of leachates in an existing municipal wastewater treatment plant is considered convenient; it has been applied in several cases, and it is the preferred disposal method for leachates, when the principal following requirements are met: availability of a sewer system, wastewater treatment plant capacity high enough to accept the heavily loaded leachates, process compatibility with the specific (composition) characteristics of leachates, and a sludge treatment facility large enough to handle the increased sludge production rates (4). Several studies of the cotreatment of municipal wastewaters and landfill leachates concluded that the overall treatment process and the effluent quality are not seriously affected by the addition of leachates up to 10% by volume at the municipal sewage, although this depends mainly on the loading strength of the leachates (6,7).

However, several problems may arise during the cotreatment that are connected to the possible negative effect and accumulation of heavy metals, the conversion of ammonia, the variations in temperature, the (much higher) sludge production, the (usually intense) foaming, and (poor) solids settleability. As a result, the cotreatment of leachates and municipal wastewaters has to be studied case-by-case, considering the significant problems that may appear due to the presence of toxic compounds, as well as the specific portion of leachate that has to be cotreated. The introduction of a pretreatment facility, such as a simple aerated lagoon, may satisfy the requirements for a preliminary polishing step in these cases.

PHYSICAL–CHEMICAL TREATMENT OF LEACHATES

Physical–chemical techniques are becoming increasingly common for treating industrial wastewater and for reclaiming municipal wastewaters, especially when intended for reuse. These techniques include mainly processes such as equalization, neutralization/pH adjustment, chemical precipitation and coagulation, chemical oxidation, activated carbon adsorption, air-stripping, ion exchange, and membrane separation. The application of physicochemical treatment methods to leachates offers the advantages of short start-up periods, relative stability to temperature variations, and the potential for automation.

Equalization

The composition and generation rates of leachates at landfills may vary widely due to their direct relationship to rainfall, storm water run-on and runoff, groundwater entering the waste-containing zone, and the moisture content and absorptive capability of disposed of wastes. To allow equalization of pollutant loadings and flow rates, the leachates are often collected, prior to treatment, in tanks or ponds that have sufficient capacity to hold the peak flows generated at the landfill facility (2). A constant flow is delivered to the treatment system from these holding tanks to dampen the variation in hydraulic and pollutant loadings to the wastewater treatment system. This reduction in hydraulic and pollutant variability increases the performance and reliability of treatment systems applied downstream and can reduce the size of subsequent treatment tanks as well as the chemical or polymer feed rates of supplementary reagents by reducing the maximum flow rates and the concentrations of pollutants to be removed.

The equalization systems consist of steel or fiberglass holding tanks or lined ponds that can provide sufficient capacity to contain peak flow. Detention times determined by using a mass balance equation and depend on site-specific generation rates and treatment design criteria. Detention times can range from less than a day up to 90 days; the median value is about 2 days. Equalization systems usually contain either mechanical mixing or aeration systems; they enhance the equalization process by keeping the tank contents well mixed and prohibiting settling of solids.

pH Adjustment

The pH of wastewater generated by landfills may have a wide range of values, depending on the specific types of wastes deposited in the landfill. In many instances, the raw wastewater may require neutralization to eliminate either high or low pH that may upset the treatment system subsequently applied, such as an activated sludge biological treatment. The landfill facilities may use neutralization systems in conjunction with chemical treatment processes, such as chemical precipitation, to adjust the pH of the wastewater and to remove metals to optimize process control. Acids, such as sulfuric acid or hydrochloric acid, are added to reduce pH, whereas alkalis, such as sodium hydroxide or lime, are added to raise the pH. Neutralization may be performed in a holding tank, in a rapid mixing tank, or in an equalization tank. Typically, the neutralization systems applied at the end of a treatment system are designed to control the pH of the final discharge between 6 and 9.

Chemical Precipitation and Coagulation

Suspended particulates and colloidal matter contained in surface waters or wastewaters can be removed by coagulation using multivalent cations, such as Ca^{2+}, Fe^{3+} or Al^{3+}. As a result, several investigations of the treatment of leachates dealt with the use of chemical precipitation and coagulation (8).

In chemical precipitation, soluble metallic ions and certain anions, found in landfill wastewaters, are converted to insoluble forms that precipitate from the solution. Most metals are relatively insoluble as hydroxides, sulfides, or carbonates. Coagulation is used in conjunction with precipitation to facilitate their removal by agglomerating suspended and/or colloidal materials. The precipitated metals can be subsequently removed from the wastewater stream by filtration, settling clarification (sedimentation), or some other type of gravity-assisted separation. Other treatment processes such as equalization, chemical oxidation, or reduction (as in the case of hexavalent chromium) usually precede chemical precipitation. The performance of the chemical precipitation process is affected mainly by other chemical interactions, temperature, pH, the solubility of waste contaminants, and mixing effects (2).

Common precipitating reagents used at landfills usually include lime, sodium hydroxide, soda ash, sodium sulfide, or alum. Other chemicals also used in precipitation and coagulation, as well as for pH adjustment, include sulfuric and phosphoric acids, ferric chloride, and polyelectrolytes (synthetic organic polymers). Often, landfills use an appropriate combination of these chemicals. Precipitation by sodium hydroxide or lime is the most conventional method for removing metals from leachates. Hydroxide and coagulant precipitation has proven effective for removing several metals, such as trivalent chromium, pentavalent arsenic, copper, lead, nickel, and zinc. However, sulfide precipitation may also be used, instead of hydroxide precipitation, to remove certain metal ions, such as mercury, lead and silver more effectively.

Carbonate precipitation is another method of chemical precipitation; it is used primarily to remove antimony or lead. Use of alum as a precipitant/coagulant agent results in the formation of aluminum hydroxides in wastewaters, containing calcium or magnesium bicarbonate. Aluminum hydroxide is an insoluble gelatinous floc, which settles slowly and entraps suspended materials. It is considered particularly effective for removing certain metals, such as arsenic or cadmium.

Lime is less expensive than sodium hydroxide, so it is used more frequently at landfills employing hydroxide precipitation. However, lime is more difficult to handle and feed, as it must be slaked, prepared in a slurry, and mixed intensively, often plugging the feed system lines. Lime precipitation also produces a larger volume of sludge.

In addition to the type of chemical agent selected for treating leachates, another important design factor in the operation of chemical precipitation is the pH. Metal hydroxides are usually amphoteric, meaning they can react chemically both as acids or bases; as such, their solubilities increase at both lower (acidic) and higher (alkaline) pH levels. Therefore, there is an optimum pH value for the precipitation of each metal, which corresponds to its minimum solubility. Another key consideration in chemical precipitation is the necessary detention time during the sedimentation phase of the process. The optimal detention time depends on the wastewater being treated and on the desired effluent quality.

The first step in chemical precipitation is pH adjustment and the addition of coagulants. This process usually takes place in separate mixing and flocculation tanks. After mixing the wastewater with the appropriate chemical reagents, the resulting mixture agglomerates in the flocculation tank, and it is mixed slowly by mechanical means, such as mixers, or by recirculation pumping. The wastewater then undergoes further separation, by clarification (by settling) or filtration, where the precipitated metals are removed from the (cleared) solution. In a clarification system, an organic flocculant, such as a synthetic polymer (e.g., polyacrylamide), is sometimes added to help the settling. The resulting sludge from the clarifier or from the filter must be further treated, disposed of, or recycled.

Several studies have been reported on the examination of coagulation–flocculation for the treating landfill leachates, aimed to optimize performance, by selection of the most appropriate coagulant, determination of experimental conditions, assessment of the pH effect, and investigation of flocculant addition (9,10). Aluminum sulfate (alum), ferrous sulfate, ferric chloride, and ferric chlorosulfate are commonly used as coagulants (3). Iron salts proved more efficient than aluminum salts, resulting in COD reductions of up to 56%, whereas the corresponding values for alum or lime were 39 and 18%, respectively (11). Additionally, high COD removal capacities have been observed during the combined action of alum and lime on stabilized leachates (12). Furthermore, the addition of flocculants together with coagulants may substantially enhance the floc settling rate (9).

The coagulation–precipitation process has been investigated mainly by using stabilized or biologically pretreated landfill leachates, as a final polishing treatment stage. However, limited information exists on the efficiency of this physicochemical process, when used to remove pollutants from leachates, partially stabilized by recirculation or from recently produced ("fresh") leachate. This technique may be important for enhancing leachate biodegradability prior to biological treatment. High COD removal capacities (about 80%) have been obtained during the addition of ferric chloride to partially stabilized leachates, whereas low COD reductions (lower than 35%) have been measured during the addition of coagulants to raw samples (13).

In general, the coagulation and/or precipitation of raw leachates by the addition of lime resulted in the removal of multivalent cations, suspended solids, and color from raw leachates, but the effect on organic matter removal was rather negligible. In an early work of Slater et al. (14), it was found that only a small percentage (about 4–6%) of organic compounds with molecular weight of 10,000 or more was contained in an industrial raw leachate, whereas most of the organics had a molecular weight of 500 or less. However, after lime addition, the higher MW fraction disappeared, whereas the other fractions of MW 500 or less and between 500 and 10,000 remained almost untouched. As a result, lime addition to "young" leachates is not expected to be effective for removing organics because this type of leachate contains mainly high amounts of lower MW volatile fatty acids. Coagulation by lime may be an efficient method for treating "older" or biologically treated leachates that contain a large fraction of high MW substances, such as humic and fulvic acids (1). However, the use of ferric salts or of alum has proven more effective than lime, possibly due to different optimum pH process conditions that range between 4.5 and 5.5.

Chemical Oxidation

Chemical oxidation processes can generally be used in wastewater treatment to remove ammonia, to oxidize cyanide, to reduce the concentration of residual organics, and to reduce the bacterial and viral content. Chemical oxidation for treating leachates has been successful, based on several oxidants, including chlorine gas, calcium hypochlorite, potassium permanganate, hydrogen peroxide, and ozone (2). Both chlorine and ozone are two chemicals that are commonly used to destroy residual organics in biologically pretreated wastewater. When these chemicals are used for leachate treatment, the resulting disinfection of the wastewater is usually an added benefit.

Chemical oxidation is a potential treatment option for removing certain organic pollutants from leachates or groundwater. The amount of oxidant required in practice is generally greater than the theoretical mass calculated. The reasons for this are numerous and include incomplete oxidant consumption and oxidant demand caused by the simultaneous presence of other oxidizable species in solution. Oxidation reactions depend on the presence of appropriate catalysts, as well as on pH control, which is an important design variable. For many facilities using chemical oxidation, partial oxidation of organics, followed by additional treatment options, may be more efficient and cost-effective than using a complete oxidation treatment scheme alone.

The use of chlorine gas in leachates has been tested and resulted in high color and iron removal rates, but in limited reduction of organic matter, which is possibly due to (1) the presence of ammonia, which has to be initially destroyed by break-point chlorination before any organic oxidation and (2) the presence of relatively difficult to oxidize organics. On the other hand, the use of hydrogen peroxide presents several benefits: control of odor from stored leachates, removal of sulfides discharged to municipal sewers, and growth control of undesirable microorganisms near discharge of leachates. In addition, the study of the MW distribution of organics in leachates treated with hydrogen peroxide showed that it enhances the percentage of compounds of MW less than 1000 and therefore, increases the possibility of further biological treatment.

Ozone treatment of leachates provides several benefits, such as the removal of color, the degradation of particular organics (such as polyaromatic hydrocarbons), and the reduction of phenols and toxicity (15,16). Furthermore, ozone application may enhance the biodegradability of leachates by converting pollutants to end products or to intermediate products that are more readily biodegradable or can be more easily removed by adsorption (17). Ozone application proved very effective for removing color and iron, but was less efficient in removing COD. It was concluded that ozonation should not be used in leachates of high volatile fatty acid content, especially when acetic acid is present, due to their strong resistance to chemical oxidation (8).

Activated Carbon Adsorption

Activated carbon adsorption is a physical separation process, in which organic and inorganic materials are removed from wastewaters by sorption, attraction and accumulation of the contaminants on the surface of carbon granules. Most organic compounds and some metals typically found in landfill leachates can be effectively removed by using granular activated carbon (GAC). Although the primary removal mechanism is adsorption, biological degradation and filtration are additional pollutant removal mechanisms, also provided by an activated carbon filter. Adsorption capacities of 0.5 to 10% by weight are rather typical in many industrial applications. Spent carbon can be either regenerated on site by thermal processes, such as wet-air oxidation or steam stripping, or for smaller operations, it can be regenerated off site or sent directly for disposal in to hazardous waste landfills.

Several studies have been presented concerning the use of activated carbon adsorption for treating landfill leachates. In general, this process is very effective in removing residual organics that remain after prior biological treatment of leachates, and thus it could be used as a final polishing step for biologically pretreated leachates and/or for well-stabilized “old” leachates (8). Furthermore, the combination of powdered activated carbon with an activated sludge system results in enhanced removal capacities of organic matter up to 98% of BOD_5 (2).

In conclusion, the adsorption of higher MW organic compounds is enhanced by the properties of these compounds. As the MW of organics increases, their polarity, solubility, and branching properties decrease, resulting in an increase in carbon adsorption. As a result, lower MW volatile fatty acids representative of “younger” leachates are poorly adsorbed on activated carbon particles, whereas higher MW compounds, such as fulvic acids, found in “old” leachates, are adsorbed on activated carbon to a greater extent. Both powdered and granular activated carbon may be used for leachate treatment, but special consideration should be given during the design period, because of the high cost of this material.

Air Stripping

Stripping is an effective method for removing dissolved volatile organic compounds from wastewater. Removal is accomplished by passing air or steam through the agitated waste stream. Air stripping is used to the treat leachates, mainly to remove ammonia. In this case, the pH must be increased to between 10.8 to 11.5, usually by adding NaOH or $Ca(OH)_2$ solutions; ammonia stripping takes place by blowing large volumes of air upward through the leachate bulk volume. This process is carried out in towers, where leachates trickle down over some type of inert material or in a shallow aerated reaction vessel. Air stripping has been proved efficient for the extensive reduction of ammonia (up to 93%); the residual concentrations no longer inhibit nitrification (18). However, this method has two drawbacks; the cost of chemicals for pH adjustment and the problem of freezing as the air and the leachate temperature approach 0 °C (2).

Ion Exchange

Ion exchange is an adsorption process that uses appropriate (usually synthetic organic) resins as media to remove charged contaminants from wastewater. Ion exchange is commonly used to remove heavy metals from relatively low-concentration waste streams. A key advantage of the ion exchange process is that it allows recovery and reuse of the removed metals. Ion exchange can also be designed to be selective for certain metals and can effectively remove them from wastewater that contains high concentrations of “background” metals, such as iron, magnesium, and/or calcium. A specific disadvantage of this treatment method is that the resins used are subjected to fouling by oils or other natural (high MW) polymers. However, the use of ion exchange to treat leachates is limited, by the high operating costs of this method, including the cost of the exchange media, the necessary chemical reagents used as regenerants, and the regenerants disposal costs. As a result, this method is appropriate for the supplementary removal of metals, as posttreatment final polishing step, that results in low residual ion concentrations of less than 1 mg/L (2,8).

Membrane Filtration

Membrane filtration systems employ a semipermeable polymeric membrane and a pressure differential to separate constituents of different size (from microparticles down to soluble ions) from an aqueous phase. Nanofiltration, ultrafiltration, and reverse osmosis are the most commonly used membrane filtration processes.

Ultrafiltration uses a semipermeable microporous membrane, through which the wastewater is passed under pressure. Water and low molecular weight solutes, such as salts and surfactants, pass through the membrane and can be removed as permeate. Emulsified oils and suspended solids are rejected by the membrane and are removed with part of the wastewater as a more concentrated liquid. The concentrate is usually recirculated through the membrane unit, until the permeate flow drops substantially. Ultrafiltration is commonly used for removing substances whose molecular weights are greater than 500, including suspended solids, oil and grease, large organic molecules, and complexed heavy metals. Ultrafiltration is commonly used, when the solute molecules are greater than 10 times the size of the solvent molecules (usually water) and less than 0.5 μm.

Reverse osmosis is a separation process that uses selective semipermeable membranes to remove dissolved solids, such as metal salts, from water. The respective membranes are more permeable to water than to contaminants or impurities. The wastewater is forced through the membrane at a pressure that exceeds the osmotic pressure caused by the dissolved solids. Molecules of water pass through the membrane as permeate, and the contaminants are rejected along the surface of the membrane and exit as a concentrated stream. The concentrate (rejection) flow from a reverse osmosis system ranges from 10–50% of the feed flow; the concentrations of dissolved solids and of contaminants within this stream approach at least 10 times that of the feed (raw) wastewater. The percentage of permeate that passes through the membrane is a function of operating pressure, membrane type, and concentration of the contaminants in the feed.

Cellulose acetate, aromatic polyamide, and thin-film composites are commonly used membrane materials. Membrane pore sizes for a typical reverse osmosis system range from 0.0005–0.002 μm, and pressures of 20–30 bars are usually required. Therefore, reverse osmosis feed water must be very low in turbidity to avoid direct blocking of the membrane. As a result, pretreatment of landfill wastewater prior to reverse osmosis may be necessary, including chemical addition and clarification or cartridge filtration (using 5-μm filters), to remove suspended particulates from the influent and protect pumps and membranes. Carbon adsorption is also recommended as a pretreatment for membranes sensitive to chlorine. Biofouling can be prevented by chlorination and dechlorination of the feed water. To maintain sufficient solubility of metals, such as calcium, magnesium, and iron, and avoid the formation of precipitates, the pH should be appropriately adjusted with acid. Aside from pH adjustment, chemical reagents may also be used as bactericides, as well as for dechlorination (2).

Several reports on the use of ultrafiltration and especially on the application of reverse osmosis membranes for treating leachates showed that these methods are best used, following biological pretreatment, or for treating "older" leachates (19). In addition, during the treatment of leachates by membranes, compounds whose MW was lower than 200 were not rejected, in comparison with those having a MW higher than 200. The performance of reverse osmosis membranes may be further optimized, after careful adjustment of pH to values around 8 and by using polythylamine membranes that results in almost 94% reduction of total organic carbon (TOC) (8). However, severe membrane fouling was experienced in several cases, suggesting that reverse osmosis is most effective as a posttreatment step (following biological treatment) for removing residual COD and dissolved solids. Trebouet et al. (20) have shown that high pollutant removal can also be achieved by nanofiltration, especially for "older" leachates. Nanofiltration can be run at lower pressures than reverse osmosis, hence presenting lower operating costs and less membrane fouling.

Recirculation of Leachates into the Landfill

The recirculation of leachates is the redistribution of leachates that have been collected at the bottom of a landfill back to the top of it. The recirculation can usually be performed by spraying leachates onto the exposed surface of the landfill or by distribution through perforated pipes, located just beneath the surface of the landfill. As the recirculated leachate trickles downward through the fill, the disposed of solid waste materials in the landfill become an appropriate medium for developing anaerobic microorganisms, and as a result, an anaerobic treatment process is initiated.

Therefore, the landfill becomes an uncontrolled anaerobic digester and the biodegradable organics in the leachates are initially converted to volatile fatty acids and then to methane. Under these conditions, an initially low BOD_5 leachate, which is similar in composition to that of "older" leachates, may be produced during periods up to 18 months of recirculation. It has been suggested that the recirculation of leachates can more rapidly develop an active anaerobic bacterial population of methane-forming bacteria within the landfill. The rate of removal of organic compounds may be further enhanced by the addition of excess sewage sludge, acting as additional carbon source, which is produced in biological wastewater treatment plants, as well as by appropriate pH control (8,21).

The problems of recirculation usually include the development of odors, the high capital and maintenance cost of the recirculation system for leachates, and the precipitation of carbonates and iron oxides that may clog both the spraying equipment and the surface of the landfill and decrease the percolation rate. However, recirculation of leachates has a number of benefits, such as production of leachates with more uniform properties, the acceleration of overall landfill stabilization, the delay in the starting time for the application of other treatment systems, and reduction in the strength of the treated leachates. Nevertheless, the recirculation of leachates does not finally result in reduction of generated wastewater volumes and cannot provide a sufficient treatment process for leachates, because the treated leachates may have relatively high COD content (higher than 3000 mg/L), as well as high ammonia concentrations (2).

In general, physical–chemical treatment methods are considered an effective means for treating leachates, which contain organic compounds of MW less than 500 and a BOD/COD ratio lower than 0.1. This is particularly important for the use of chemical coagulation and activated carbon adsorption because these methods are very sensitive to the MW distribution of organics. Chemical oxidation may be used for removing dissolved metals (mainly iron), but has little effect on COD, when applied separately. Air stripping can be highly effective in removing ammonia, but at highly alkaline pH. Finally, membrane separation processes may have some potential for the treating leachates, but they are subject to membrane fouling.

In conclusion, neither physical–chemical treatment alone, nor biological methods may be able to treat leachates completely, when applied separately. As a result, the integration of several treatment processes is required to produce an effluent of acceptable quality; the selection of the most appropriate treatment train is very significant for an integrated leachate management system.

SELECTING THE APPROPRIATE COMBINATION OF TREATMENT PROCESSES

The characteristics of leachates may vary from place to place, as well as with time; thus, the construction of an appropriate treatment scheme is a difficult task, requiring the development/design of appropriate processes, consisting of the following subsequent steps: the first step involves assessment of leachate quality, an estimate of the (seasonal) quantity, and the type of treatment techniques available; the second step includes selection of the optimum biological treatment method for removing major pollutants from the leachate, followed by selection of the applicable polishing (final) stages as a third step (4,22).

Selecting Treatment Techniques Based on Leachate Quality

During this phase, the influent leachate quality is assessed, and the corresponding effluent characteristics are determined, based on the estimates of BOD_5, COD, nitrogen (as ammonia, i.e., NH_3-N), phosphorous, and metal content. Additional data that might be used in this phase include the concentration of volatile fatty acids, TOC, and total suspended solids.

The most important parameter for the preliminary screening of treatment techniques for leachates is the BOD_5/COD ratio. Leachates from a relatively new landfill have high COD values, usually higher than 10,000 mg/L; low NH_3-N content; and BOD_5/COD ratios ranging from 0.4–0.8. These leachates are representative of "young" leachates, containing high amounts of easily biodegradable organic substances, which are amenable to both aerobic and anaerobic biological treatment. However, physical–chemical treatment may not be an appropriate method for such leachates due to the presence of low molecular weight volatile fatty acids, prevailing over higher molecular weight compounds.

"Old" (mature) leachates are characterized by lower COD values, usually less than 3000 mg/L; higher NH_3-N concentrations, due to the anaerobic decomposition of organic nitrogen content within the landfill; and BOD_5/COD ratios lower than 0.4. In this case, aerobic biological treatment is required because it can provide extensive nitrogen removal through nitrification, in addition to removing organic matter (COD values). However, for BOD_5/COD ratios lower than 0.1, the remaining organics consist mainly of nonbiodegradable materials, and physical–chemical treatment becomes a more attractive option.

A second parameter, which can be used as an indicator for the preliminary selection of a treatment process, is the molecular weight partitioning of the organic content. In this case, biological treatment would be an effective technique for leachates that contain organic substances of MW lower than 500, whereas physical–chemical treatment is favored for removing organics, of molecular weights higher than 1000. However, this parameter is not easily measured in samples of leachates, and it is not used as a general index. Other less important parameters may include the BOD_5/NH_3-N ratio and the metal content, which are usually considered in the following steps of the design procedure.

Selecting the Appropriate Biological Treatment Method

To treat "young" leachates that have high BOD_5/COD ratios and high amounts of low MW (i.e., easily biodegradable) organics, biological treatment is the most efficient technique for reducing organic (carbonaceous) matter. The first option in this case is the examination of recirculation as a cost-effective method for preliminary reduction of leachate strength. However, when recirculation is not feasible, then aerobic or anaerobic biological treatment should be used.

Anaerobic biological treatment is the most appropriate method for handling leachates of high BOD_5/COD ratio, low NH_3-N content, high temperature, and high VFA content; the optimum process in this case is the application of anaerobic filters. The effluents from anaerobic processes would be similar to "old" leachates that have COD values between 1000 to 3000 mg/L and require an additional posttreatment step to reduce residual organics.

Aerobic biological treatment is a common method, which may be applied either for anaerobically pretreated or for raw leachates. In addition, biological denitrification may also be included in the aerobic process for effective removal of nitrates. Two significant problems are associated with the aerobic treatment of leachates; the first is the phosphorous deficiency in leachates that requires supplementary phosphorous, and the second is the high ammonia content that may inhibit the nitrification capacity of the system. In this case, the initial high ammonia concentration should be reduced by preliminary air stripping of the leachate. Additional problems include possible high metal content; long sludge retention time (up to 30 days), hence requiring the use of larger basins; foaming of leachates during aeration; and the potential for metal precipitate formation that affects the operation of aeration systems. The effluents from the aerobic processes usually have low BOD_5 values, lower than 100 mg/L, but rather high COD values, up to 1500 mg/L, that require subsequent physical–chemical treatment (22).

Selection of Physical–Chemical Treatment Method

The third step in the treatment design procedure for leachates is selecting a process for posttreating the effluent. "Old" and biologically pretreated leachates may contain nonbiodegradable high MW organic compounds, particulates, and metal ions. Residual organics may be removed by chemical oxidation, using hydrogen peroxide and/or ozone, but these techniques are expensive, due to the high dosages of the necessary chemicals. Coagulation is an alternative method, which is effective for removing higher MW organics that represent about 50% of the residual organic matter. Activated carbon adsorption is also a viable process for removing lower MW organics. Membrane separations may be used for removing organics, but these methods are best applicable as final polishing stages, due to high costs and problems of membrane fouling.

Chemical precipitation using lime or chemical oxidation followed by sedimentation and/or filtration has been suggested to decrease the metal content of leachates. Similar techniques can be also used to reduce particulates and metals content, such as coagulation followed by sedimentation/filtration, chemical oxidation, membrane separation, or ion exchange.

Several alternative units for treating leachates are operating currently worldwide, consisting of a combination of subsequently applicable treatment steps. The

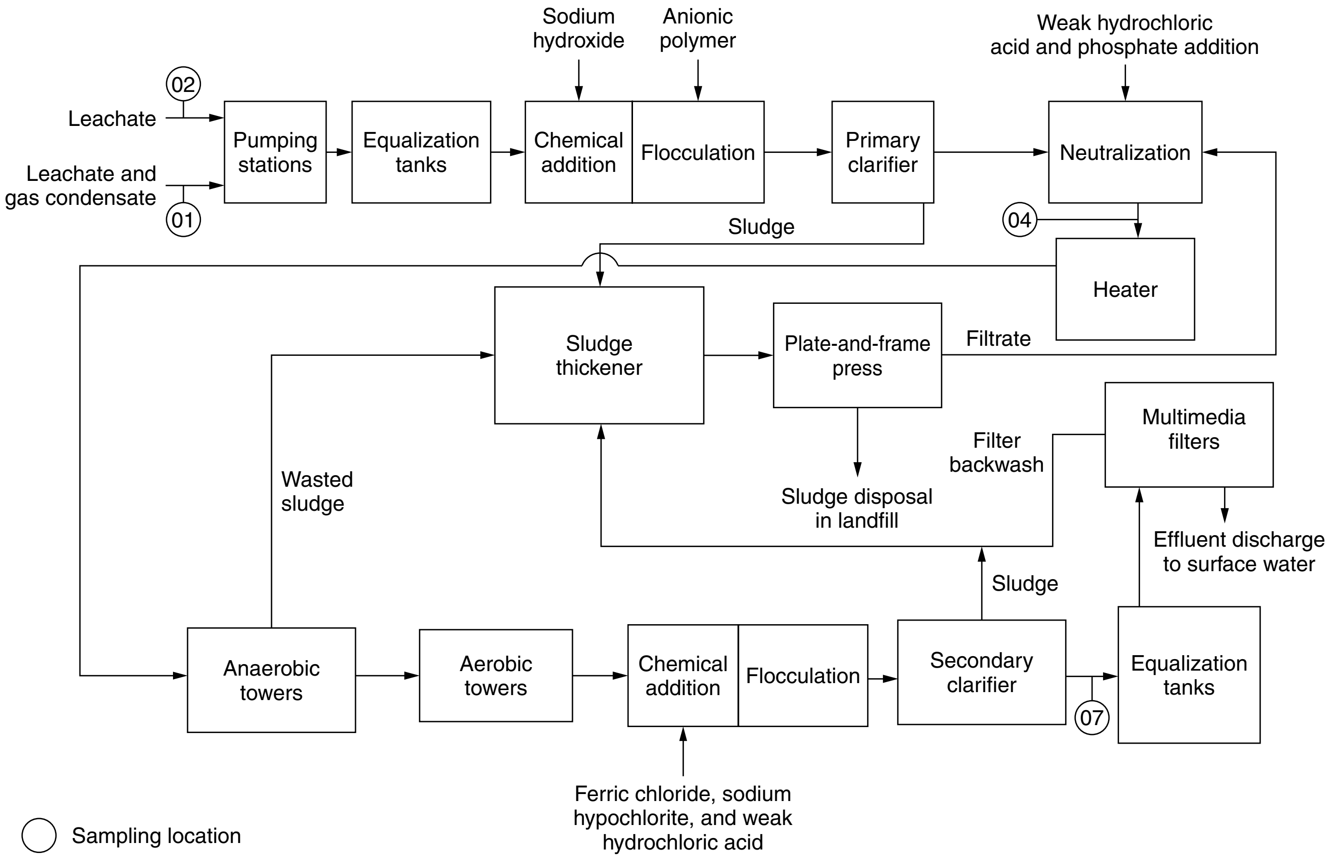

Figure 1. Flow sheet of a typical leachate treatment plant (2).

U.S. EPA (2) has evaluated the performance of a number of treatment systems and representative results are presented in the following. A typical treatment system for leachates from a sanitary landfill is shown in Fig. 1 (2). The system employs equalization tanks, coagulation/sedimentation, pH adjustment, biological treatment consisting of anaerobic towers followed by aerobic ones, coagulation/sedimentation, and multimedia filtration; the sludge treatment unit includes a sludge thickener and a plate-and-frame filter press. The results of the system operation are presented in Table 2.

As shown in Table 2, the biological treatment unit experienced good overall removal for TOC (93%), COD (90.9%), and NH_3-N (99.1%). The biological unit operation alone did not demonstrate high removals of BOD_5 (10.2%), TSS (9.3%), or for various metals (showing in general less

Table 2. Performance Data of a Typical Leachate Treatment Plant

	Biological Unit			Entire System		
Parameter	Influent, mg/L	Effluent, mg/L	Removal, %	Influent, mg/L	Effluent, mg/L	Removal, %
BOD_5	39.2	35.2	10.2	991	35.2	96.5
Total suspended solids	11.8	10.7	9.3	532.8	10.7	98.0
NH_3-N	135	1.1	99.1	193.3	1.1	99.4
COD	1742	159.4	90.9	4028	159.4	96.0
NO_3-N	1.5	130.5	0.0	0.693	130.5	0.0
TDS	5960	5181	13.1	5012	5181	0.0
TOC	758	52.8	93.0	1316	52.8	96.0
Total phenols	0.2	0.05	72.5	1.2	0.05	95.9
Barium	0.010	0.022	0.0	2.43	0.022	99.1
Boron	3	2.9	8.9	4.33	2.9	32.5
Chromium	0.012	ND[a]	—	0.036	ND[a]	70.3
Strontium	ND[a]	0.082	0.0	2.9	0.082	97.2
Zinc	ND[a]	0.012	0.0	0.144	0.012	91.6

[a] ND = not detected.

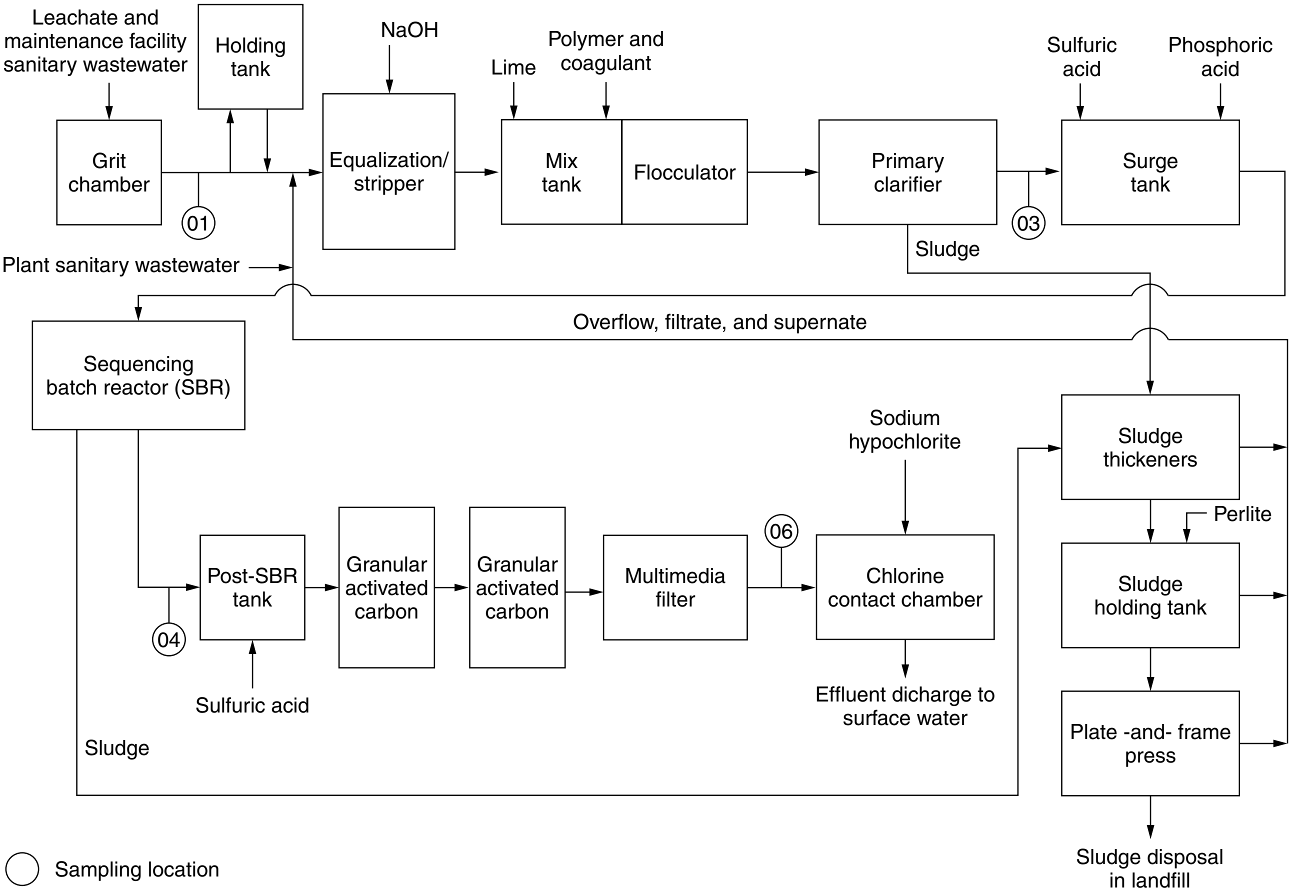

Figure 2. Flow diagram of an alternative leachate treatment plant using an SBR biological treatment unit.

than 10% removal) because the pollutants were generally not present in the biological treatment unit influent at treatable levels. The influent BOD_5 in the treatment unit was rather low (39.2 mg/L), TSS was 11.8 mg/L, and most metals were not at detectable levels, even though the raw wastewater at this facility exhibited an initial BOD_5 of 991 mg/L, TSS of 532.8 mg/L, and several metals at treatable levels.

The biological treatment unit influent had low concentrations of pollutants because this facility employed large aerated equalization tanks and a chemical precipitation system prior to biological treatment. The equalization tanks had a retention time of approximately 15 days and were followed by a chemical precipitation system using sodium hydroxide. Due to the long retention time and the aeration of wastewater, significant biological activity also occurred in these tanks. The resulting insoluble pollutants were removed in the primary clarifier prior to entering the biological towers. The entire treatment system showed good removals for BOD_5, TSS, NH_3-N, COD, TOC, and total phenols. Most metals had good percentage removals or were removed to nondetectable levels.

Another leachate treatment plant was evaluated by the EPA, including ammonia removal, hydroxide precipitation, biological treatment using a sequencing batch reactor, granular activated carbon adsorption, and multimedia filtration. A flow diagram of the landfill wastewater treatment system is presented in Fig. 2 (2). The wastewater treatment process used at this (nonhazardous) facility was primarily treated landfill generated wastewater and a small amount of sanitary wastewater flow from the on-site maintenance facility. A summary of percentage removal data collected for the biological treatment unit operation (SBR) and for the entire treatment system is presented in Table 3.

As shown in this table, the SBR treatment unit showed moderate overall removals for TOC (43.45%), COD (24.7%), and BOD_5 (48.7%). Improved removal efficiencies were observed for TSS (82.9%), total phenols (74.2%), and NH_3-N (80.7%). Metals, such as barium, chromium, and zinc had low removal efficiencies. However, these metals in the influent of the biological treatment system were measured at low concentrations, often close to the detection limit. Other metals also had poor removal efficiencies, including boron and silicon. The entire treatment system showed good removals for BOD_5, TSS, NH_3-N, COD, TOC, and total phenols. Each of the metal parameters also experienced good removal rates through the treatment system.

An alternative system for treating leachates from a nonhazardous facility was also constructed; it employed a two-stage reverse osmosis system and a multimedia filter. The flow diagram of this unit is shown in Fig. 3, and the corresponding performance data are given in Table 4.

Table 3. The Performance Data of an Alternative Leachate Treatment System that Employed an SBR Biological Treatment Unit

	Biological Unit			Entire System		
Parameter	Influent, mg/L	Effluent, mg/L	Removal, %	Influent, mg/L	Effluent, mg/L	Removal, %
BOD_5	232.6	119.3	48.7	1088	201	81.5
TSS	59.6	10.2	82.9	93.4	ND[a]	95.7
NH_3-N	134.8	26.04	80.7	295.9	12.06	95.9
COD	635.0	478.2	24.7	2932	251	91.4
NO_3-N	14.4	87.8	0.0	0.494	87	0.0
TDS	4024	3987	0.9	6232	3834	38.5
TOC	212.6	120.4	43.4	1098	82	92.5
Total Phenols	0.2	0.052	74.2	0.940	ND[a]	94.7
Barium	0.019	0.032	0.0	0.283	0.0426	85.0
Boron	2.842	2.483	12.6	6.7	2.334	65.2
Chromium	0.010	0.011	0.0	0.0906	ND[a]	87.7
Strontium	0.193	0.237	0.0	1.935	0.249	87.1
Zinc	0.025	0.058	0.0	0.494	0.027	94.5

[a] ND = not detected.

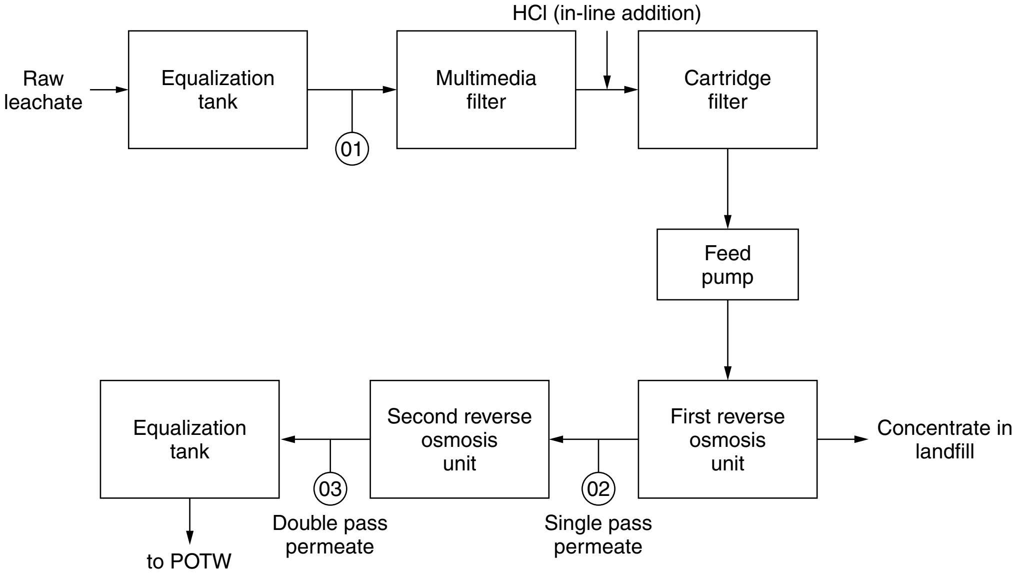

Figure 3. Flow diagram of a leachate treatment plant using a two-stage reverse osmosis unit.

As shown in Table 4, the single-pass reverse osmosis treatment system demonstrated good overall removals for a number of parameters, including TSS, TOC, BOD_5, TDS, and COD. Total phenol and NH_3-N% removals were observed at 75.1 and 76.7%, respectively. Metals with quantitative percentage removals included arsenic (87.4%), boron (54.1%), and strontium (92.9%). The additional polishing reverse osmosis unit caused the removal efficiency of most parameters to increase further. These parameters include BOD_5, NH_3-N, COD, TDS, TOC, and total phenols. The percentage removal for boron also increased from 54.1% in the single-pass reverse osmosis system up to 94.4% in the two-stage reverse osmosis treatment system.

In general, selecting the most appropriate treatment train should be based on leachate characteristics and cost estimates. For "young" leachates, which have BOD_5/COD ratios higher than 0.4, biological treatment will prevail in the overall treatment system. For the highest BOD_5/COD ratios (in the range of 0.6 to 0.8), recirculation of leachates should be included as a preliminary treatment stage, followed by anaerobic or aerobic treatment. For BOD_5/COD ratios lower than 0.4, aerobic biological treatment becomes the most important method, especially when nitrification is required; in all cases, physical–chemical treatment is necessary, as a polishing step for biologically pretreated effluents.

In some cases, physical–chemical treatment may precede aerobic treatment, aiming, for example, to reduce ammonia or metals. When the BOD_5/COD ratio is lower than 0.1, physical–chemical methods are the most appropriate, and aerobic biological treatment may be additionally used for nitrification/denitrification. During the design period, it is very important to consider the variation of

Table 4. Performance Data of a Leachate Treatment Unit, Including a Two-Stage Reverse Osmosis System

	Single-stage Reverse Osmosis[a] System			Entire Treatment System[a]		
Parameter	Influent, mg/L	Effluent, mg/L	Removal, %	Influent, mg/L	Effluent, mg/L	Removal, %
BOD_5	1182	54	95.4	1182	5.4	99.5
TSS	171.8	ND	97.7	171.8	ND	97.7
NH_3-N	58.48	13.6	76.7	58.48	0.608	99.0
COD	1526	72.2	95.3	1526	11.4	99.3
NO_3-N	1.3	0.666	48.8	1.3	0.502	61.4
TDS	2478	116.6	95.3	2478	ND	99.6
TOC	642.6	25	96.1	642.6	ND	98.4
Total phenols	1.26	0.316	75.0	1.26	0.063	95.0
Barium	0.28	0.006	98.0	0.28	0.001	99.5
Boron	1.808	0.83	54.1	1.808	0.10	94.4
Chromium	ND	ND	—	ND	ND	—
Strontium	1.406	ND	92.9	1.406	ND	92.9
Zinc	ND	ND	—	ND	ND	—

[a] ND = not detected.

leachates properties over time that requires particular attention to the treatment plant design to achieve operating flexibility to cope with varying influent characteristics.

BIBLIOGRAPHY

1. Lema, J.M., Mendez, R., and Blazquez, R. (1988). Characteristics of landfill leachates and alternatives for their treatment: A review. *Water Air Soil Pollut.* **40**: 223–250.
2. Environmental Protection Agency. (2000). Development document for final effluent limitations guidelines and standards for the landfills point source category. EPA-821-R-99-019, Washington, DC.
3. Ehrig, H.J. (1984). Treatment of sanitary landfill leachate: biological treatment. *Waste Manage. Res.* **2**: 131–152.
4. Qasim, S.R. and Chiang, W. (1994). *Sanitary Landfill Leachate: Generation, Control and Treatment*. Technomic, Lancaster, PA.
5. Forgie, D.J.L. (1988). Selection of the most appropriate leachate treatment methods. Part 1. A review of potential biological leachate treatment methods. *Water Pollut. Res. J. Can.* **20**(2): 308–328.
6. Kelly, H.G. (1987). Pilot testing for combined treatment of leachate from a domestic waste landfill site. *J. Water Pollut. Control Fed.* **59**(5): 254–261.
7. Diamadopoulos, E., Samaras, P., Dabou, X., and Sakellaropoulos, G.P. (1997). Combined treatment of landfill leachate and domestic sewage in a sequencing batch reactor. *Water Sci. Technol.* **36**(2–3): 61–68.
8. Forgie, D.J.L. (1988). Selection of the most appropriate leachate treatment methods. Part 2. A review of recirculation, irrigation and potential physical-chemical treatment methods. *Water Pollut. Res. J. Can.* **20**(2): 329–340.
9. Amokrane, A., Comel, C., and Veron, J. (1997). Landfill leachates pre-treatment by coagulation flocculation. *Water Res.* **31**(11): 2775–2782.
10. Sletten, R.S., Benjamin, M.M., Horng, J.J., and Ferguson, J.F. (1995). Physical–chemical treatment of landfill leachate for metals removal. *Water. Res.* **29**(10): 2376–2386.
11. Diamadopoulos, E. (1994). Characterization and treatment of recirculation-stabilized leachate. *Water Res.* **28**(12): 2439–2445.
12. Loizidou, M., Kapetanios, E.G., and Papadopoulos, A. (1992). Assessment of leachate characteristics and its treatability. *Fresenius Environ. Bull.* **1**: 748–753.
13. Tatsi, A., Zouboulis, A.I., Matis, K.A., and Samaras, P. (2003). Coagulation-filtration pretreatment of sanitary landfill leachates. *Chemosphere* **53**(7): 737–744.
14. Slater, C.S., Uchrin, C.G., and Ahlert, R.C. (1985). Ultrafiltration processes for the characterization and separation of landfill leachates. *J. Environ. Sci. Health A* **20**(1): 97–111.
15. Wenzel, A., Gahr, A., and Niessner, R. (1999). TOC removal and degradation of pollutants in leachate using a thin-film photoreactor. *Water Res.* **33**(4): 937–946.
16. Marttinen, S.K. et al. (2002). Screening of physical–chemical methods for the removal of organic material, nitrogen and toxicity from low strength landfill leachates. *Chemosphere* **46**: 851–858.
17. Beaman, M.S., Lambert, S.D., Graham, N.J.D., and Anderson, R. (1998). Role of ozone and recirculation in the stabilization of landfills and leachates. *Ozone Sci. Eng.* **20**: 121–132.
18. Cheung, K.C., Chu, L.M., and Wong, M.H. (1997). Ammonia stripping as a pretreatment for landfill leachate. *Water Air Soil Pollut.* **94**: 209–221.
19. Peters, T. (1999). Past and future of membrane filtration for the purification of landfill leachate. *Proc. 7th Int. Waste Manage. Landfill Symp.*, Cagliari, Italy, pp. 335–344.
20. Trebouet, D. et al. (1999). Effect of operating conditions on the nanofiltration of landfill leachates: Pilot scale studies. *Environ. Technol.* **20**: 587–596.
21. Morris, J.W.F., Vasuki, N.C., Baker, J.A., and Pendleton, C.H. (2003). Findings from long-term monitoring studies at MSW landfill facilities with leachate recirculation. *Waste Manage.* **23**(7): 653–666.
22. Forgie, D.J.L. (1988). Selection of the most appropriate leachate treatment methods. Part 3. A decision model for the treatment train selection. *Water Pollut. Res. J. Can.* **20**(2): 341–355.

MACROPHYTES AS BIOMONITORS OF POLYCHLORINATED BIPHENYLS

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INTRODUCTION

The freshwater, estuarine, and marine ecosystems around the world are now being increasingly subjected to greater stress from various human activities. As a result of several contaminants, significant changes in freshwater and marine plant communities have occurred (1).

Polychlorinated biphenyls (PCBs) are one of the more ubiquitous and toxic organic pollutants. Altogether, some 209 different individual PCB compounds exist, although only about 130 of these are found in commercial mixtures. PCBs have a number of physical and chemical characteristics that have contributed to their persistence in the environment, such as low aqueous solubility, resistance to oxidation and hydrolysis, and high volatility (2). The use of PCBs is now restricted to nondispersive systems (e.g., as dielectric fluids in condensers and transformers), but until few years ago, they were important constituents of a number of industrial chemical formulations, including paints, inks, plastics, pesticides, and copying papers.

In most industrialized countries, the use of PCBs has been banned since the late 1970s, resulting in a decline in PCB releases in the environment. However, in several aquatic ecosystems, the biota contamination remained relatively stable since the mid-1980s (3–5).

The concern about the presence and effects of PCBs on the biota and, ultimately, on human health, have mobilized worldwide research in order to find remediating PCB levels in the environment and therefore prevent possible future undesirable consequences. Toxic effects in animals include reproductive impairment, mutagenesis, carcinogenesis, and teratogenesis (6). Recently, several studies have demonstrated the ability of PCBs to induce oxidative stress (a cellular situation characterized by an elevation in the steady-state concentration of reactive oxygen species) (7) in fishes, birds, reptiles (8), and dinoflagellates (9); but in plants, a lack of studies about this subject exist. PCBs are very hydrophobic contaminants and preferentially adsorb onto sediment particles. Particle size distribution and organic carbon content seem to be important factors in determining the extent of partitioning of PCBs to natural sediment (10). In particular, the high octanol/water partition coefficient (Kow) indicates that PCBs have a high affinity for suspended solids, especially those rich in organic carbon. Mobilization of PCBs from sediments is one of the causes of the persistence of these contaminants (11,12), because sediments were, in the past, the most important sink of these pollutants.

THE ROLE OF MACROPHYTES IN THE AQUATIC ECOSYSTEM

Macrophytes include various emergent, submergent, and floating leaved species. Together with algae, periphyton, and phytoplankton, macrophytes form the base of most aquatic food chains. Macrophytes are important in nutrient cycling and respond rapidly to water quality changes. It is well known that aquatic vascular plants can enhance a freshwater ecosystem in many ways, such as by improving water clarity, contributing oxygen via photosynthesis, and providing spawning sites and protection for fish, mollusks, crustaceans, and other invertebrate species (13,14).

Plants interact with their environment through processes that include contaminant bioconcentration and excretion, shading, and organic matter production and decomposition. As a result of these interactions, aquatic plants may significantly affect water and sediment quality (15).

As plants are the base of most food chains, they will experience the effects of toxic compounds released into the aquatic media sooner than will organisms occupying higher trophic levels. In this respect, plants may be able to act as an “early warning signal” of impending contaminant impacts on other trophic levels of aquatic environments.

Contaminants present in aquatic macrophytes may be transferred to higher levels of the food chain, when consumed as live plants by herbivores or as detritus by detritivores (16,17).

Aquatic macrophytes in the littoral zones of lakes have two fundamental properties, which make them attractive as limnological indicators. First, they react slowly and progressively to changes in nutrient conditions, in contrast to bacteria and microalgae, i.e., over several years. Macrophytes, therefore, function as integrators of environmental conditions to which they are subjected, and thus can be used as long-term indicators with high spatial resolution. Second, the littoral zone may experience patterns of nutrients and pollutant concentrations (18,19), caused by natural or artificial inflows as well as by diffuse and nonpoint sources. The latter are difficult to localize and quantify, but even chemical analysis of point sources is often neglected in limnological routine work (20).

Vascular plants like bulrushes (*Schoenoplectus* spp.), duckweeds (*Lemna* spp.), and pickerel weed (*Pontederia* spp.) are the more common species used in North American wetlands treatment systems to improve water quality in a variety of ways, including binding soil and reducing the resuspension of muds (15). Bioaccumulation by plants can remove substantial quantities of potential toxicants (like organochlorines) and nutrients of water entering and passing through wetlands. Thus, Menone et al. (21) calculated that about 75 μg of Heptachlor-epoxide per square meter of cordgrass marsh exists, or over the 32 km^2 of cordgrass marsh, roots of *Spartina* densiflora concentrates 2 Kg of this contaminant. Total PCBs in the same estuary can be estimated as 22 μg per square meter or 0.7 Kg over the 32 km^2 of cordgrass marsh.

EXPOSURE AND UPTAKE OF MACROPHYTES TO CONTAMINANTS

The uptake of contaminants depends on the physicochemical characteristics of the compounds and on the life form of the macrophyte (floating-leaved, free-floating, well-rooted, or rootless species). Free-floating plants, such as *Lemna spp., Eichornia spp.*, and *Pistia spp.*, take up contaminants from the water by roots and/or leaves. Likewise, the rootless *Ceratophyllum spp.* takes up contaminants mainly through its finely divided leaves. The situation of species with a well-developed root-rhizome system and totally submersed foliage, such as *Myriophyllum spp., Potamogeton spp.*, and *Vallisneria spp.* species, is much more complex. Thus, these submersed aquatic macrophytes grow at the interface of two distinct environments, being their leaves exposed to the water column while their roots are in contact to the sediment. Both media (the water column and the sediment pore water) are potential sources of uptake of contamination (22,23). Indeed, the rooted aquatic macrophyte *Hydrilla verticillata*—common throughout the southern United States—has been shown to take up contaminants from both the sediment pore water and the overlying water column. It also has the ability to translocate sediment-incorporated contaminants from the roots into the vegetative portion of the plant (24).

Other species, such as *Schoenoplectus californicus, Spartina densiflora* (mainly from the Southern Hemisphere), and *Spartina alterniflora* (mainly from the Northern Hemisphere), have the root-rhizome system well developed, but have not totally submersed foliage. The first two macrophytes form the bulk of the emergent vegetation in many of the shallow lakes and estuarine areas of the Southern America regions. The pollutant sequestration in these macrophytes occur across many interfaces, sediment, water, and air (21,25,26).

Several environmental factors, including water and sediment pH, water current, sediment texture, organic carbon, and mineral composition, are known to influence contaminant adsorption by sediments and macrophytes growth, so they may contribute to overall site quality.

BIOMONITORING

During the past, direct chemical measurement of the concentrations of toxic and hazard substances have been carried out for the evaluation of water quality in contaminated natural environments. However, for environmental management, contaminant concentrations do not necessarily account for, or enable prediction of, the impairment of biota. If the objective is to monitor and improve environmental quality of the ecosystems, biotic measurements of contamination are more useful than only measures of water or sediment contaminant concentrations. Furthermore, the cost of evaluation and measurement of persistent and toxic organochlorines, such as PCBs, is substantial. Therefore, for ecologic and economic reasons, it is important to develop biological monitoring that is useful and valuable. The use of biomonitoring to assess and control discharges of toxic chemicals into the environment has been promoted as being a desirable alternative to more expensive, less realistic, and time-consuming chemical analysis (27). Thus, the presence of indicator organisms (biomonitors) provides a measure of cumulative exposure to contaminants over time and avoids the need for frequent sampling. The use of biomonitors *in situ* to identify and quantify toxicants in an environment is referred to as biomonitoring (28). This technique takes advantage of the ability of organisms to accumulate contaminants in their tissues through bioaccumulation and bioconcentration. The primary objective of biomonitoring investigations is to assess the quality of water in an area by relating observed responses of organisms that live within a suspected polluted site to the concentrations of contaminants detected within their tissues. An additional and very significant advantage of biomonitoring is that the bioaccumulated sublethal levels of contaminants within the tissues of organisms indicate the net amount of contaminants that have been integrated over a period of time (27).

The response of biota to pollution stress can be observed at the ecosystem, community, population, individual, and suborganismal levels of organization (29). Environmental assessments may be made by establishing quantitative relationships between (a) concentrations of pollutants that are accumulated within the tissues of organisms residing within a particular area and (b) manifest biological effects (30).

In general, three historical stages exist in the biomonitoring with plants, based on the use of different parameters:

1. various physiological, morphological, and community parameters (pigment content, photosynthetic activity, diversity indices, biomass, etc.)
2. environmental concentrations of pollutants in plant tissues
3. early warning systems or biomarkers for assessing contaminant exposure and effects (histological, biochemical, or genetic)

The presence of certain toxicants may induce a physiological response in an organism, often involving a heightened production of enzymes that are capable of metabolizing and/or degrading the toxicant in question. In this way, the quantity and activity of such xenobiotic-metabolizing enzymes may be used as indicators of the bioavailability of a specific contaminant in the environment. An increasing number of studies have used biochemical as well as physiological endpoints for assessing toxic effects on plants. These effects are often more sensitive, but their environmental relevance and their relationship to the impact of toxic chemicals on biomass are not known. However, they can be combined with other parameters of chemical exposure to predict the ecological consequences of chemical-specific contamination (31). For a biomarker to be applied in the field, it should be correlated with a significant effect, such as survival, growth, or reproduction. Although many biomarkers have been validated for use in evaluating animal health and exposure to toxic substances, both in the laboratory and in natural ecosystems, very few biomarkers have been validated and used to assess plant exposure and health effects under field conditions (31). Padinha et al. (32) has shown that variations in some indices of physiological stress, like thiolic protein concentrations in *Spartina maritima*, could be used as a tool to monitor contamination by heavy metals. On the other hand, Wall et al. (33) have found no adverse influences of PCBs in terms of peroxidase activity (POD), glutathione concentration (tGSH), photosynthesis, and transpiration on *S. alterniflora* from a Superfund site contaminated with $46.0 \pm 52.7\ \mu g\, g^{-1}$ dry weight in sediments. Therefore, the utility of POD as well as other detoxication enzymes as biomarkers of PCB stress deserves attention but needs further study.

In addition, laboratory research can complement and contribute to the best understanding of data from field studies (biomonitoring). Among laboratory experiments, we can mention:

— *Toxicity tests*: Toxicity tests involve exposing a well-defined test organism to a dilution series of a suspected toxicant under controlled laboratory conditions. The goal of toxicity tests is to correlate the level of toxicants to observed organismal responses. Of the multitude of organismal responses that could be observed as endpoints in toxicity test, the one most frequently used is survivorship. In ecotoxicology, survivorship is usually expressed as LD_{50}, which is the dosage of the suspected toxicant that is seen to cause mortality in half of the individuals tested within a specified time period.

— *Bioassays*: Bioassays are often used to assess the toxic effects of mixtures of compounds on biota by exposing test organisms to naturally contaminated water or sediment samples.

When a pollutant enters an aquatic environment, it is expected that its initial effect on an exposed organism will be a suborganismal one—either biochemical or genetic. In this manner, biochemical and genetic indicators may be able to detect the presence of minimum contaminant concentrations compared with the levels of toxicants required to elicit a response at the level of the entire organism (e.g., death) (28).

MACROPHYTES AS BIOMONITORS

Plant biomonitors provide an integrated description of pollution within an ecosystem (34). Freshwater species were used as sentinels of contaminant stress for many years, such as in the biomonitoring study of Wang and Williams (35), who used *Lemna minor* to examine the phytotoxicity of industrial effluents. Macrophytes have also proved to be useful for assessing organochlorine contamination in laboratory experiments (36,37) and in the field (27,28). The organochlorine bioaccumulation in submersed macrophytes may be very high; macrophytes may be three to four times more contaminated than sediment, and 6000 to 9000 times more contaminated than the water (38).

Under field conditions, *Schoenoplectus californicus* has already shown potential as a biomonitor of organochlorine pesticides. Moreover, this species has demonstrated the ability to function as phytoremediator—plant use for the remediation of contaminated environments—of these pesticides, because, in combination with other aquatic biota, about 40% of the more hydrophobic pesticides have been retained in the lake environment, leading to their lower release through the effluent creek (25,26,39). *Spartina densiflora* grows abundantly and contributes significantly to the primary productivity of the estuarine ecosystems on the Southern America coast. In Mar Chiquita coastal lagoon (Argentina), it can bioaccumulate both organochlorine pesticides and PCBs, and the total amount of these compounds in cordgrass biomass may represent a significant proportion of the total PCBs burden in the estuary system (21). The same species is the dominant plant in Humboldt Bay salt marshes. *S. densiflora*'s ability to rapidly expand in bare areas has implications for marsh mitigation and restoration activities (40).

Other known macrophytes, like *Vallisneria americana*, var. americana—one of the most abundant macrophyte in the Great Lakes (41,42)—*Potamogeton spp., Najas spp., Myriophyllum spp.*, and *Elodea spp.*, accumulate contaminants within its tissues and have also shown potential as biomonitors of organic contaminants in the field (27,28).

MACROPHYTES AND PCBS

Laboratory studies indicate that uptake of PCBs from contaminant water or sediments in aquatic macrophytes is expected (43). In addition, considering their limited mobility and their abundance in many aquatic systems, they could function as *in situ* biomonitors of water contaminants, like PCBs. However, the extent of sequestration in natural populations remains almost unknown. Thus, little impetus has developed for studying the role of submersed aquatic macrophytes in PCBs biogeochemical cycling in freshwater ecosystem, as evidenced by our literature survey, which revealed a lack of field data documenting the incidence of hydrophobic organic contaminants in feral aquatic macrophytes.

Exposure to sediment-borne PCBs is particularly important for rooted macrophytes. As a result of the hydrophobicity of these compounds, sediments frequently contain higher concentrations of contaminants than the surrounding water (44,45). Thus, plants grown in contaminated environments typically have higher concentrations of hydrophofobic pollutants in below-ground tissues than in foliage and, because their mobility within the plant tissues is very limited (23), they tend to accumulate in roots (28). Macrophytes collected from different sites may contain different concentrations of contaminants within their tissues, reflecting sediments, water, and air loads at each location (26,28). In a shallow lake from Argentina, it has been demonstrated that *S. californicus* accumulate PCBs in direct relationship to the sediment PCB concentrations. Moreover, the higher PCB levels were found in root tissues revealing the high ability of this macrophyte to function as PCB biomonitor (Miglioranza, personal communication).

The Bioaccumulation Factor (BF) is the ratio of the concentration in the biota and the concentration in the soil/sediment. It primarily depends on the properties of the soil/sediment and the biota, particularly the ratio of lipid in the biota and the organic carbon content of the soil/sediment (2). Root Bioaccumulation Factors (RBF) have been calculated for *Schoenoplectus californicus* and *Spartina densiflora* from Los Padres lake and Mar Chiquita coastal lagoon, respectively. The values in *S. californicus* ranged between 49 and 600 for different congeners of PCBs, being the highest RBF for the lower chlorinated congeners. In *S. densiflora*, the RBF ranged between 0.75 and 26.5. These results show the magnitude of bioaccumulation of PCBs in freshwater and estuarine macrophytes species and their importance in the ecology of these environments.

The investigations of Butler et al. (46) demonstrated for the first time that plant cells are capable of hydroxylating and glycosylating a chlorinated biphenyl in a manner similar to what has been reported for animals (47). The metabolism of PCBs varies between the plant species and is affected by the substitution pattern and the degree of chlorination (48,49). Wilken et al. (49) analyzed 12 different terrestrial plant species and showed that lower chlorination grade is associated with higher metabolism rates. Recent studies (50,51) have shown the important role of plant cytochrome P450 in metabolism of different toxicants, but have admitted involvement of peroxidases too (52,53).

Despite the scarce information about PCB concentrations in macrophytes under field conditions, we can conclude that macrophytes can play a crucial role in the biomonitoring and remotion of these toxic organic compounds from the environment, not only accumulating but also transforming them. For this reason, phytoremediation has been proposed as an alternative or complementary technique to treat sediment polluted by PCBs, but still needs much basic research.

BIBLIOGRAPHY

1. Orth, R.J. (1994). *Lake Reservoir Manage.* **10**: 49–52.
2. Connell, D.W. (1997). Lewis Publishers, New York, p. 505.
3. Borgmann, U. and Whittle, D.M. (1992). *J. Great Lakes Res.* **18**: 298–308.
4. Picer, M. and Picer, N. (1995). *Water Res.* **29**: 2707–2719.
5. Stow, C.A., Carpenter, S.R., Eby, L.A., Amrhein, J.F., and Hesselberg, R.J. (1995). *Ecol. Appl.* **5**: 248–260.
6. Rand, G.M. (1995). Ecological Services Inc., North Palm Beach, FL, p. 1125.
7. Scandalio, J.G. (1990). *Advances in Genetics* **28**: 1–12.
8. Cheung, C.C.C., Zheng, G.J., Lam, P.K.S., and Richardson, B.J. (2002). *Marine Pollution Bull.* **45**: 181–191.
9. Leitao, Ma da S., Cardozo, K.H.M., Pinto, E., and Colepicolo, P. (2003). *Arch. Environ. Contam. Toxicol.* **45**: 59–65.
10. Reid, B.J., Jones, K.C., and Cemple, K.T. (2000). *Environmental Pollution* **198**: 103.
11. Mac Donalds, C.R., Metcalfe, C.D., Balch, G.C., and Metcalfe, T.L. (1993). *Environ. Toxicol. Chem.* **12**: 195–224.
12. Larsson, P., Lennart, O., and Cronberg, G. (1998). *Can. J. Fish. Aquat. Sci.* **55**: 1926–1937.
13. Kilgore, K.J., Morgan, R.P., II, and Rybicki, N.B. (1989). *Nat. Amer. J. Fish. Manag.* **9**: 101–111.
14. Posey, M.H., Wigand, C., and Stevenson, J.C. (1993). *Estuarine Coast. Shelf Sci.* **37**: 539–555.
15. Lewis, M.A. and Wang, W. (1997). In: W. Wang, J.W. Gorsuch, and J.S. Hughes (Eds.). Lewis Publishers, New York, pp. 141–175.
16. Lodge, D.M. (1991). *Aquat. Bot.* **41**: 195–224.
17. Wetzel, R. (1995). *Freshwater Biol.* **33**: 83–89.
18. Dave, G. (1992). *Water, Air Soil Pollut.* **63**: 187–200.
19. Drake, J.C. and Heaney, S.I. (1987). *Freshwater Biol.* **17**: 513–523.
20. Melzer, A. (1999). *Hydrobiologia*. **395/396**: 181–190.
21. Menone, M.L. et al. (2000). *Estuaries*. **23**: 583–592.
22. Barko, J.W., Gunnison, D., and Carpenter, S.R. (1991). *Aquat. Bot.* **41**: 41–65.
23. Guilizzoni, P. (1991). *Aquat. Bot.* **41**: 87–109.
24. Byl, T.D., Sutton, H.D., and Klaine, S.J. (1994). *Environ. Toxicol. Chem.* **13**: 509–515.
25. Miglioranza, K.S.B. et al. (2002). *Environ. Sci. Pollut. Res.* **9**: 250–256.
26. Miglioranza, K.S.B., de Moreno, J.E.A., and Moreno, V.J. (2004). *Water Res.* **38**: 1765–1772.
27. Lovett-Doust, L., Lovett-Doust, J., and Biernacki, M. (1994). *J. Great Lakes Res.* **20**: 333–354.
28. Lovett-Doust, J., Schmidt, M., and Lovett-Doust, L. (1994). *Biologic. Rev.* **69**: 147–186.
29. Cairns, J. and Niederlehner, B.R. (1992). *J. Environ. Sci.* **4**: 1–9.
30. Sandhu, S.S. and Lower, W.L. (1992). In: S.S. Sandhu, D.M. DeMarini, M.J. Mass, M.M. More, and J.L. Munford (Eds.). Plenum Press, New York, pp. 145–160.
31. Lytle, J.S. and Lytle, T.F. (2001). *Environ. Toxicol. Chem.* **20**: 68–83.
32. Padinha, C., Santos, R., and Brown, M.T. (2000). *Marine Environ. Res.* **49**: 67–78.
33. Wall, V.D. et al. (2001). *Arch. Environ. Contam. Toxicol.* **40**: 10–17.
34. Dennison, W.C. et al. (1988). *Biosciences* **43**: 86–94.
35. Wang, W. and Williams, J.M. (1988). *Environ. Toxicol. Chem.* **7**: 645–652.
36. Biernacki, M., Lovett-Doust, J., and Lovett-Doust, L. (1995). *J. Appl. Ecol.* **32**: 761–777.
37. Biernacki, M., Lovett-Doust, J., and Lovett-Doust, L. (1995). In: *Ecovision Worls Monograph Series*. M. Munawar, T. Edsall, and J. Leach (Eds.). S.P.B. Academic Publishing, The Netherlands, pp. 413–426.

38. Painter, S. (1990). In: *Proc. Aquat. Ecosystem Health Sympos*. Waterloo, Ontario.
39. González Sagrario, M.A., Aizpún de Moreno, J.E., Moreno, V.J., and Escalante, A.H. (1998). *Environ. Sci.* **6**: 153–169.
40. Kittelson, P.M. and Boyd, M.J. (1997). *Estuaries* **20**: 770–778.
41. Schloesser, D.W., Edsall, T.A., and Manny, B.A. (1985). *Can. J. Bot.* **63**: 1061–1065.
42. Catling, P.M., Spicer, K.W., Biernacki, M., and Lovett-Doust, J. (1994). *Can. J. Plant Sci.* **74**: 883–897.
43. Gobas, F.A.P.C., McNeil, E.J., Lovett-Doust, L., and Haffner, G.D. (1991). *Environ. Sci. Technol.* **25**: 924–929.
44. Di Toro, D. et al. (1991). *Environ. Toxicol. Chem.* **10**: 1541–1583.
45. Burton, A. (1992). In: A. Burton (Ed.). Lewis Publishers, Boca Raton, FL, Ch. 8, pp. 167–181.
46. Butler, J.M., Groeger, A.W., and Fletcher, J.S. (1992). *Bull. Environ. Contam. Toxicol.* **49**: 821–826.
47. Sandermann, H. (1982). In: *Environmental Mutagenesis, Carcinogenesis, and Plant Biology*. E.J. Klekowski (Ed.). Vol. 1, Praeger, New York, pp. 2–32.
48. Lee, I. and Fletcher, J.S. (1992). *Plant Cell Reports* **11**: 97–100.
49. Wilken, A., Bock, C., Bokern, M., and Harms, H. (1995). *Environ. Toxicol. Chem.* **14**: 2017–2022.
50. Pflugmacher, S., Geissler, K., and Steinberg, C. (1999). *Ecotoxicol. Environ. Safety* **42**: 62–66.
51. Stiborová, M., Schmeiser, H.H., and Frei, E. (2000). *Phytochemistry* **54**: 353–362.
52. Koller, G., Moder, M., and Czihal, K. (2000). *Chemosphere* **41**: 1827–1834.
53. Chromá, L., Kucerová, P., Macek, T., and Macková, M. (2002). *Book of Abstracts, The Second PCB Workshop*. I. Holoubek, and I. Holoubkova (Eds.). Masaryk University Brno, p. 153.

WASTEWATER MANAGEMENT FOR DEVELOPING COUNTRIES

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INTRODUCTION

A country is characterized as a developing one according to specific economic indicators. The World Bank has linked gross domestic product (GDP) to pollution for developing nations (1) (Fig. 1). This link breaks when incentives to protect the environment are introduced, followed by the adoption of cleaner and more efficient technologies, which can be adjusted to the case of water pollution originating from the disposal of untreated wastewater. Once increasing pollution has had negative effects on the wellbeing and economy of an area, incentives for wastewater treatment are induced. Legislation is introduced requiring polluters to pay for the treatment of wastewater at a certain level. Construction of wastewater treatment plants (WTPs) in compliance with legislation reduces pollution from wastewater and has a positive effect on a quality index based on a combination of treated effluent qualitative parameters.

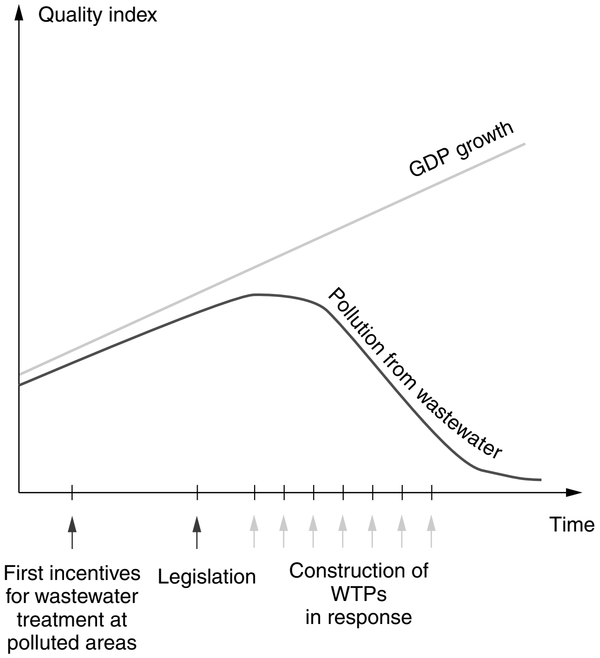

Figure 1. Breaking the link between economic growth and pollution from wastewater (1).

Wastewater management involves collection treatment and disposal/reuse. Potable water supply is inevitably related to them, hence some principles discussed below will include or directly apply to such issues. Ujang and Buckley (2) summarize sanitation problems for developing countries as lack of environmental awareness, insufficient expertise, inappropriate policies, insufficient funding, insufficient water resources, inappropriate management systems, and institutional support.

Following this introduction, the application of existing technologies to developing countries (DC) is discussed, focusing on technology and knowledge transfer and the role of international experts. Some differences over wastewater production and its quality are stressed with special reference to the high standards often set by decision makers in DC. Finally, issues on sustainable technology selection and key points referring to methodologies and indexes are discussed.

APPLICATION OF EXISTING TECHNOLOGIES TO DEVELOPING COUNTRIES

Wastewater management must be considered as an integral part of the development process and national plans should be formulated (3). Conditions applicable when planning wastewater treatment facilities for DC are not identical to those prevalent during planning in developed countries in the past. Although some similarities exist, many differences also exist. One reason is that water pollution issues are not the main concern in DC because of other more pressing issues such as national or racial security, food availability, and epidemic control (2).

Technology Transfer

Today, technology is available for the treatment of wastewaters of any origin and strength. DC cannot be expected to play a key role in the development of cutting edge technology in wastewater management or water research. However, research is needed in order for available technology to be applied to specific country-region conditions. This kind of research is an investment for those countries concerned. The existing transfer of technology should be done wisely because today, developed countries are regarded as an area of investment for water companies. For example, the design approach in rural Egypt was to select well-established technologies; little stress was placed on selecting more innovative technologies. However, less sophisticated treatment technologies, such as stabilization ponds, have proven capable of meeting the required effluent standards (4). A similar situation was reported in Greece. From the 147 small (<10,000 p.e.) WTPs, 80% were activated sludge systems, resulting in one out of three being out of operation. If some natural treatment technologies had been properly installed instead of activated sludge systems, failures would have been less frequent (5).

An approach by UNIDO (6), for the acquisition of foreign technology in DC, recommends the following steps:

a. It should be determined that the technology has been commercially proven yet is not obsolete;
b. Alternative technologies that may be available should be evaluated comparatively covering the following points: cost of obtaining such technologies, principal inputs required and their local availability, and estimation of manufacturing costs and profitability.
c. When a country cannot use a certain technology because of foreign exchange limitations or other constraints, a comparative evaluation should still be made, as in (b) above, for purposes of negotiation.

In most cases, when a project is to be evaluated for a DC, shadow pricing should be undertaken to adjust market prices to reflect opportunity costs. A conversion factor, i.e., shadow rate, should be calculated, which then needs to be multiplied with the market prices for unskilled labor wage, the foreign exchange rate, the opportunity cost of capital, and the shadow price of land, water, and other direct inputs (7).

In DC, institutional barriers often exist for hampering the effective application of projects. In many countries, emphasis has been given to increasing the coverage of service facilities to all parts of the population. However, the absence of institutional safeguards, at both the community and government levels, to ensure that these service facilities can be operated and maintained in a sustainable way has caused the facilities to deteriorate, creating an unacceptable financial burden on governments using traditional supply-driven projects (8).

Knowledge Transfer

Knowledge is less available in DC than in developed countries. At the same time, contemporary means of communication have made knowledge more accessible. The World Wide Web, international organizations, networks of excellence, and textbooks all play a positive role in its availability. Textbooks and other sources of knowledge are invaluable tools for design engineers but should always be used wisely. Not all information is applicable to all areas without screening. In fact, if necessary adjustments to local conditions are not made, projects may face serious problems (9).

International Experts and Advisors

Very commonly, advice is sought from international experts/advisors who are asked to give assistance on a specific project. Such assistance is useful when it applies to the technology itself, but to make any wastewater project or plan work, the adaptation should incorporate local conditions. Local experts should therefore always be involved. International experts or advisors can also be employed for solving specific operational problems. The selection of international experts/advisors should be done carefully. Reid (3) pinpoints nine cases of problems associated with advisors. He discusses how some may act like promoters of specific projects to a government resulting in low returns or even losses. In addition, too many advisors on the same project can cause confusion. When advisors are given a difficult task but not given all the information they need to solve a problem, no solution may be found. Although donor countries may offer financial and technical assistance for projects, this can be a misallocation of funds if they do not also take the recipient country's more immediate needs into account.

WASTEWATER QUALITY AND QUANTITY FOR DEVELOPING COUNTRIES

Wastewater Production and its Quality

Historical data on the flow rate is necessary for design purposes, therefore daily, seasonal, and annual variations should be acquired where possible. Reid (3) supports urging each country to establish their own resources agency with responsibility to collect pertinent data and to plan with a regional approach rather than a case-by-case approach.

Where this is not possible, accurate estimations should be taken according to local conditions and information. Crites and Tchobanoglous (10) proposed a domestic base flow rate of 245–300 L/inh.·d. These values apply mostly to developed countries. Uncritical adoption of the above values or other values may lead to overdesigning of the installation. The size of the community served, its socioeconomic conditions, and other parameters may influence the per inhabitant flow rate. Pujol and Lienard (11) proposed 150 (±50) L/inh.·d for rural areas of less than 5,000 population equivalent (p.e.). Campos and Von Sperling (12) developed a model for wastewater production in Brazil that showed significant variation according to the income of the people served (74–210 L/inh.·d). For Greek urban and rural communities, these values are on average 165 L/inh.·d and 100–120 L/inh.·d, respectively, and for Turkish cities 170 L/inh.·d (13,14). Wastewater production may also vary with time and conditions in the same area. Shaheen (15) reports that, in the West Bank, the water consumption was 58 l/inh.· d in 1991, but under a specific scenario, this will rise to 122 l/inh.·d by 2010.

Usually, wastewater in DC is characterized by having high concentrations of basic pollutants. A study in Jordan showed that the average values for 5 WTP in terms of BOD_5, COD, and TSS, were 616–1419 mg/L, 1159–3707 mg/L, and 458–1647 mg/L, respectively (16). In contrast, average BOD_5/COD/SS concentrations were 187/477/236 mg/L, 268/634/302 mg/L, 171/450/237 mg/L, and 267/581/426 mg/L for Belgium-Flanders, France, Netherlands, and Slovenia, respectively (17). One of the major problems in DC is the illegal discharge of industrial effluents into public sewers, unauthorized connections, and unregistered population (18).

Effluent Quality and Standards

Low levels for effluent requirements and standards are frequently introduced in DC, but these levels are, in reality, rarely met. No means exists of imposing any kind of effluent requirements or of adopting the most advanced technology of wastewater treatment, when no mechanism exists to safeguard the maximum possible efficiency.

Many of the high standards used in the developed world have only superficial environmental justification, and the costs of implementation are often not considered by the quality regulators. The regulation and monitoring of standards carries a cost to society that is often considered or appreciated by those setting standards (19).

A list of common problems associated with setting up and implementing standards in developing countries are discussed by von Sperling and Chernicharo (20). Of those, the most important are:

- Standards are often copied by developed countries.
- Protection measures that do not lead to immediate compliance with the standards do not obtain licensing or financing.
- Developing countries attempt to reach developed countries' status too quickly.
- No institutional development exists that could support and regulate the implementation of standards, thus standards are not actually enforced.

von Sperling and Chernicharo (20) propose a sustainable approach for several situations whereby wastewater treatment systems (and effluent standards) should first implement a less efficient process, or a process that removes fewer pollutants. This entails transferring to a second stage the improvement toward a system more efficient or more wide-reaching in terms of pollutants, and so on.

CENTRALIZED AND DECENTRALIZED TREATMENT

Cities in DC, if no wastewater facilities have been established, usually manage their wastewaters in septic tanks, absorption pits, or collect the wastewater and discharge untreated effluent into the environment. To establish a new treatment plant, they need the support of the population that is to be served.

In order to gain this support, people should be informed about the environmental benefits and be willing to pay for the construction and the O&M costs of the WTP. The acceptability of such projects may decline when direct costs are applied to the population to be served (21).

The task of wastewater treatment comes after the collection of the wastewater. Onsite technologies do not have some of the barriers on efficient wastewater management in DC as management is on the owners. The number and location of the WTP is determined by taking two main directions into consideration. The first is that the centralization of the wastewater produced in a large region will give an additional cost per capita, as more meters of sewer and pumping are needed and second, the larger a plant is, the less per capita it will cost because of economies of scale. Therefore, this will give an optimum degree of centralization as shown in the theoretical case of (Fig. 2).

Centralization indicates an increasing number of houses or clusters of houses connected to a main sewerage network instead of being treated onsite. Each cluster of houses, suburb, or neighboring village has an additional cost for connecting itself to a main sewerage network. Although an economy of scale exists in treatment, this is not the case with the cost of centralization of sewers when remote areas are added to the main network. In centralized treatment, extra costs are needed for pumping stations and piping. Furthermore, during the transport of wastewater over long distances, hydrogen sulphide is produced. Extra costs are then needed for odor prevention or reduction. In addition, extra costs are necessary for maintaining the system and pumping energy (22,23). In any case, the cost of centralization should be considered on top of the cost of treatment, with an economic analysis to investigate its feasibility. In a hypothetical case study, after a number of agglomerations have been centralized, it is not worth including others, because the additional cost of connecting them would offset the economy of scale achieved by the treatment of the wastewater.

A combination of onsite and centralized treatment cannot be overruled. In rural areas with a number of

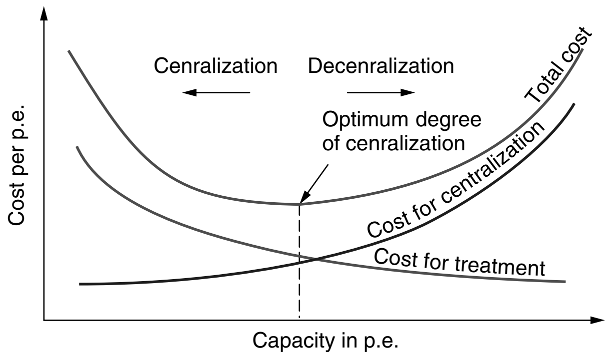

Figure 2. Effect of centralization to the total economic cost of sanitation projects.

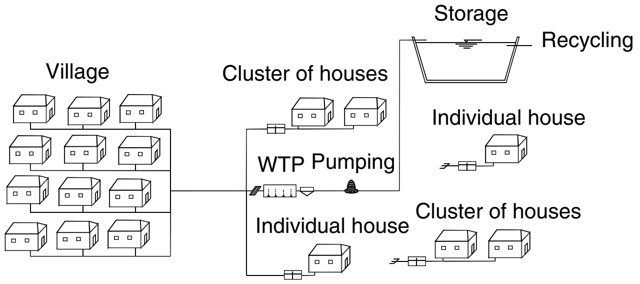

Figure 3. Combined centralized and decentralized wastewater management approaches.

villages, centralized treatment for the villages can exist together with onsite treatment for houses away from the WTP. For some other villages or cluster of houses, onsite septic tanks can be used adjacent to the villages, and then effluent can be carried to the WTP as shown in (Fig. 3).

In a study focusing on small communities of the MENA region, it is proposed that solids are removed in an interceptor tank, which is part of a household connection. Settled sewerage costs are quite low in comparison with conventional sewerage, mainly because of the shallow excavation depths, use of small diameter PVC paperwork, and simple inspection chambers (24).

TECHNOLOGY SELECTION

Sustainable Solutions

A great range of technical solutions are available today. From them are selected those that can produce such effluent quality as to protect receiving surfaces and underground water bodies, in all cases having no negative effects on the environment. These solutions must also protect public health and be acceptable to society. They should be affordable to the users and be operated effectively. The environment, society, and economy are the three aspects that must be given priority when selecting among different solutions (25,26) (Fig. 4).

Reid (3) defines as an appropriate technology for wastewater treatment the one that is acceptable to users and can be maintained by the community. No ideal solution applicable to all conditions exists, and each situation/project should be considered individually (27,28).

Society barriers and limitations may develop from social acceptance, amenity value, community participation, public awareness institutional requirements, local parameters, and stimulation of sustainable behavior (29).

The effluent destination is also a critical factor in the choice of technology for wastewater treatment. Reuse should be encouraged where possible. It is necessary to carry out careful investigations, which are based on local requirements and conditions, rather than uncritically adopting practices from abroad (30).

Methodologies/Indexes

It is possible to use indicators and methodologies to evaluate the different alternatives. These should be used as case study tools and should never lead to a universal classification of all different options. Balkema

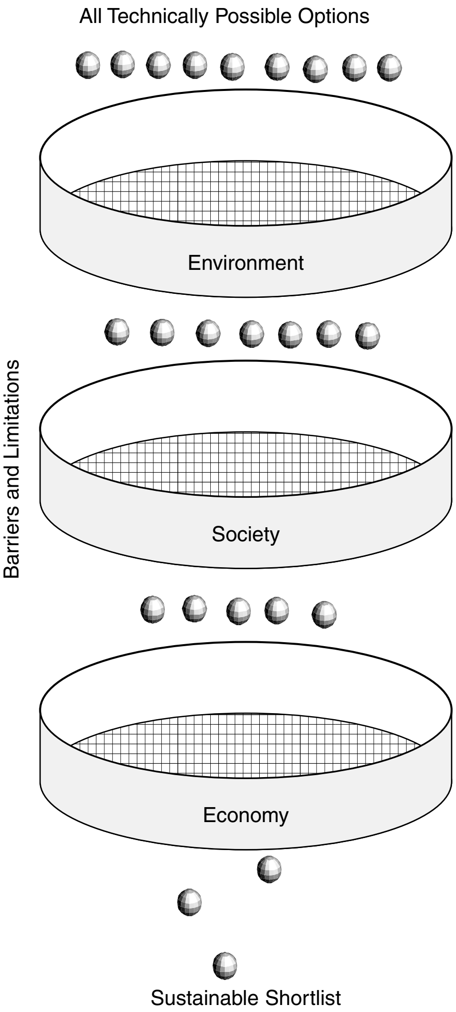

Figure 4. Sustainable short listed wastewater management solutions.

et al. (25) point out that some of the indicators are hard to quantify and ensure the integration and multidimensional character of the sustainability assessment.

Phybus and Schoeman (31) present various monitoring and performance indicators for developing areas. They conclude that the adoption and use of performance indicators at the community level should be made a stimulating experience for the players involved. It should introduce an element of competition within the initial stages and can lead from there to comparison with neighboring communities.

Schutte (32) suggests that for an organization responsible for water supply and sanitation services in developing areas, five key success factors should be applied:

- Create an organization-wide culture of service to customers.
- Ensure reliability in the water supply.
- Ensure community involvement.
- Create a culture of awareness for focusing on generation and collection of income.
- Create a culture of cost consciousness and focus on minimization of losses.

BIBLIOGRAPHY

1. World Bank. (1992). *World Development Report 1992: Development and the Environment*. Oxford University Press, Oxford, UK.
2. Ujang, Z. and Buckley, C. (2002). Water and wastewater in developing countries: present reality and strategy for the future. *Water Sci. Technol.* **46**(9): 1–9.
3. Reid, G.W. (1978). Introduction: interface for decision. In: *Appropriate Methods of Treating Water and Wastewater in Developing Countries*. G.W. Reid and K. Coffey (Eds.). Bureau of Water and Environmental Resources Research, Univ. of Oklahoma, Washington, DC.
4. Gaber, A., Antill, M., Kimball, W., and Wahab, R.A. (1993). Planning replaceable small flow wastewater treatment facilities in developing nations. *Water Sci. Technol.* **28**(10): 1–8.
5. Tsagarakis, K.P., Mara, D.D., Horan, N.J., and Angelakis, A.N. (2000). Small municipal wastewater treatment plants in Greece. *Water Sci. Technol.* **41**(1): 41–48.
6. UNIDO. (1973). *Guidelines for the Acquisition of Foreign Technology in Developing Countries*. United Nations Industrial Development Organization, Vienna, Austria, p. 43.
7. Mara, D. (1996). *Low Cost Urban Sanitation*. John Wiley, Chichester, UK, pp. 171–192.
8. Garn, H.A. (1997). *Lessons from Large-Scale Rural Water and Sanitation Projects: Transition and Innovation*. Water and Sanitation Program Working Paper. World Bank, Washington, DC.
9. Tsagarakis, K.P., Mara, D.D., Horan, N.J., and Angelakis, A.N. (2001). Institutional status and structure of wastewater quality management in Greece. *Water Policy* **3**(1): 81–99.
10. Crites, R. and Tchobanoglous, G. (1998). *Small and Decentralised Wastewater Management Systems*. WCB and McGraw-Hill, New York.
11. Pujol, R. and Lienard, A. (1990). Qualitative and quantitative characterisation of wastewater for small communities. *Water Sci. Technol.* **22**(3–4): 253–260.
12. Campos, H.M. and von Sperling, M. (1996). Estimation of domestic wastewater characteristics in a developing country based on socio-economic variables. *Water Sci. Technol.* **34**(3–4): 71–77.
13. Tsagarakis, K.P., Mara, D.D., and Angelakis, A.N. (2001). Wastewater treatment in Greece: experience and lessons for developing countries. *Water Sci. Technol.* **44**(6): 163–172.
14. Karagözoglu, B., Altin, A., and Degirmenci, M. (2003). Flowrate and pollution characteristics of domestic wastewater. *Int. J. Environ. Pollut.* **19**(3): 259–270.
15. Shaheen, H.Q. (2003). Wastewater reuse as means to optimize the use of water resources in the West Bank. *Water Int.* **28**(2): 201–208.
16. Jamrah, A.I. (1999). Assessment of characteristics and biological treatment technologies of Jordanian wastewater. *Bioprocess Engineering* **21**: 331–340.
17. Pons, M.N., Spanjers, H., Baetens, D., Nowak, O., Gillot, S., Nouwen, J., and Schuttinga, N. (2004). *Wastewater Characteristics in Europe - A Survey*. European Water Management Online, Official Publication of the European Water Association (EWA), Brussels, Belgium.
18. Karn, S.K. and Harada, H. (2001). Surface water pollution in three urban territories of Nepal, India, and Bangladesh. *Environ. Manag.* **28**(4): 483–496.
19. Johnstone, D.W.M. and Horan, N.J. (1994). Standards, costs and benefits: an international perspective. *J. IWEM.* **8**: 450–458.
20. von Sperling, M. and Chernicharo, C.A.L. (2002). Urban wastewater treatment technologies and the implementation of discharge standards in developing countries. *Urban Water*. **4**: 105–114.
21. Roomratanapum, W. (2001). Introducing centralised wastewater treatment in Bangkok: a study of factors determining its acceptability. *Habitat Int.* **25**: 359–371.
22. Townley, G. (1978). Cost effectiveness of the socio-cultural and health benefits of sewerless alternatives for domestic waste disposal in developing countries. In: *Appropriate Methods of Treating Water and Wastewater in Developing Countries*. G.W. Reid and K. Coffey (Eds.). Bureau of Water and Environmental Resources Research, Univ. of Oklahoma, Washington, DC, pp. 521–619.
23. Leeuw, E.J. and Van't, E. (1996). Oever, process selection, design and operation of the EDE WWTP. *Water Sci. Technol.* **33**(12): 57–63.
24. Bakir, H.A. (2001). Sustainable wastewater management for small communities in the Middle East and North Africa. *J. Environ. Manag.* **61**: 319–328.
25. Balkema, A.J., Preisig, H.A., Otterpohl, R., and Lambert, F.J.D. (2002). Indicators for the sustainability assessment of wastewater treatment systems. *Urban Water*. **4**: 153–161.
26. Bradley, B.R., Daigger, G.T., Rubin, R., and Tchobanoglous, G. (2002). Evaluation of onsite wastewater treatment technologies using sustainable development criteria. *Clean Techn. Environ. Policy* **4**: 87–99.
27. von Sperling, M. (1996). Comparison among the most frequently used systems for wastewater treatment in developing countries. *Water Sci. Technol.* **33**(1): 59–72.
28. Tsagarakis, K.P. (1999). *The Treatment of Municipal Wastewater in Greece*. PhD. Thesis, University of Leeds, School of Civil Engineering, Leeds, UK.
29. Burhard et al. (2000).
30. Tsagarakis, K.P., Tsoumanis, P., Charzoulakis, K., and Angelakis, A.N. (2001). Water resources status including wastewater treatment and reuse in Greece: related problems and prospectives. *Water Int.* **26**(2): 252–258.
31. Phybus, P. and Schoeman, G. (2001). Performance indicators in water and sanitation for developing areas. *Water Sci. Technol.* **44**(6): 127–134.
32. Schutte, C.F. (2001). Managing water supply and sanitation services to developing countries: key success factors. *Water Sci. Technol.* **44**(6): 155–134.

MERCURY REMOVAL FROM COMPLEX WASTE WATERS

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The Remediation Technology Group in the Chemical Technology Division at Oak Ridge National Laboratory obtains information on mercury contamination throughout

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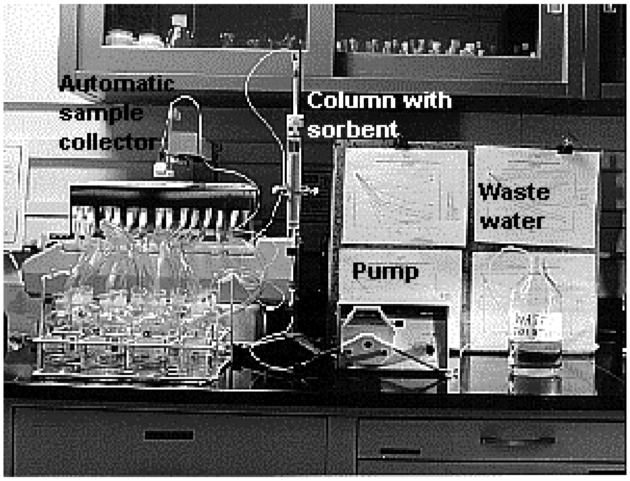

Figure 1. The typical experimental setup for long-term studies employs a continuous flow of waste water through a column packed with sorbent.

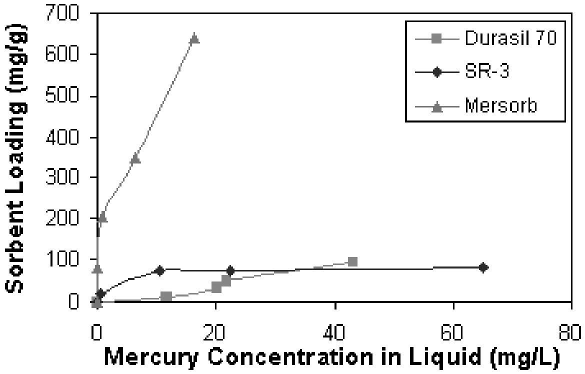

Figure 2. These data are from an experiment conducted with a waste water similar to tho one stored at the Savannah River Site. The original mercury concentration was 108 mg/L. Various amounts of sorbent were placed in contact with 50 mL of water for 24 h before the mercury was measured in the free liquid. The purpose of the experiment was to determine the isotherms.

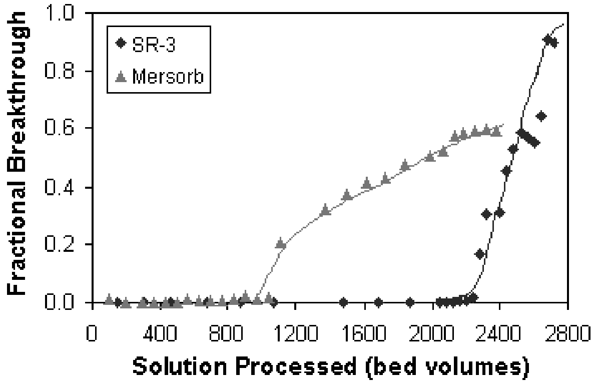

Figure 3. These data are from an experiment conducted with surrogate SRS waste passed through a column packed with a sorbent. As is noted, the effluent from the column is free of mercury until the sorbent becomes saturated.

the Department of Energy (DOE) complex, and conducts research and development activities to serve end-users.

Mercury-contaminated soils, sludges and aqueous residues at DOE sites usually contain sufficient radioactivity to invoke special handling under the Atomic Energy Act and Resource Conservation and Recovery Act. Typical examples are high-salt acidic wastes stored at Idaho Chemical Processing Plant, alkaline waste stored at Savanah River Site (SRS), and mercury-bearing lithium hydroxide and low-salt neutral pH groundwater at the Oak Ridge Y-12 Plant. Difficulties in removing mercury from these wastes are due to its concentration, speciation, interference from other dissolved species, and pH of the bulk media.

Figures 2 and 3 shows data from a feasibility study conducted on a surrogate waste similar to the SRS waste water. Typically, a large number of sorbents are screened for applicability before an isotherm study is conducted. Based on the results from these experiments, sorbents are selected for continuous column experiments in which data are collected to determine the long-term performance of sorbents. The data collected in these type of experiments can be used to design full-scale systems.

Every waste is different, so there is always a need for these type of experiments. We prefer to work with the actual waste whenever possible; however, sometimes the cost is prohibitive.

In Fig. 2, are the results of isotherm studies with SRS waste. The three sorbents performed quite differently; the Mersorb (sulfur impregnated activated carbon pellets) appeared to be able to adsorb far more mercury than the other sorbents.

Column studies bring another dimension into the project. In Fig. 3, the concentration of the mercury in the effluents from columns packed with SR-3 or Mersorb sorbent are displayed. There is no mercury exiting the column until about 2200 bed volumes (BV) had passed through the system when SR-3 was used as sorbent. The breakthrough was sharp, indicating efficient use of the column and the mass transfer zone was 6.2 mm deep. The flow rate was about 11 BV per hour. In the case of Mersorb about 1000 BV could be processed before mercury appeared in the effluent. In this case the breakthrough was more gradual over time, which is less desirable.

METAL SPECIATION AND MOBILITY AS INFLUENCED BY LANDFILL DISPOSAL PRACTICES

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Currently, landfills are constructed of a system of liners, leachate collection systems, and gas venting and collection systems. Hazardous wastes normally have two synthetic liners on the bottom and two leachate collection systems, one within the waste and one between the liners. These bottom liners typically rest on bentonite clay. Landfills have one bottom liner (New York requires two) resting on clay and one leachate collection system within the waste. A schematic of a typical landfill system is shown in Fig. 1. The landfill has a top cover system consisting of a synthetic liner with a topsoil cover designed to deflect precipitation. Not all of the liner components are shown, geotextiles and sands are used in various combinations for cushioning and inducement of preferential flow paths.

The following discusses and summarizes the mechanisms involved in metal speciation and mobility, modeling including references that provide more modeling information, and specific research in some of the areas.

Some precipitation inevitably enters the waste from liner permeation, holes, and cracks. However, most precipitation is deflected to stormwater collection, called runoff in Fig. 1. The dominant flow mechanisms into the waste are from the construction defects and not diffusion through the synthetic liners (1).

The precipitation that enters landfill wastes interacts with waste components and leaches metals and other substances. There are very complex interactions between the leachate and waste components that depend on pH, the metal and other component speciation, the presence of ligands, overall waste composition, redox potential, and others. Most of the leachate is collected in the leachate collection and treatment system. However, some of the leachate penetrates the bottom liner system from mechanisms similar to infiltration, and enters the soil column, and subsequently enters the groundwater.

Metal speciation and mobility are influenced by physical, chemical, and biological processes, and complex interactions between these processes may result in transporting specific contaminants at different rates (1). Attenuation of mobile metals depends on the amount of time that the contaminant is in contact with the material, the physical and chemical characteristics of the material, and the characteristics of the leachate.

Physical processes that control the transport of contaminants in the subsurface include advection (convection), the mixing effects of dispersion and diffusion, and physical sorption. Chemical processes that are important in controlling subsurface transport include precipitation/dissolution, chemical sorption, redox reactions, ion exchange, and complexation. These processes are generally reversible. The reversible processes tend to retard transport but do not permanently remove a contaminant from the system. Sorption and precipitation are generally the dominant mechanisms retarding contaminant transport (1). However, as discussed later, complexation can be dominant in landfills.

One model commonly used in chemical and environmental engineering that is often used to estimate leachate concentrations as a function of time and space, $C(t,x,y,z)$, is

$$\left(1+\frac{\rho_B}{\alpha}K_D\right)\frac{dC}{dt} = \nabla\bullet D\nabla C - \vec{v}\bullet\nabla C + R \qquad (1)$$

If the diffusion coefficient is constant and a single dimension is used, this becomes

$$\left(1+\frac{\rho_B}{\alpha}K_D\right)\frac{dC}{dt} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} + R \qquad (2)$$

where

C	concentration, M/L^3
D	diffusion (or dispersion) coefficient, L^2/t
K_D	leachate/solid distribution coefficient, L^3/M
R	reaction rate, M/L^3/t
x	spatial variable, L
t	time
v	velocity, L/t
α	solid porosity
ρ_B	solid bulk density, M/L^3

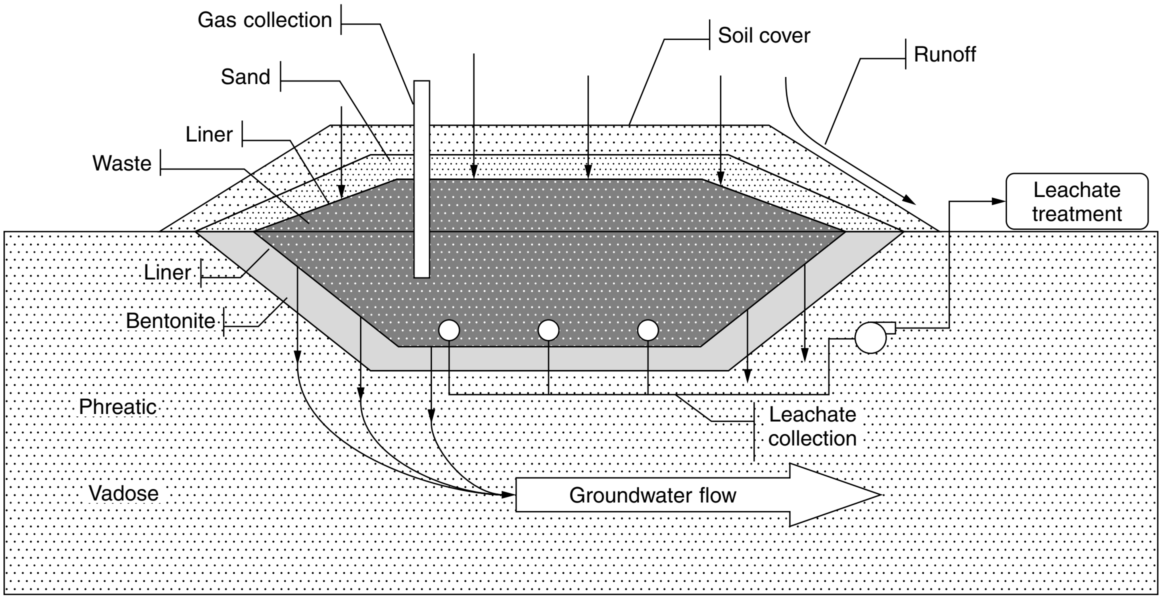

Figure 1. Schematic of landfill system.

The term on the left is the rate concentration change with time modified by the retardation based on sorption. The distribution coefficient for organic compounds can be estimated from the organic carbon content of the waste (2) but is likely to require measurement for metals. The first term on the right is the diffusion and/or dispersion. The second term on the right is the advection and the third term is the chemical reaction term. Equation 2 does not account for all phenomena. However, lumped sum parameters can be used, for example, the reaction rate R can include several types of generation and degradation terms lumped together. This equation or a variation thereof is normally solved numerically using appropriate boundary conditions.

Mathematical models to simulate the expected fate and transport of leachate metals are frequently used in groundwater and waste piles. Travers and Sharp–Hansen provide a thorough review of pertinent factors (3). Each facility is different, and no one generic model is appropriate in all situations. The conceptual model and data are used to select a mathematical model that accurately represents the conceptual model (4). A number of groundwater models, including saturated flow, solute transport, heat transport, fracture flow, and multiphase flow models, are summarized in van der Heijde et al. (5). A report by van der Heijde and Beljin provides detailed descriptions of 64 groundwater flow and solute transport models that were selected for use in determining wellhead protection areas (6). Reviews of groundwater flow and transport models for the unsaturated zone is presented in Oster (7). Groundwater flow and transport models are summarized by Bond and Hwang (8). Finally, Travers and Sharp-Hansen summarize models that may be applicable to problems of leachate generation and migration from landfill units (3). In an idealized situation (e.g., no complexation), metal mobility is controlled by the solubility of the species in the leachate. Precipitation is incipient when the metal exceeds its solubility, for the solubility product constant of a divalent metal,

$$K_{\mathrm{sp}} = [\mathrm{M}^{+2}][\mathrm{OH}^{-}]^{2} \qquad (3)$$

The precipitation of a dissolved substance may be initiated by changes in pressure, temperature, pH, concentration, or redox potential (9).

Chemical adsorption/desorption is a common mechanism that affects metal contaminant migration in soils. Solutes become attached to the solid phase by adsorption. Adsorption/desorption and precipitation/dissolution are reversible processes. However, adsorption/desorption generally occurs at a relatively rapid rate compared to precipitation reactions (1).

Oxidation and reduction (redox) reactions involve the transfer of electrons. Depending on the redox potential, metals may exist in various oxidation states that can impact their solubility. An example is iron that is very insoluble in the plus-three valence state. The valence state of iron depends on the redox potential and the pH, as shown in Eq. 4 (10):

$$4\mathrm{Fe}^{2+} + \mathrm{O}_2 + 4\mathrm{H}^{+} = 4\mathrm{Fe}^{3+} + 2\mathrm{H}_2\mathrm{O} \qquad (4)$$

Redox reactions and pH affect the solubility, complexing capacity, and sorptive behavior of constituents and thus control the presence and mobility of many substances in water. Microorganisms are responsible for a large proportion of redox reactions that occur in groundwater and, by inference, wastes in landfills.

Ion exchange occurs primarily at exchange sites on layered silicate clays and organic matter that have a permanent negative charge. The ability of soils and other solids to exchange cations is measured by the cation exchange capacity. The type and quantity of clay mineral present, the amount of organic matter present, and the pH of the soil or solids affect cation exchange capacity. Major cations in leachate (Ca, Mg, K, Na) usually dominate the exchange sites, resulting in little attenuation in soils of trace metals in the leachate, depending on the material selectivity and leachate metals concentrations. A smaller ion exchange effect for anions is associated with hydrous oxides. Soils typically have more negatively charged clay particles than positively charged hydrous oxides. Therefore, the transport of cations is attenuated more than the transport of anions.

Complexation reactions occur when metal ions react with inorganic anions or organic ligands to form coordination compounds. Complexation can either increase the concentration of a constituent in solution by forming soluble complex ions or decrease the concentration by forming a soluble ion complex with a solid. It is often difficult to distinguish among sorption, solid–liquid complexation, and ion exchange. Therefore, these processes are usually grouped together as one mechanism.

The biological degradation cycle of landfills normally occurs in four phases, aerobic, acetogenic, methanogenic that last on the order of 15 years, followed by a humic phase where the relatively refractory humic substances are stable. The degradation refers to organic compounds. The last phase is the phase in which no more organic degradation occurs and the remaining organic compounds consist of humic substances. The aerobic decomposition phase is short; it lasts approximately 1 month when all of the oxygen is used up (11). The second phase can last several years producing simple compounds such as fatty acids with high BOD_5 and an acidic leachate of pH approximately 5–6. The leachate contains high levels of mobile metals. Methanogenesis is slower than acetogenesis, so simple organic compounds are consumed during the third phase. Sulfates can be reduced to sulfides during the third phase that subsequently precipitate metals and hence change their speciation and reduce their mobility. The pH during the third phase is of the order of 7–8.

Recent work provides some specific examples of the way landfill practice influences speciation and mobility of metals. A plethora of information exists in the literature. Therefore, only some of the references found are cited. The general conclusion of the studies is that metal speciation and mobility are highly dependent on the landfill phase. The humic phase of the landfill is when the metals are least mobile and are speciated by chelation with humic substances. This phase may be short or long-lived, depending on the waste exposure to air. Humic oxidation can likely be minimized and/or eliminated by precluding air infiltration. The phase of a landfill can be accelerated by recycling water thus rendering metals less mobile sooner. It is also concluded that metals can exist in colloidal form and can complex with dissolved organic and/or inorganic compounds.

Several of the studies cited below correlate the speciation and mobility with chelation by humic compounds. Therefore, some discussion of these substances is needed. Humic compounds are derived from the amorphous part of dark brown to brown-colored substances in soil, lignite, peat, and brown coal produced during the humification of decaying organic materials. A conceptual model of a humic acid structure (12) is shown in Fig. 2. Figure 2 shows a possible sequestration mechanism of nickel, cadmium, and plutonium by humic acid. Humic acid/humic substance chemical structures have not yet been clearly defined. Approximate models describe humic acids as three-dimensional macromolecules whose molar mass is between 25,000 and 100,000. Their basic structure always has two distinctive features: (1) a central core with high aromaticity and (2) strong cross-linkage and peripheral functional groups linked by bridge binding (13). A substantial fraction of the mass of the humic acids is in carboxylic acid functional groups, which endow these molecules with the ability to chelate positively charged multivalent ions (Mg^{2+}, Ca^{2+}, Fe as well as hazardous metals such as Cd^{2+} and Pb^{2+}) (14). A major effect of humic acids in the speciation and mobility of metals is detoxification of heavy metals by chelation.

Organic matter degradation and hence the potential efflux of heavy metals in a long-term perspective was studied by defining some scenarios for waste deposits containing organic compounds, different longevity and functions of covers, and different water and air intrusion rates. The scenarios were based on various transport processes as well as different landfill constructions. The main conclusion is that the degradation of humic matter and hence the release of toxic metals can be substantially decreased if potential buildup of hydraulic gradients is avoided and if the landfill is located below the water surface (15). The amount of oxygen available for oxidation of the humic material and sulfides is reduced by water saturation. The assumption is that humic material and sulfides are readily oxidized and thus release the metals upon oxidation. The fifth phase of the landfill is the humic oxidation stage, if sufficient air can contact the waste and oxidation rates are fast. Additional research is needed in this area.

A conceptual model has been developed for waste deposits (16). The important processes occurring during the humic phase were quantified. The scenarios included the main mechanisms based on various transport processes as well as different landfill constructions, for example, binding capacities of sulfides and humic substances. They also included transport mechanisms by which the reactant oxygen can intrude into a deposit, sorption capacities of hydrous ferric oxides, and pH-buffering reactions. Scoping calculations have shown that the binding capacity of humic substances is sufficient to bind all toxic metals Cd, Cr, Pb, Zn, and Hg. In addition, the humics could also bind a smaller part of Ca, Fe, and Al, provided that much of the organic wastes remain as humic substances. Sulfides, on the other hand, can bind approximately twice the amount of all toxic metals. The binding capacity of hydrous ferric oxides, which can be formed by oxidation reactions during the humic phase, is estimated at three times the total content of metals that can sorb on hydrous ferric oxides. The alkalinity of the wastes is high enough to buffer the acidity produced by the oxidation of sulfides and by the degradation of organic matter, as well as that added by acid precipitation. Therefore, the main conclusion is that higher remobilization rates of heavy metals due

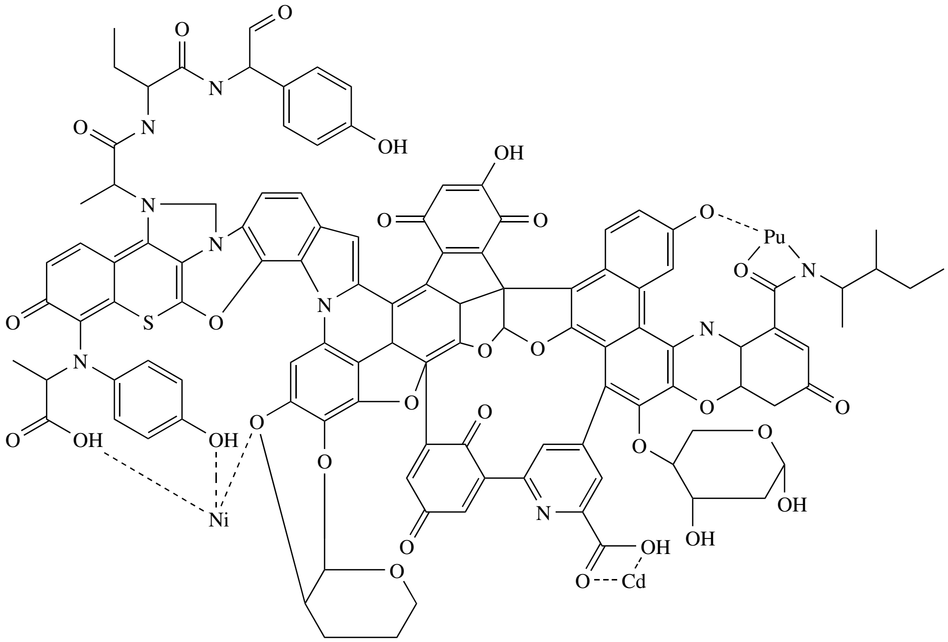

Figure 2. Model structure for humic acid.

to lowering of pH are not expected for many thousands of years.

Dissolved organic compounds can also complex with metals that increase mobility. Leachates after treatment from a landfill in Japan contain the same order as the influent (17). This was attributed to complexation with organic compounds, as treatment by elevated pH precipitation was effective when the organic compounds were removed. The ability of dissolved organic carbon (DOC) from landfill leachate-polluted groundwater to form complexes with the heavy metals cadmium (Cd), nickel (Ni), and zinc (Zn) was investigated (18). The DOC samples originated from the leachate pollution plume at Vejen Landfill, Denmark, and were studied in the original matrix with a minimum of manipulation. The results showed that DOC from landfill leachate-polluted groundwater can form complexes with Cd, Ni, and Zn and that the distribution coefficients were a factor of 2–6 lower in the presence of DOC. The migration velocity of the metals was increased by the presence of DOC but did not exceed 1.2% of the water migration velocity, indicating that the effect of DOC on the mobility of Cd, Ni, and Zn may have only minor environmental importance.

Rainfall and the recycling of leachate impact landfill leachate metal speciation and mobility. Leachate volume increases linearly with rainfall, and the leaching coefficient decreases, according to studies in Taiwan (19). Landfill bioreactor technology offers important advantages in managing and treating municipal solid waste, including accelerated waste stabilization rates, enhanced gas production, facilitated leachate management, volume reduction, and minimized long-term liability. These advantages have been documented in laboratory, pilot, and full-scale investigations. Although challenges remain in implementing the technology, bioreactor landfills are designed and operated at increasing frequency (20). Metal washout is initially one of the important mechanisms in conventional landfills, but sulfide and hydroxide precipitation followed by complexation with humic compounds are the primary mechanisms in recirculating landfills. However, metals can be remobilized, once humic oxidation starts. Recycling of leachate and/or addition of water through the waste accelerates stabilization. Water addition is a means of decreasing the degradation time span and thus accelerating metal stability. The water helps spread nutrients and bacteria to other parts of the landfill (21) and provides a medium conducive to biochemical reactions.

The physical forms of the species are also important in considering leachate metal speciation and mobility. Some of the metals can exist in colloidal form as, very small particles that are not easily filterable. This can have a large impact on characterization and leachate treatment processes. According to research on Danish landfills, metals exist in colloidal form. The dominant part of the colloidal material was in the smallest colloidal size fraction (0.001–0.40 mm); total organic carbon (TOC) was one of the major components of the colloidal mass. Si, Al, Ca, Fe, and S were also found in the colloidal fractions. This indicated that clay type particles, organic matter, and precipitates (most likely sulfides) were present in the leachate samples (22). The behavior of the colloidal mass can be markedly different from a dissolved metal speciation and needs to be accounted for in leachate treatment systems. In another similar study, anaerobic leachate-polluted groundwater samples were collected downgradient of a Danish landfill (23). The groundwater samples were spiked with heavy metals at concentrations within the range of metal concentrations found in landfill leachates and divided under anaerobic conditions into colloidal (screen-filtration and cross-flow ultrafiltration), organic (anion-exchange), and dissolved inorganic species of the heavy metals. The distribution of the heavy metals among the different size fractions showed that a substantial, but highly varying part of the heavy metals was associated with the colloidal fractions. These colloidally bound metals were, furthermore, associated primarily with the organic fraction, except for Zn, which was associated mainly with the inorganic fractions. Dissolved Cd, Cu, and Pb were mainly associated with dissolved organic carbon; Ni was also present as carbonate complexes and Zn as carbonate complexes and free divalent Zn. The results indicate that heavy metals in leachate-polluted groundwater are strongly associated with small-size colloidal matter and organic molecules.

BIBLIOGRAPHY

1. US EPA. (1987). *Background Document on Bottom Liner Performance in Double-Lined Landfills and Surface Impoundments*. EPA/530/SW-87/013. US EPA, Washington, DC. NTIS PB-87-182291.
2. Hemond, H.F. and Fechner, J.F. (1994). *Chemical Fate and Transport in the Environment*. Academic Press, San Dicego, CA.
3. Travers, C.L. and Sharp-Hansen, S. (1991). *Leachate Generation and Migration at Subtitle D Facilities: A Summary and Review of Processes and Mathematical Models*. Prepared for US EPA, Environmental Research Laboratory, Athens, GA.
4. Donigian, A.S. and Rao, P.S.C. (1990). Selection, application, and validation of environmental models. *Proc. Int. Symp. Water Quality Modeling Agric. Non-Point Sources*. Part 2.
5. van der Heijde, P.K., Bachmat, Y., Bredehoeft, J., Andrews, B., Holtz, D., and Sebastian, S. (1985). *Groundwater Management: The Use of Numerical Models*. American Geophysical Union, Washington, DC.
6. van der Heijde, P.K. and Beljin, M.S. (1988). *Model Assessment for Delineating Wellhead Protection Areas*. EPA-440/6-88-002. US EPA, Washington, DC.
7. Oster, P.A. (1982). *Review of Ground-Water Flow and Transport Models in the Unsaturated Zone, NUREG/CR-2917, PNL-4427*. Pacific Northwest Laboratory, Richland, WA.
8. Bond, F. and Hwang, S. (1988). *Selection Criteria for Mathematical Models Used in Exposure Assessments: Groundwater Models*. EPA/600/8-88/075. US EPA, Washington, DC.
9. Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., and Hackett, G. (1987). *A Standardized System for Evaluation of Ground Water Pollution Potential Using Hydrogeologic Settings*. EPA 600/2-87-035. Kerr Environmental Research Lab, US EPA, Ada, OK.
10. Tchobanoglous, G. and Schroeder, E.D. (1987). *Water Quality*. Addison-Wesley, Reading, MA.

11. Irene, M. and Lo, C. (1996). Characteristics and treatment of leachates from domestic landfills. *Environ. Int.* **22**(4): 433–442.
12. Adaptation from a structure by Kickuth on a German Website, http://www.pharmawerk-weinboehla.de/english/humine/humin2.html.
13. http://www.pharmawerk-weinboehla.de/english/humine/humin2.html.
14. http://www.thekrib.com/Chemistry/humic.html.
15. Bozkurt, S., Moreno, L., and Neretnieks, I. (1999). Long-term fate of organics in waste deposits and its effect on metal release. *Sci. Total Environ.* **228**: 135–152.
16. Bozkurt, S., Moreno, L., and Neretnieks, I. (2000). Long-term processes in waste deposits. *Sci. Total Environ.* **250**: 101–121.
17. Urase, T. et al. (1997). Effect of high concentration of organic and inorganic matter in landfill leachate on the treatment of heavy metals in very low concentration level. *Water Sci. Technol.* **36**(12).
18. Christensen, J.B., Jensen, D.L., and Christensen, T.H. (1996). Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. *Water Res.* **30**(12): 3037–3049.
19. Paris, H.C. (1996). Assessment of leachates from sanitary landfills: impact of age, rainfall, and treatment. *Environ. Int.* **22**(2).
20. Reinhart, D.R. and Al-Yousfi, B.A. (1996). The impact of leachate recirculation on municipal solid waste landfill operating characteristics. *Waste Manage Res.* **14**(4): 1.
21. Mosher, F.A., McBean, E.A., Crutcher, A.J., and MacDonald, N. (1997). Leachate recirculation for rapid stabilization of landfills. *WQI*.
22. Jensen, D.L. and Christensen, T.H. (1999). Colloidal and dissolved metals in leachates from four danish landfills. *Water Res.* **33**(9): 2139–2147.
23. Jensen, D.L., Ledin, A., and Christensen, T.H. (1999). Speciation of heavy metals in landfills-leachate polluted groundwater. *Water Res.* **33**(11): 2642–2650.

MICROBIAL FOAMING IN THE ACTIVATED SLUDGE PROCESS

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The production and accumulation of microbial (bacterial) foam in activated sludge processes is common and often contributes to increased operational costs and permit violations for total suspended solids (TSS), biochemical oxygen demand (BOD), and floating solids. There are several significant operational conditions that permit foam production in the aeration tank and its accumulation throughout numerous tanks in the treatment process. Each condition allows for the production of foam with its own characteristic texture and color (Table 1). Operational conditions responsible for microbial foam production include the undesired growth of foam-producing filamentous organisms, the presence of a nutrient deficiency, increasing sludge age, and undesired zoogloeal growth or viscous floc.

Table 1. Operational Conditions Associated with the Production of Microbial Foam

Operational Condition	Microbial Foam
Foam-producing filamentous organisms	Viscous chocolate-brown
Nutrient deficiency at a young sludge age	Billowy white
Nutrient deficiency at an old sludge age	Greasy gray
Sludge aging (young to old)	Billowy white to crisp white to crisp brown to viscous dark brown
Zoogloeal growth	Billowy white

Foam consists of entrapped air or gases beneath a thin layer of solids or biological secretions. Gases entrapped in foam consist of those released during the aerobic and anaerobic degradation of carbonaceous wastes. These gases include carbon dioxide (CO_2), molecular nitrogen (N_2), and nitrous oxide (N_2O).

Microbial foam is produced in the aeration tank and is discharged from the aeration tank to other treatment units such as the secondary clarifier, thickener, digester, dewatering facilities, and chlorine contact tank. In these units the accumulation of foam often results in increased operational costs. As foam is discharged from the aeration tank to other treatment units, the air and gases escape, and the foam collapses. The collapsed foam is sometimes referred to as scum.

FOAM-PRODUCING FILAMENTOUS ORGANISMS

In order of occurrence in activated sludge processes in North America, foam-producing filamentous organisms include nocardioforms, *Microthrix parvicella*, and type 1863. These organisms produce viscous, chocolate-brown foam.

Foam production by filamentous organisms is due to the presence of a large population of living organisms and a large population of dead organisms. The living organisms release insoluble lipids that coat floc particles and entrap air and gases. Dead organisms undergo autolysis and release surfactants (biosurfactants) that reduce the surface tension of the wastewater and permit microbial foaming. Surfactants released include ammonium ions ($NH_4{}^+$) and fatty acids. Because dead organisms release surfactants, control measures that destroy large numbers of foam-producing filamentous organisms over a relatively short time period often result in the rapid production of a copious quantity of foam.

The rapid and undesired growth of each foam-producing, filamentous organism can be associated with specific operational conditions (Table 2). By monitoring and preventing these conditions, the undesired growth of these organisms and their production of foam can be reduced.

Nocardioforms are a specialized group of bacteria that are known as actinomycetes. These organisms display some growth characteristics such as true branching that are found in the fungi. Nocardioforms and related

Table 2. Operational Conditions Associated with the Undesired Growth of Foam-Producing Filamentous Organisms

Operational Condition	Filamentous Organism		
	Nocardio-forms	*Microthrix parvicella*	Type 1863
High MCRT (>10 d)		X	
Fats, oils, and grease	X	X	X
High pH (>8.0)		X	
Low DO and high MCRT		X	
Low F/M (<0.05)	X	X	
Low MCRT and high F/M			X
Low nitrogen or phosphorus	X		
Low pH (<6.5)	X		
Readily degradable substrates	X		
Slowly degradable substrates	X	X	
Winter proliferation		X	

genera that are most often associated with foam production in activated processes include *Actinomadura, Arthrobacter, Corynebacterium, Micromonospora*, and *Nocardia. Nocardia* is the most commonly observed foam-producing actinomycetes, and the most frequently reported species of *Nocardia* include *N. amarae, N. asteroides, N. caviae, N. pinesis*, and *N. rhodochrus*. These organisms are relatively short (<50 μm), highly branched, and gram-positive. Nocardioforms can be found in the foam and mixed liquor within floc particles, extending into the bulk solution from the perimeter of the floc particles, and free-floating between the floc particles. Usually, nocardioforms as well as *Microthrix parvicella* and type 1863 are found in higher concentration in the foam than in the mixed liquor.

Because foam-producing filamentous organisms are found in high concentrations in the foam, the foam represents a source of "reseeding" of the mixed liquor with filamentous organisms. Therefore, treatment of the foam should be addressed when attempting to control the growth of foam-producing filamentous organisms (Table 3).

Microthrix parvicella is a nonbranched, relatively short (<200 μm), gram-positive filamentous organism. Intracellular granules in the filamentous organism may appear as a string of "beads." *Microthrix parvicella* usually is found in tangled mats in the floc particle or bulk solution.

Table 3. Treatment Measures for the Control of Filamentous Organism Foam

- Collapsing foam with the application of cationic polymer
- Collapsing foam with the application of effluent through "bib" sprinklers
- Collapsing foam with nonpetroleum-based defoaming agent
- Digesting foam with the application of bacterial cultures that contain the lipid-digesting enzyme lipase
- Physically removing the foam
- Spraying foam with a 10–15% sodium hypochlorite solution and spraying foam with effluent after 2–3 h of foam exposure to the sodium hypochlorite solution

Blooms of *Microthrix parvicella* often are associated with cold wastewater temperatures (winter proliferation). The proliferation of *Microthrix parvicella* during cold wastewater temperature may be due to the congealing of fats, oils, and grease. These compounds are preferred substrates for this filamentous organism.

Type 1863 also is a nonbranched, relatively short (<50 μm), gram-negative filamentous organism. Type 1863 is found free floating in the bulk solution and extending into the bulk solution from the perimeter of the floc particles. The filamentous organism possesses "chains" of rod-shaped cells that are constricted at each end.

NUTRIENT DEFICIENCY

Nutrient deficiencies are commonly observed in activated sludge processes and usually are due to the presence of nutrient-deficient industrial wastewater (Table 4). Nutrients that are most often deficient are nitrogen and phosphorus.

During a nutrient deficiency, soluble substrate that is absorbed by bacterial cells in floc particles cannot be degraded. The nondegraded food is converted by bacterial cells to insoluble polysaccharides and stored outside the bacterial cells. The polysaccharides are less dense than water and hinder the settleability of floc particles. Often, polysaccharides are deposited in the floc channels that permit the moving of water, air, and gases through the floc particle. When these channels become heavily laden with polysaccharides, air and gases are entrapped in the channels and desired settleability continues to deteriorate and foam appears on the surface of the aeration tank.

Foam produced during a nutrient deficiency is billowy white at a young sludge age and greasy gray at an old sludge age. The difference in texture and color of nutrient-deficient foam is due to the accumulation of oils in the floc particles. Young bacterial cells produce relatively little oil that accumulates in floc particles as compared to old bacterial cells. The transfer of oil to the foam from the floc

Table 4. Nutrient-Deficient Industrial Wastewaters for Nitrogen or Phosphorus

Industrial Wastewater	Nutrient Deficient	
	Nitrogen	Phosphorus
Bakery	X	
Beverage—alcoholic and soda drink	X	X
Citrus	X	
Chemical		X
Coffee	X	
Corn	X	
Cotton kerning	X	
Dairy—milk		X
Dairy—cottage cheese	X	
Food processing	X	X
Fruit and vegetable	X	X
Leather tanning		X
Petroleum refining		X
Pharmaceutical		X
Pulp and paper	X	X
Textile	X	

particle results in the production of greasy gray foam as the sludge age increases.

A nutrient deficiency within an activated sludge process can be corrected by identifying nutrient-deficient industrial wastewaters and ensuring that adequate nutrients are added to these wastewaters. Also, nutrients can be added to the activated sludge process as needed. Chemical compounds that release ammonium ions (NH_4^+) or orthophosphate (HPO_4^{2-}) can be added to the mixed liquor influent or primary clarifier effluent. Appropriate recycle streams also can be discharged to the activated sludge process when needed, if these streams contain adequate quantities of ammonium ions or orthophosphate and relatively low quantities of soluble wastes. Recycle streams include decant from digesters, centrate, and filtrate.

INCREASING SLUDGE AGE

Several types of foam are produced through changes in microbial activity with increasing sludge age. Billowy white foam is produced at a young sludge age when the bacterial population or mixed liquor suspended solids (MLSS) value is relatively small, that is, <1000 mg/L. This small population of bacteria lacks sufficient enzymatic ability to adequately degrade the surfactants that are discharged to the activated sludge process. The nondegraded surfactants produce billowy white foam.

With increasing sludge age the bacterial population or MLSS value increases. This population has sufficient enzymatic ability to adequately degrade the surfactants. With degradation of the surfactants, the foam becomes crisp white.

As the bacterial population (or MLSS) continues to age, large quantities of oils secreted by the bacteria accumulate in floc particles. The color of the oils darkens crisp white foam to crisp brown foam.

Finally, as the bacterial population becomes very old, large numbers of slow-growing filamentous organisms such as nocardioforms and *Microthrix parvicella* may proliferate. The growth of these lipid-producing organisms contributes to the production of viscous dark brown foam.

Undesired quantities of foam as a result of young or old sludge ages can be corrected by decreasing or increasing the sludge age by regulating sludge wasting rates. Sludge wasting rates should be uniform over as long a period of time as possible in order to prevent the development of pockets of young bacterial growth and old bacterial growth. If these pockets of growth do develop, concentric circles of light foam and dark foam can be observed on the surface of the aeration tank when aerators are turned off.

ZOOGLOEAL GROWTH

Zoogloeal growth or viscous floc is the rapid and undesired proliferation of floc-forming bacteria such as *Zoogloea ramigera*. This growth is associated with the production of large quantities of insoluble gelatinous material that entrap air and gases. The gelatinous material and entrapped air and gases result in the production of billowy white foam.

The occurrence of zoogloeal growth in activated sludge processes is due to high MCRT, long HRT, nutrient deficiency, organic acids, and significant changes in F/M. Zoogloeal growth and its foam can be controlled by exposing the growth to anoxic periods.

The texture and color of foam may vary due to changes in operational conditions. Generally, foam becomes more billowy and lighter in color with decreasing sludge age and more viscous and darker in color with increasing sludge age. Also, several operational conditions for the production of foam can occur at the same time, resulting in a mixture of textures and colors. For example, nutrient-deficient foam and filamentous organism foam can occur simultaneously.

Additional foaming conditions that often occur in activated sludge processes include surfactant foam, alkalinity foam, and polymer foam. If surfactants are not quickly degraded in the aeration tank, surfactants change the surface tension of the wastewater and produce billowy white foam. Also, an increase in alkalinity in the wastewater changes the surface tension of the wastewater, resulting in the production of billowy white foam.

If cationic polymers containing amino groups ($-NH_2$) are applied in an excess quantity for sludge thickening or sludge dewatering, and the excess quantity of polymer enters the aeration tank, billowy white foam is produced. When the polymer is degraded in the aeration tank, ammonium ions are produced from the release of amino groups. The ammonium ions represent an increase in alkalinity and a change in the surface tension of the wastewater. The change in the surface tension of the wastewater results in the production of billowy white foam.

INTRODUCTION TO WASTEWATER MODELING AND TREATMENT PLANT DESIGN

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INTRODUCTION

There are many ways of approaching the design of a wastewater treatment plant. Of the many methods, the field of practice generally uses three or four: design codes, rules of thumb, simple Monod calculations; and rigorous mathematical modeling. Most states still subscribe to variants of the first two methods because they work and are written in code documents. Depending on the backgrounds of designers, they may or may not have been exposed to the Monod equation and/or mathematically rigorous approaches to development of a static or dynamic model.

We confine this article to discussing readily available activated sludge and related models. Anaerobic digestion or film type of biological treatment systems is not discussed because the modeling effort for film modeling is not well enough defined to permit accurate modeling, and anaerobic modeling is still relatively new and has not become widely available. Another reason is that many of the models would require a full book to summarize adequately, and their use and calibration are often the subject of Ph.D. theses.

The older design code approach is often characterized by reference to individual state and national design codes such as the Ten States Standards. This approach is acceptable but produces a design which is between 30 and 50% in excess of that required and leads to sloppy and wasteful operation.

The rationale model is a group of codified experience based principally on food to microorganism ratio, mixed liquor suspended solids (MLSS), and a number of rules of thumb about the amount of air to supply per pound of waste treated, the quantity of cells produced per pound of biochemical oxygen demand treated, and hydraulic retention time.

For example, one could find rationale in the literature and the codes for designing a treatment plant with an F/M ratio of 0.4 to 0.05, a retention time between 12 and 30 hours, an MLSS of between 1000 and 4000 mg/L, and an oxygen transfer rate of 2.2 lb oxygen supplied per horsepower/hour per pound of BOD removed. That plant would probably work well, but under the ranges of the assumptions given, one could wind up with tankage that varies by a factor of 10 times or more. Still, no discussion of the rules for designing a clarifier system to remove solids has occured. The clarifier design can vary over a smaller range of perhaps 4:1. There is a wide latitude in what works, but the principal objective is to get the best combination of size and efficiency for the cost.

To varying degrees, the individual and company design groups have computerized their designs on spreadsheets (principally Excel®) or in limited versions for numerical calculators. These programs are adequate as far as they go, but designing an expensive and energy-intensive facility should consider the dynamic behavior of the wastewater and the performance of the plant.

It can be argued, because I have done so, that repeated running of the static models at varying conditions is an adequate substitution for dynamic modeling. At one time I believed that. However, the static models available are just not up to the performance of the dynamic models, and they do not address the different types of conditions and alternatives that can be evaluated using dynamic models.

Modeling the operation of a wastewater treatment plant is neither easy nor simple. Rather, it requires a concerted effort to acquaint oneself with the process of model development, the development of a mindset, and a willingness to research the somewhat arcane area of mathematical modeling formulations and development.

Modeling a wastewater treatment plant requires mastery of the elements of modeling and a basic understanding of the fundamentals of model development and chemistry. It also requires understanding the limitations of the model(s) used and their interactions.

STATIC AND DYNAMIC MODELS AVAILABLE

A number of wastewater models are currently available. The principal static models are available on the World Wide Web or from individuals via e-mail:

The Steady© model was developed by Luis Aburto Garnica and Gerald E. Speitel, Jr. It is available from the University of Texas via its website. It solves the activated sludge equations by an iterative approach. The graphics are limited, and the model is also very limited, but it is free. It can be obtained from: http://www.ce.utexas.edu/prof/speitel/steady/steady.htm.

Dr. William McHarg developed a spreadsheet model that is also free. The documentation is available online from Dr. McHarg, and a copy of the spreadsheet is available from him. The documentation is very good, and it is available at: http://www.wideopenwest.com/~bmcharg/bioxmdl/bioxmdl.htm.

The Wisconsin Department of Natural Resources has developed a model for the activated sludge process, named ENBIR. The ENBIR model is available from the following web address: http://www.dnr.state.wi.us/org/water/wm/ww/biophos/enbir.htm. The model is DOS-based and may not run under all versions of Windows. The documentation and theory development are available in a Power Point® slide from the following address: http://www.dnr.state.wi.us/org/water/wm/ww/biophos/remproc.ppt. The model was developed by Dr. Jim Park in 1996 to address Wisconsin's concerns about cold weather effects on wastewater treatment plants and the decrease of nutrient removals during cold weather. The documentation is reasonably good but does not consider all the ramifications of design and has limited ability to handle industrial wastes and nonstandard conditions.

Dynamic models come in all shapes and sizes. As far as can be ascertained, the only two free dynamic models are from Clemson University, called simulation of single sludge Processes (SSSP), and the corresponding program from University of Uppsala, Sweden, called Java activated sludge process simulator (JASS).

The SSSP model was developed by Dr. Les Grady and one of his graduate students around 1986. It is a DOS-based model. It was one of the earliest works that incorporated dynamic modeling and is now available free from Clemson. As far as can be ascertained, it was developed about the same time as the ASM1 model (see below), and it can model a multitank activated sludge plant. Steven Birstrip was one of Dr. Grady's graduate students, and he developed the DOS code for the model. The model is relatively easy to use, has good documentation, and can be learned and used in a matter of hours. It is limited in that it does not model the clarifier portion of the wastewater treatment plant well, but other than that, it is functional. The model can be obtained from the following website at the Rich Environmental Research Center of Clemson University: http://www.ces.clemson.edu/ees/sssp/index.htm.

The JASS model can be found at http://www.syscon.uu.se/~psa/. It is free, but it runs on their network and cannot be downloaded to a private personal computer. The graphics are unsophisticated, and the modeling is based on the ASM1 model. In times past, when the site was under development, some of the comments on the bulletin board accompanying the site indicated that there were mistakes in the program that were being fixed. The site is not necessarily convenient, nor is it reliable, and it lacks the power and flexibility of some of the commercial software packages.

Based on my own research, I prefer the SSSP program to the JASS program. This does not say that others cannot and have not developed free spreadsheet and other dynamic models, but none are as well documented as the SSSP Model.

For those of you who have the Mathcad® program, there is an activated sludge simulator that can be freely downloaded, but can be used only with Mathcad®.

The next group of programs is available for operation on mainframe computers where the base operating program is Matlab. Matlab is designed for solving large groups of complex equations, and a number of models of the activated sludge programs are available on Matlab. Matlab is not for everyone and is primarily a research tool. A single site license for Matlab costs in excess of $2500 per year.

The last group of programs is commercially available. They are made by several different groups. The principal programs are BIOWIN, GPS-X, SIMBA, STOAT, and WEST. All models have good graphical interfaces. Some are slightly easier to use than others. Depending on the desires and personal tastes of the user, one particular program may suit a user need better than others. The pricing structure and the modeling capabilities are somewhat similar but differ in outcome and computation time, graphical interface, and ease of use. All products allow the user to develop plant configurations of any type or size and readily make changes in the configuration.

Some programs offer a variety of models and configurations; others offer only a single model with adapted differences for enhanced performance. The real advantage of dynamic modeling lies in its ability to model an entire plant and show the designer or operator how the system operates. In all programs, it is possible to come up with an almost infinite variety of configurations and plant arrangements. For example, there are at least six dynamic models of clarifiers. Some models are only for primary clarifiers, others are for secondary clarifiers. When combined with the many variants of activated sludge and other process models, there is almost an infinite variety of plant configurations one can develop for modeling an activated sludge process before one has to consider tank and reactor dynamics and before one considers the various control systems and parameters. The result can often be quite overwhelming because the models construct and then solve more than 50 differential equations for a simple plant configuration.

The differences in the software are qualitative: power, flexibility, user base, development, features, and pricing structure. There is also a trend toward using a simulator software as a supervisory control and data acquisition system (SCADA), but, at this time, only WEST offers that capability.

The author of this article is affiliated with HEMMIS, the producer of WEST software, and, accordingly, all descriptions of competitors could be construed as commercial criticism or endorsements, but are very general in nature. Nothing should be construed as either an endorsement or as a criticism of a particular software product.

BIOWIN® is produced by EnviroSim Associates in Canada. The web address is http://www.envirosim.com/products/. It is very popular and has a reasonable interface.

GPS-X has a very good graphical icon interface, and it is reasonable to work with. It is produced by Hydromantis in Toronto, Canada. The Web address is http://www.hydromantis.com.

SIMBA is a German product produced by Ifak System GmbH, Schleinufer 11, D-39104 Magdeburg, Germany. SIMBA 4.0 is shipped together with the Matlab®/Simulink™ software of MathWorks Inc.; it runs under the Windows 9x, 2000, and NT 4.0 operating systems.

STOAT is produced by WRc Plc Ltd. in England. It is a very intuitive program, and one can quickly set up a configuration, but the targets on the connecting graphical elements are a bit small. The completed program creates an output to an Excel® file, and all the calculations are done at one time. The program is mathematically rigorous and good to use. It was designed by engineers, so it is quite intuitive, and the documentation is very good. Because it does the computation at one time, it is relatively quick compared with other programs. The Internet link for information on the WRc program is http://www.wrcplc.co.uk/asp/wastewater_tmnt.asp.

WEST® is the product of HEMMIS in Kortrijk, Belgium. It is an extremely rigorous and powerful program and has good graphics. Several features of WEST® include the ability to adjust the modeling parameters (such as oxygen uptake rate) on the fly; to adjust flow, control, and other parameters during the run; and instantaneously see the output. The program has a wide variety of models and options, including all the IWA models, plus others that have been rigorously tested by the Biomath Department at the University of Ghent. On the HEMMIS website, there is a free download of a sample of WEST®. The website is http://www.hemmis.com.

A word about pricing. Prices vary significantly with user needs. Base prices start at somewhere around $3,000 and go up to about $20,000 or higher depending on the user needs and the package. The cost of an adequate system for modeling a variety of conditions is between $10,000 and $15,000. Do not be fooled by different marketing offers, and make sure that the program you buy has the features you need and want. Some sites provide a simple matrix of programs at a modest to low price, and then if you want more complexity and power, you have to buy advanced models at a much higher price. Plan on a $10,000–$22,000 price tag for a complete system.

IWA

In the software packages discussed, all models have been developed by, or are based on, work performed by the International Water Association (formerly the International Water Quality Association) in London. The oldest of the models is Activated Sludge Model Number 1 (ASM1). The model formulation and description are presented by the IWA, and anyone who wishes can take the documentation and prepare an individual version of the model. If one is planning on doing any modeling, it is imperative that one has the IWA model documentation.

The available models are:

Activated Sludge Model Number 1 (ASM1), the oldest model and the most widely accepted. It allows computation of nitrification and denitrification.

Activated Sludge Model Numbers 2 and 2d. These models are similar but not identical to ASM1. The models were developed to consider nitrification, denitrification, and phosphorous uptake and release by the cells. The difference between Model 2 and Model 2d is that ASM2d allows for chemical precipitation and removal as well as for uptake and removal by the biomass.

Activated Sludge Model Number 3 is a BOD-based model that differs in formulation from the other three models. It has been tested and produces reliable results, but many of the experienced modelers do not like the general formulation of the model, and to date, it has not gained wide acceptance. It is handy because it is a BOD-based model, whereas all other models are COD based. In the United States, where the standards are BOD based, it is a bit easier to use because the model outputs can be used directly and do not have to be converted from COD back into BOD.

Anaerobic Digestion Model Number 1 is the newest of the IWA models. It has been released relatively recently and has not yet gained wide acceptance.

OTHER DYNAMIC MODELS AVAILABLE

This discussion has been primarily about modeling an entire plant, so a brief digression is in order. Most of the IWA models deal with the aeration portion of the plant and do not deal with the clarifier or other portions of the plant. Of specific interest are the associated or "ancillary" programs that often make up a plant configuration. These include the selection of primary and secondary clarifiers, sludge thickeners, dissolved air flotation units, centrifuges, filters, filter presses, disinfection units, and various types of headworks such as degritters and equalization systems. A word about these models and their characterization is necessary.

First, degritters and some headworks devices are nice showy pieces for modeling but do not really affect the plant modeling effort very greatly because we, as engineers and scientists, often do not characterize the grit and sand loads in the wastewater stream for two reasons. First, grit and sand often fall to the bottom of a pipe and are not sampled or characterized. Second, they are not characterized in models because they represent inert solids and the driving models for wastewater treatment are mostly COD based, not TSS based. In many systems, they represent a distraction as they add some numbers but affect the outcome by less than 5%.

Sand does not have any measurable COD, and most degritters are designed to remove particles of sand and rocks. The removal is proportional to the difference in settling velocities by Stokes' law and is proportional to the difference between the fluid and the particle density. Organic particles often have a specific gravity of 1.01–1.15; sand and rock have SG of 2.65. So, a model designed to remove sand may look impressive, but it provides only a minimal removal of the organic loading for the dynamic modeling of the wastewater treatment plant.

Clarifier models are for primary or secondary treatment. To some extent, they may be the same model with slightly different applications or literature on which the model was built. For example, the Lessard–Beck primary clarifier model (1) is similar in many aspects to the Takacs secondary clarifier model (2) and the Mars–Libelli clarifier model. The similarities include the manner in which the mass balance in the clarifier is analyzed, the location of the inlet port, and the approach to settling versus upward bulk flow. The clarifier is analyzed in ten layers in all models, and the mass balance is taken across the layers. The solids settle against the rising bulk velocity of the fluid and, as they reach the lower levels of the clarifier, depending on the model used, they collect and compress and generally follow the research work of Vesilind on sludge accumulation and compression (3).

When the sludge reaches the bottom of the clarifier, it is drawn off by different methods. Lessard–Beck uses a scour coefficient for primary clarifiers that could just as easily be adapted to a secondary clarifier. Mars–Libelli uses a slightly different configuration, and Takacs still a different configuration for sludge withdrawal and thickening. The point is that the model assumptions do make a difference in behavior. Where thickening behavior is to be investigated, the Mars–Libelli model is often preferred. For general behavior, the Takacs model is preferred, and for primary treatment, use the Lessard–Beck Model.

Where sludge thickening and centrifugal processing are involved, it is well to look carefully at the equations. The modeling assumptions often come down to a complex set of equations and elaborate calculations with a very interesting simplifying assumption. For example, several of the dissolved air flotation system and centrifugal models look very complex, but finally resolve down to a "stickiness factor" or a collection or efficiency factor, often experimentally determined, which controls the degree of separation. After all the trouble in the calculations, one finally has a simple constant on which the removal hangs, and that can be simulated by a single line equation or a simple clarifier model without any difficulty.

COD, BOD, and Modeling

BOD is a common but useless parameter. Unfortunately, we use it for much of our historical data and much of the permit work in the United States and elsewhere. It is useless because it is so unreliable. A quick check of Standard Methods indicates that the BOD test has a variability of around 20% at a 200 mg/L level. At lower levels, it is so unreliable that the issue of using it for permits is laughable, which makes for bad control and even worse permitting. Single-digit BOD permit values may be unrealistic, but, unfortunately, they are finding their way into the permit structure in some watersheds.

Another reason that BOD is useless as a control parameter is that the test takes too long for the results. Given that most tests take 5 days or 20 days (ultimate BOD), we still have to adjust the BOD test to prevent oxidation of ammonia and make sure that the seed is acclimatized. Even under extreme conditions, the retention time of wastewater in a treatment plant, except for very large lagoons, is seldom over 48 hours and is often between 4 and 24 hours; a standard activated sludge plant takes 12 hours.

As a control or performance parameter, it is also useless. Hoover, Jacewizc, and Porges made this appropriate comment about the BOD test in 1953 (4):

> The BOD test is paradoxical. It is the basis of all regulatory actions and is used routinely in almost all control and research studies on sewage and industrial waste treatment. It has been the subject of a tremendous amount of research, yet, no one appears to consider it adequately understood or well adapted to his own work.

Question: How do you control a plant when you can only find out what happened 5 days later?

Answer: You cannot, which is one reason why many plants are not operated but are maintained and marginally operated. There is a fundamental lack of understanding and appreciation of the basics underlying the operation and the value and the role of the operator. When an operator only finds out what happened to his plant a week later, there is no positive feedback. Dissolved oxygen and ammonia and VSS/TSS are more important control parameters. But we cannot run a plant intelligently on those parameters alone.

There are many other reasons for a lack of operation as well, but fundamentally underlying all of them is the idea that we cannot control the process, and it is a series of operator experience and guesses that get the plant through rather than any intelligent control decisions. About the only reason that an operator will get out of the air-conditioned office on a hot Friday afternoon is if the air conditioner breaks, the plant is in crisis, or the office catches fire. And who can blame them. We have set up our systems with so much slop that a typical design has between 30% and 50% excess capacity before any allowance for expansion or population growth (5).

This discussion is about how to get better process control and how to set up and evaluate a plant for this control and evaluation.

Relating BOD and COD

Both BOD and COD are measures of the amount of carbon in wastewater. There are two types of COD in use, permanganate and dichromate. Permanganate is a weaker oxidizer and gives lower results than dichromate COD. The U.S. standard is dichromate oxidation. If you apply European or foreign COD data, you have to make sure that you know the basis for the test.

For many municipal wastewaters, the relationships in Table 1 apply (6).

Table 1. Various Indicator Strengths

	Concentration		
	Weak	Medium	Strong
TSS	350	720	1200
TDS	250	500	850
Fixed TDS	145	300	525
Volatile TDS	105	200	325
BOD-5	110	220	400
COD	250	500	1000
TOC	80	160	290
TKN	20	40	85
NH_3	12	25	50
P-Total	4	8	15
Organic P	1	3	5
Inorganic P	3	5	10

The BOD does not measure ammonia uptake because we inhibit the test to prevent ammonia demand. COD does not measure ammonia either.

Various sources have estimated the relationships between COD and BOD. The overall range is that the BOD is between 40% and 60% of the COD. In Table 1, the three ratios are approximately 40%. A rough figure of BOD = 50% COD is not a bad estimate and depends on whose text is used. A standard figure of about 50% has often been employed. Figure 1, from Eckenfelder (7), would seem to contradict that, but given the variability of the BOD test, the 50% figure holds reasonably well. If one is considering the effluent BOD after biological treatment, then it is about 25% of the COD.

For modeling purposes, however, BOD is generally not used because it does not represent what is happening in the reactor tanks, it is not a consistent parameter, and the

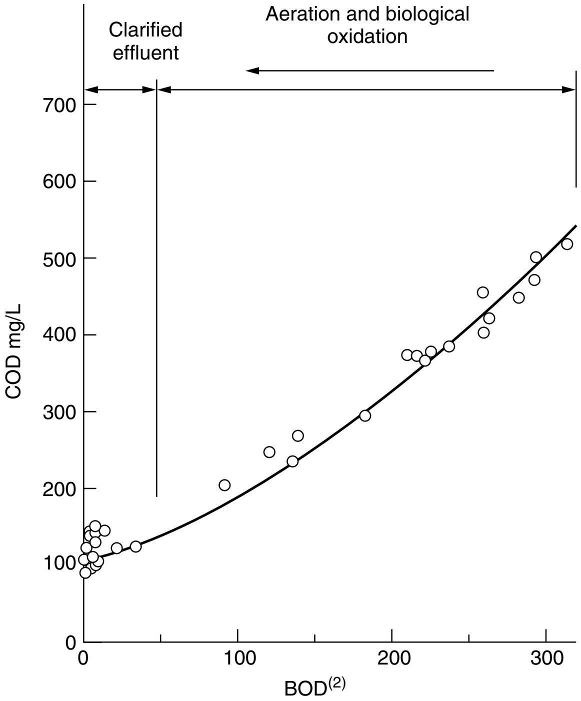

Figure 1. Relationship between COD and BOD (7).

Table 2. Various Indicator Strengths

Ratio	Low	Typical	High
COD/BOD	1.5–2.0	2.0–2.5	2.5–3.5
COT/TKN	6–8	8–12	12–16
COT/Tot. P	30–35	35–45	45–60
BOT/TKN	3–4	4–6	6–8
BOD/Tot. P	10–15	15–20	20–30
VSS/SS	0.4–0.6	0.6–0.8	0.8–0.9
COD/TOC	2–2.5	2.5–3	3–3.5

reproducibility of the test is uncertain. It does not make a good basis for modeling.

Additional Guidance on BOD/COD Relationships

Table 2 gives typical values for BOD/COD and other relationships in wastewaters. A high COD/BOD ratio indicates that organic matter is difficult to degrade. A high COD/TKN ratio indicates a waste that may require denitrification. A high VSS/SS ratio indicates a high organic matter relationship in the suspended materials (8).

MODELING THE BIOLOGICAL PROCESS

In the material that follows, we look briefly at the Monod equation and some of the mass balances around a typical activated sludge system. Then we continue briefly through the model development associated with the Peterson Matrix—which is used by the IWA in presenting and describing the mathematical development of the various models. Finally, we look at some of the balances around an activated sludge plant and consider the variables in the ASM1- Activated Sludge Model Number 1, which handles both nitrification and denitrification. The notation used and the pictures are taken from some of the modeling documents associated with HEMMIS' WEST® modeling platform and software and are used by permission.

Biological Growth Occurs According to the Monod Equation

The Monod equation is

$$\mu = (\lambda S)/(K_s + S)$$

where μ = specific growth rate coefficient

λ = maximum growth rate coefficient, which occurs at $0.5\ \mu_{max}$

S = concentration of limiting nutrient: BOD, COD, TOC, etc.

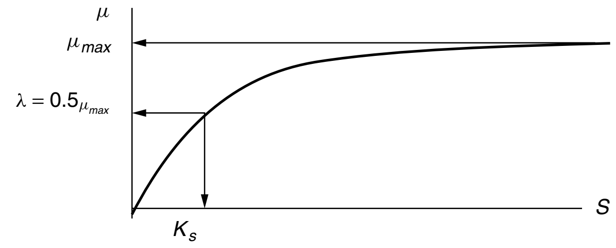

Figure 2. Graph of Monod equation.

K_s = Monod coefficient, also called the half-saturation coefficient because it corresponds to the concentration at which μ is one-half of its maximum, which can be seen from the Monod equation by setting S equal to K_s. K_s occurs at $\lambda = 0.5\ \mu_{max}$ (Fig. 2).

The curve is a plot of specific growth rate coefficient versus concentration of growth-limiting substrate when there is no inhibition.

$$\text{Organics} + \text{Bacterial} + \text{Nutrients} + \text{Oxygen} \longrightarrow \text{New Bacteria} + CO_2 + H_2O + \text{Residual organics} + \text{Inorganics}$$

$$\text{Rate of bacterial growth} = Rg = \mu X$$

where X is the microorganism concentration in mass/volume and μ = specific growth rate per unit of time.

$$\text{Cell Yield Coefficient} = Y_{obs} = \frac{-R_g}{R_{su}}$$

where Y_{obs} = observed yield coefficient, R_{su} = substrate utilization rate, and R_g = cell growth rate.

If we are looking only at the carbon variable, we get the following relationships:

$$Q = \text{Influent} = \text{Effluent} - \text{waste} = Q - Q_w + Q_w$$

= or if we define a new variable, Q_e, as the effluent, then

$$Q = Q_e + Q_w$$

For convenience, define the flow between the aeration tank and the clarifier as Q_2 with variable X_2. X_2 representing the combined flow of MLSS out of the tank and S_2 representing the substrate in the tank.

COD Relationships in Modeling

The models for activated sludge and biological processes use COD. The following are the relationships of the variables, and they will walk you through the formulation of the basics of the activated sludge models (ASMs).

In this example, we will first look at the carbon variable and then at the fractionation of the wastewater for treatment.

The basic activated sludge plant looks something like the schematic shown in Fig. 3.

Starting with a water balance, $Q_1 = Q_3 + Q_w$.

Running a mass balance around the system, we get

$$Q_1C_1 - r_{vs}V_2 = Q_3C_3 + Q_wC_r$$

where r_{vs} is the reaction rate for substrate utilization.

Note that in the above equation, no specific definitions are implied, so C can be NO_2, NH_3, COD, or anything else. However, one must define the unit of volume as well as the reaction rate, which means that the reaction rate can be r_{vs} or r_{xs} together with the unit of the volume V_2 and for r_{sx}, the activated sludge concentration X_2.

The units must be internally consistent. The activated sludge concentration X_2 can be measured in kg of SS/m^3,

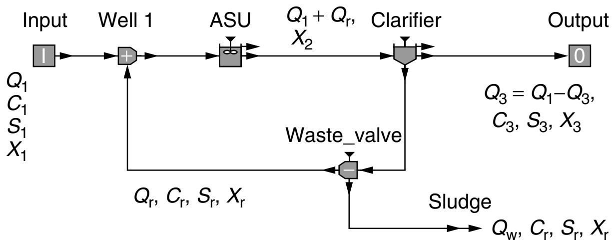

Figure 3. Activated sludge plant. Plant model was created using graphics from WEST® Software.

kg of VSS/m^3, or kg of COD/m^3, but the units must be consistent in the numerator and denominator.

Another way of looking at the mass balance is the following. The materials must be hydrolyzed before they can be accessed by the bacteria. So if you have some substrate such as BOD or COD, it cannot be used until it is solubilized, which means that the basic balance will look like the following when we consider the same mass balance as in Fig. 3, only now we have added the growth and hydrolysis terms to the equations:

$$\text{input} + \text{hydrolysis} + \text{growth} = \text{effluent}$$

$$\text{Input} + \text{sludge return} + \text{growth}$$

$$Q_1 S_{s1} + K_h * X_{S2} V_2 + [-(1/Y)]\mu[\text{Ss}2/(S_{sw} + K_s)]$$
$$[S_{O_2}/(K_{sO_2} + S_{O_2})] X_{BH} V_2 = Q_3 S_3 + C_r$$

(note that the growth term removes the substrate).

X_{BH} is the heterotrophic biomass and S_{O_2} is the oxygen concentration, etc as shown below.

We can also add other terms to the equations to compensate for the oxygen and substrate terms, and those are most conveniently multipliers expressed in the form of the Monod equation: $S/(S+K)$. A few of them are shown below, and you will note that a few of them act as "switches" because when S goes below a specific value, the term tends toward zero, and the entire multiplier falls out of the balance equation.

Some of those terms are:

Now the Matrix:

Component	S_s	X_s	X_I	X_{BH}	S_{O_2}	Reaction Rate r_v
Process						
Aerobic heterotrophic growth	$-(1/Y)$			1	$(1-Y)/Y$	$\mu[S_s/(S_s+K_s)]*$ $[S_{O_2}/(K_{sO_2}+S_{O_2})]$ X_{BH}
Heterotrophic decay		$1-f_{XB}$	f_{XB}	-1		$b_H * X_{BH}$
Hydrolysis	1	-1				$K_h * X_s$
Units	kg COD/m^3					
	Easily degraded organic matter	Slowly degradable organic matter	Inert suspended organic matter	Heterotrophic biomass	Oxygen	

This is the start of formulating the equations for most of the activated sludge models developed by the IWA.

How to Use the Matrix and the Equations. Given the plant depicted in Fig. 3 and an effluent concentration of 10 mg/L COD (about 20 mg/L BOD). Arbitrarily, we use a flow rate of 5 million gallons per day which is a Q of 3.785 L/Gal*5 MGD= 18.925 M L/D = 18925 m^3/D at a strength of 500 mg/L (= 0.5 kg COD (S)/m^3. The plant has no recycle. Find the aeration tank volume.

Moreover, we have the following information provided: $r_{xs} =$ 3 kg COD (S)/kg(B) COD 3 kg of substrate consumed per kg of bacteria, and the yield for substrate is 0.4 g COD(B)/kg COD (S) − 0.4 kg COD of bacteria per kg of substrate consumed.

Look at the equations above, and find the necessary volume for the tank:

$$\text{V} = (Q_1 C_1 - Q_3 C_3)/(r_x X_b)$$

and

$$X_b = Y * (C_1 - C_3)$$
$$X = 0.4(500 - 10) = 0.4 \times 490 = 196.0$$

and

$$V = (Q_1 C_1 - Q_3 C_3)/(r_x X_b)$$
$$= (18925 \times 500 - 18925 \times 10)/(3 \times 196)$$
$$= 15770.83 \text{ cubic meters}$$

Now if the plant has recycle, $Q_w > 0$.

We can go on and look at the overall process doing mass balances in any of a number of ways and at various points. The critical element is to take the internal tank reactions and the recycle rate into consideration.

If we performed a mass balance around the aeration tank and use that to calculate the tank effluent concentration, we get the following:

$$X_1 C_1 + X_r C_r + (Q_1 + Q_r)(C_{\text{ATIn}} - C_{\text{ATOut}})$$
$$Y = (Q_1 + Q_4) * X_2$$

Obviously, that requires a bit more information.

The overall substrate removal rate is

$$r = (\mu/Y)(S_2/(S_2 + K_s)(S_{O_2}/(S_{O_2} + K_{sO_2}) * X_2$$

where S_2 is the concentration of organic matter in the aeration tank.

The mass balance for the entire plant is

$$\text{Input} + \text{hydrolyzed} - \text{removed} = \text{Output}$$
$$Q_1 * S_1 + r_x V_2 v_{xs} - r_{vs} V_2 = Q_3 S_3$$

where v_{xs} is the hydrolysis coefficient.

All the above is for a simple set of reactions, but it forms the basics for modeling.

The IWA models currently in use are ASM1, ASM2, ASM2d, and ASM3. ASM1 is the oldest, dating from about 1987, and ASM3 is the newest. The problem with ASM1 is that it is difficult to fractionate the influent in the manner required for the model without a lot of trouble. ASM1 and ASM3 can be used to model nitrate removal.

ASM2 and 2d are written with the phosphorous variable in mind. They are rewritten rather to consider the fact that activated sludge is comprised of cellular biomass that has the ability to store and use phosphorous. ASM2d is specifically for phosphorous removal with the addition of precipitates (metal hydroxides).

ASM3 is a BOD-based model, and it is somewhat easier to use but still requires a basic understanding of how the model works and the kinetics. ASM3 is not as widely used because it is newer and because of the model formulation with regard to cellular internal storage.

The ASM models are written in the same matrix notation used above in the table, and in the simplest model, ASM1, there are eight rate equations: aerobic growth of heterotrophs, anoxic growth of heterotrophs, aerobic growth of autotrophs, anoxic growth of autotrophs, decay of heterotrophs, decay of autotrophs, ammonification of soluble organic nitrogen, hydrolysis of entrapped organics, and hydrolysis of entrapped organic nitrogen. So, eight equations that have 13 variables all expressed in matrix form.

The use of the words heterotroph and autotroph refers to the wastewater bacteria that can use exterior or interior sources of carbon to oxidize the wastewater.

Heterotrophs are assumed to be the utility organisms, capable of doing a wide variety of things in a biomass system. They grow aerobically, anoxically, and may be active in anaerobic fermentation. They are responsible for hydrolysis of particulate substrates and can use all degradable organic substrates under all conditions.

Autotrophs are nitrifying organisms that are responsible for nitrification. They are obligate aerobes, classified as chemo-litho-autotrophs, and are responsible for ammonia oxidation to nitrate (*Nitrosomonas* and *Nitrobacter*).

The variables and their notation in WEST are as follows:

For ASM1

Note that the IWA model description uses almost identical notation, but uses subscripts: thus S_i would be expressed by the IWA rather than the S_I notation used here

Name	Description
H2O	Water
S_I	Inert soluble matter
S_S	Readily biodegradable matter
S_O	Dissolved oxygen
S_NO	Nitrate and nitrite
S_NH	Free and ionized ammonia
S_ND	Soluble biodegradable organic nitrogen
S_ALK	Alkalinity
X_I	Inert particulate matter
X_S	Slowly biodegradable matter
X_BH	Heterotrophic biomass
X_BA	Autotrophic biomass
X_P	Particulate products resulting from biomass decay
X_ND	Particulate biodegradable organic nitrogen

These components are also used to characterize the influent of the wastewater treatment plant.

Additionally, the following parameters are also required for specifying the state variables in the modeling process.

Variable	Description	Units
Y_H	Yield For heterotrophic biomass	g COD/g COD
i_XB	Mass of nitrogen per mass of COD in biomass	g N/g COD
Y_A	Yield for autotrophic biomass	g COD/g N
f_P	Fraction of biomass converted to inert matter	—
i_XP	Mass of nitrogen per mass of COD in products formed	g N/g COD
K_S	Half-saturation coefficient for heterotrophic biomass	g COD/m^3
K_OH	Oxygen half-saturation coefficient for heterotrophic biomass	g O_2/m^3
K_NO	Nitrate half-saturation coefficient for denitrifying heterotrophic biomass	g NO_3-N/m^3
b_H	Decay coefficient for heterotrophic biomass	1/day
mu_H	Maximum specific growth rate for heterotrophic biomass	1/day
n_g	Correction factor for anoxic growth of heterotrophs	—
K_OA	Oxygen half-saturation coefficient for autotrophic biomass	g O_2/m^3
K_NH	Ammonia half-saturation coefficient for autotrophic biomass	g NH_3-N/m^3
b_A	Decay coefficient for autotrophic biomass	1/day
mu_A	Maximum specific growth rate for autotrophic biomass	1/day
k_a	Maximum specific ammonification rate	m^3/(g COD.d)
K_X	Half saturation coefficient for hydrolysis of slowly biodegradable substrate	g COD/g COD
k_h	Maximum specific hydrolysis rate	g COD/(g COD.d)
n_h	Correction factor for anoxic hydrolysis	—
-Kla	Oxygen transfer coefficient	1/day
S_O_Sat	Oxygen saturation concentration	g/m^3

Y_H and Y_A must be larger then zero (Y_H > 0 and Y_A > 0).

Fortunately, many of these values are published in the IWA Model and are constant for many waste streams. The documentation considers published values plus ranges of these values in the models.

In the next article on plant modeling and hydraulics, we consider some of the challenges and opportunities associated with setting up a plant model.

BIBLIOGRAPHY

1. Lessard, P. and Beck, M.B. (1988). Dynamic simulation of primary sedimentation. *J. Environ. Eng.* **114**: 753.
2. Takacs, I., Patry, G.G., and Nolasco, D. (1991). A dynamic model of the thickening/clarification process. *Water Res.* **25**: 1263–1271.
3. Vesilind, P.A. (1979). *Treatment and Disposal of Wastewater Sludges*. Ann Arbor Science, Ann Arbor, MI.
4. Gaudy, A.F., Jr. (1972). Biochemical oxygen demand. In: *Water Pollution Microbiology*. R. Mitchell (Ed.). Vol. 1, John Wiley & Sons, New York, pp. 305–332.
5. Russell, D.L., Dudley, J., and Amerlinck, Y. (2002). Does your plant need an upgrade? *Water Environ. Technol.* October.
6. Liu and Liptak. (1994). *Environmental Engineer's Handbook*. Lewis, Boca Raton, FL, Table 7.18, p. 520.
7. Thackston, E. and Eckenfelder, W. (Eds.). (1972). *Process Design in Water Quality Engineering*. Jenkins, New York.
8. Henze, M., Harromotes, P., la Cour Jansen, J., and Arven, E. (2002). *Wastewater Treatment—Biological and Chemical Processes*. Springer-Verlag, New York, p. 31.

PRACTICAL APPLICATIONS OF WASTEWATER MODELING AND TREATMENT PLANT DESIGN

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INTRODUCTION

In this article, we consider some of the specifics for setting up a model and plant hydraulics, and some of the practical considerations and limitations of modeling.

NOTES ON PLANT MODELING

The following notes on setting up a mathematical model of a wastewater treatment plant were prepared as a part of a training document for using WEST software. The proprietary parts have been removed, and the generic suggestions and ideas have been incorporated as a trial procedure based on personal experience. The procedure is designed for an ASM 1 model.

By following the steps outlined below, you will be able to set up and run a model and either match existing conditions or proposed conditions:

1. Information gathering
2. Model selection
3. Reactor hydraulics
4. Laboratory and other data organization
5. Flow sheet setup & model organization in WEST—the WEST C
6. Model compilation and setup—the WEST-S
7. Input and output file preparation
8. Initialization of model parameters and first runs
9. Parameter adjustments

Step 1: Information Gathering

Your objective is to make a model that represents a form of reality. That reality may represent either the dynamic behavior of a new facility or the dynamic behavior of an existing facility. The purposes are predictive and or historical. In the first case, you may want to find out how the facility will work and whether a specific design is adequate. In the second case, you may be looking to duplicate the performance of a real plant by preparing a model and matching the data from the model to the data from the real plant. In this latter instance, you can then use the data to predict future performance or investigate plant modifications.

Modeling is a very good but imperfect process. In the process of gathering information about a facility, you may never have enough information to satisfy your requirements. It will be easier to make assumptions about a new facility than to model the behavior of an existing one.

When you are dealing with an existing facility, you will almost never have enough information about the facility to satisfy your model and requirements. You will have to make some intelligent and reasonable guesses at certain things. You also may never know all that you want about a particular facility, but at the same time, you may know more about the facility than you ever dreamed of knowing because the data are often in the wrong place or of the wrong type.

This is not quite an "abandon all hope—ye who enter here" type warning, but rather a practical admission that you will be trying to reconstruct an event or make estimates of what may be happening with a model in an imperfect world.

You will need:

- An initial idea of which model you might want to use and the requirements of that model.
- Plant drawings and flow sheets.
- Aerator sizes and capacities.
- Physical dimensions of units.
- Maximum flow to each unit, which is particularly important in pumped flow where you have maximum capacities for pumps. Locations include clarifier underflow, and in nitrification plants, the return rates or recirculation rates for the system.
- Chemical data on the plant:
  - Influent data
  - Effluent data
  - Water quality data and effluent requirements
  - Internal plant operating records and logs
  - Chemicals added and operating set points

Most of the models are based on COD and most of the data you have are BOD. You may have to go back into the laboratory for more information to establish the necessary correlations to create the partition for the influent file.

Depending on how the model is established, you may or may not need additional data. If there is a system to enable you to transform your data into corresponding data for the model, it may be used after examination and careful consideration. One of the problems you may encounter is that the conversion routine makes some arbitrary decisions about the relationship between BOD and COD and the other parameters, and so you may have to consider that in the setup of the model. Also, the relationships (parameters and fractions) may change over time and with temperature and other influences. The program does not make those changes.

If you are working on a new design, you can make many choices about the type and kind of data you use.

Depending on the need for accuracy and performance, you may have to go into the laboratory and reproduce oxygen uptake rate (OUR) data, as well as yield and specific growth data, and also data for settling characteristics. If you are not going to be reproducing data from an existing plant, the effort in gathering detailed data may not be worth the trouble or expense.

A major caution should be raised here. If you are seeking to model any type of industrial waste, you probably should perform some minimum characteristics testing and should include some pilot plant testing as well as testing for settling characteristics because toxicity and hindered settling can often be associated with industrial waste treatment systems.

Step 2: Model Selection

Table 1 lists the input variables for each of the three principal activated sludge models, ASM1, ASM2d, and ASM3.

Model ASM1 is the oldest and has the most history behind it. It can be used for nitrogen removal in BNR plants. ASM2 and ASM2d were formulated later to consider the specific ability of the cell to store food materials. The ASM2d is formulated to allow the addition of metal hydroxides for phosphorous precipitation.

The ASM3 model is the newest, and many in the modeling community do not like it because of its formulation. They have indicated that the lumping of wastewater fractions and overall formulation of the model away from observed cellular behavior is objectionable. The difference in model formulation between ASM1 and ASM3 is substantial. ASM3 was formulated to address some of the deficiencies and difficulties with ASM1 resulting from assignment of the COD fractions of the influent. (See the discussion on COD and BOD and preparation of the influent file.)

Quoting and paraphrasing from the IWA description of ASM3 and ASM1 differences:

- ASM1 does not include kinetic expressions that can deal with the nitrogen and alkalinity limitations of heterotrophic organisms. The result is that the computer code cannot be based on the original form of ASM1, where a negative concentration of ammonia may occur under certain circumstances.
- ASM1 includes biodegradable soluble and particulate organic nitrogen as model compounds. These cannot be easily measured.
- ASM1 differentiates inert particulate organic material depending on its origin, influent or biomass decay, but it is impossible to differentiate these two fractions in reality.
- ASM1, ASM2, and AMS3 do not directly predict the MLSS or TSS concentration or the BOD concentration in a waste stream.
- In ASM1, hydrolysis has a dominating effect on predicting oxygen consumption and denitrification by heterotrophs. In reality, the process contains a number of coupled reactions.

ASM3 is a different model formulation all together.

An example of the differences among the models is shown in Table 1. These are the listed variables in the ASM1, ASM2d, and ASM3 models (not the parameters) expressed in the notation used in the WEST modeling platform.

Before we leave model selection, a couple of points are particularly important.

- The models do not define the conventional parameters as conventionally measured by the wastewater treatment industry. Everything is related to COD, and moving backward and forward through COD may introduce errors in modeling that are both frustrating and easily made.
- In most experiments, the researcher is often interested in modeling reductions in BOD, TSS, ammonia, phosphorous, and, perhaps, MLSS and COD. MLSS is often a control parameter for plant operations. The problem is that the values for many of these parameters are ‘reconstructed’ or measured indirectly from the COD. Ammonia and phosphorous are often directly modeled and measured, but MLSS, TSS, and BOD are calculated from COD data, and they can be difficult to obtain for control purposes.

In a recent modeling experiment, this point was again driven home by the frustration of trying to model conventional parameters. The experimenter was trying to model TSS accumulation in a membrane bioreactor system and was being frustrated by the model’s internal composition.

The ASM2 model (and the other models as well) has a complex definition of TSS. The definition of TSS includes part of the soluble and insoluble fractions of the particulates; part of the heterotrophic and autotrophic bacterial mass; and part of the internal storage product of phosphorous accumulating organisms, metal phosphates, and polyphosphates. Each factor is multiplied by partitioning coefficients, and a change in heterotrophic concentration or other parameters may influence the measurement of TSS. In the other models, the definition of TSS is somewhat less complex and more easily measured.

Table 1. Variables in ASM Models

ASM1 Variables		ASM2d Variables		ASM3 Variables	
Name	Description	Name	Description	Name	Description
H2O	Water	H2O	Water	H2O	Water
S_I	Inert soluble matter	S_I	Inert soluble matter	S_I	Inert soluble organic matter
S_S	Readily biodegradable matter	S_O	Dissolved oxygen		
		S_N2	N_2	S_S	Readily biodegradable organic substrate
S_O	Dissolved oxygen	S_F	Fermentable, readily biodegradable organic matter		
S_NO	Nitrate and nitrite			S_O	Dissolved oxygen
S_NH	Ionized and un-ionized ammonia			S_NH	Ammonia
		S_A	Fermentation products considered to be acetate	S_N2	Dinitrogen
S_ND	Soluble biodegradable organic nitrogen			S_NO	Nitrate
				S_ALK	Alkalinity
S_ALK	Alkalinity	S_NO	NO_2^- and NO_3^- nitrogen	X_I	Inert particulate organic matter
X_I	Inert particulate matter				
X_S	Slowly biodegradable matter	S_PO	Inorganic soluble phosphorus, primarily orthophosphates	X_S	Slowly biodegradable substrates
X_BH	Heterotrophic biomass			X_H	Heterotrophic organisms
X_BA	Autotrophic biomass	S_NH	Ammonium nitrogen, NH_4-N	X_STO	Cell internal storage product of heterotrophic organisms
X_P	Particulate products resulting from biomass decay	S_ALK	Alkalinity of the wastewater	X_A	Nitrifying organisms
X_ND	Particulate biodegradable organic nitrogen	X_I	Inert particulate matter	X_TS	Total suspended solids
		X_S	Slowly biodegradable matter		
		X_H	Heterotrophic biomass		
		X_PAO	Phosphate accumulating organisms: PAO		
		X_PP	Polyphosphate		
		X_PHA	A cell internal storage product of phosphorus accumulating organisms		
		X_AUT	Autotrophic biomass		
		X_TSS	Total suspended solids TSS		
		X_MeOH	Metal hydroxides		
		X_MeP	Metal phosphate ($MePO_4$)		

This is also true of BOD. In some of the models, BOD is calculated through the COD where it factors into the ultimate BOD, and then to the 5-day BOD. Needless to say, the conversion factors play a large part in the conversion. Another example is that the COD to BOD conversion formula is different for the influent and effluent parameters.

- At least one company, WRc, Ltd., in England, has a model that is formulated strictly on BOD (STOAT).
- The ASM3 model is still COD based, but it is a lot easier to use than ASM1 and ASM2. The ASM3 model has its limits, discussed above, but it is generally more forgiving, if, arguably, less accurate than the ASM1 and ASM2 models.

Step 3: Reactor Hydraulics

Reactor hydraulics is an extremely important consideration in modeling. Reactor hydraulics are critical in determining both the type of model used and the relationships involved in the plant design. For complete mix plants, the concentration of solids in the aeration tank is the same at both influent and effluent, or $X_{\text{in}} = X_{\text{out}}$.

But for a plug flow plant, the concentration of X varies through the aeration tank. The characteristics of the concentration in the effluent depend on the reactions and the tank hydraulics.

The computer models of activated sludge systems use continually stirred tank reactors (CSTRs). The ideal flow pattern in a long narrow tank approaches plug flow. The reactor flow patterns need to be addressed in the model so that the hydraulics of the model match the hydraulics of the wastewater tankage.

The subjects of reactor hydraulics and dispersion are beyond the scope of this article but need to be considered to ensure adequate hydraulic modeling for the plant.

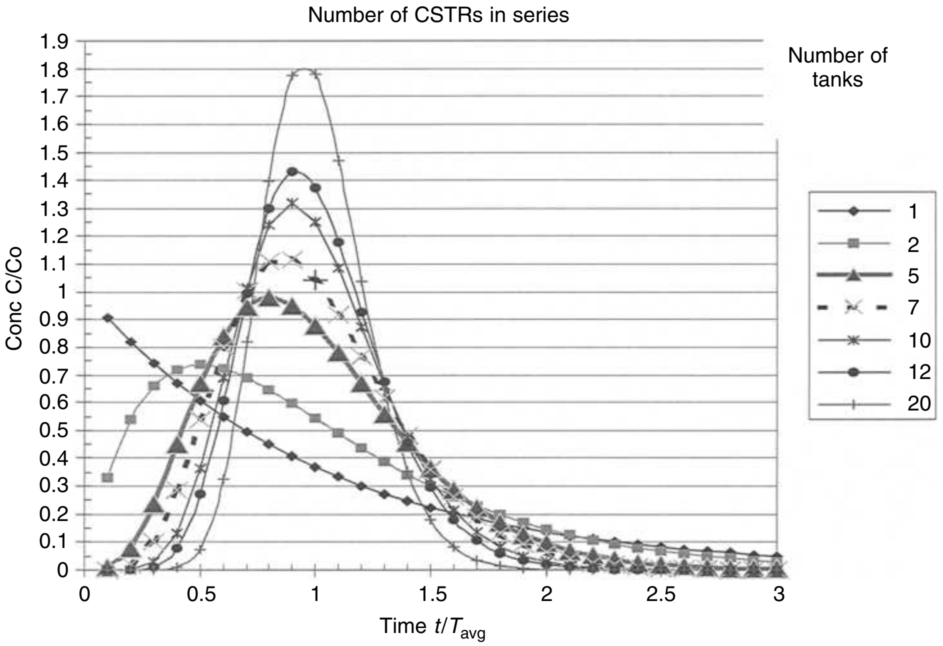

Figure 1. Changes in concentration with time.

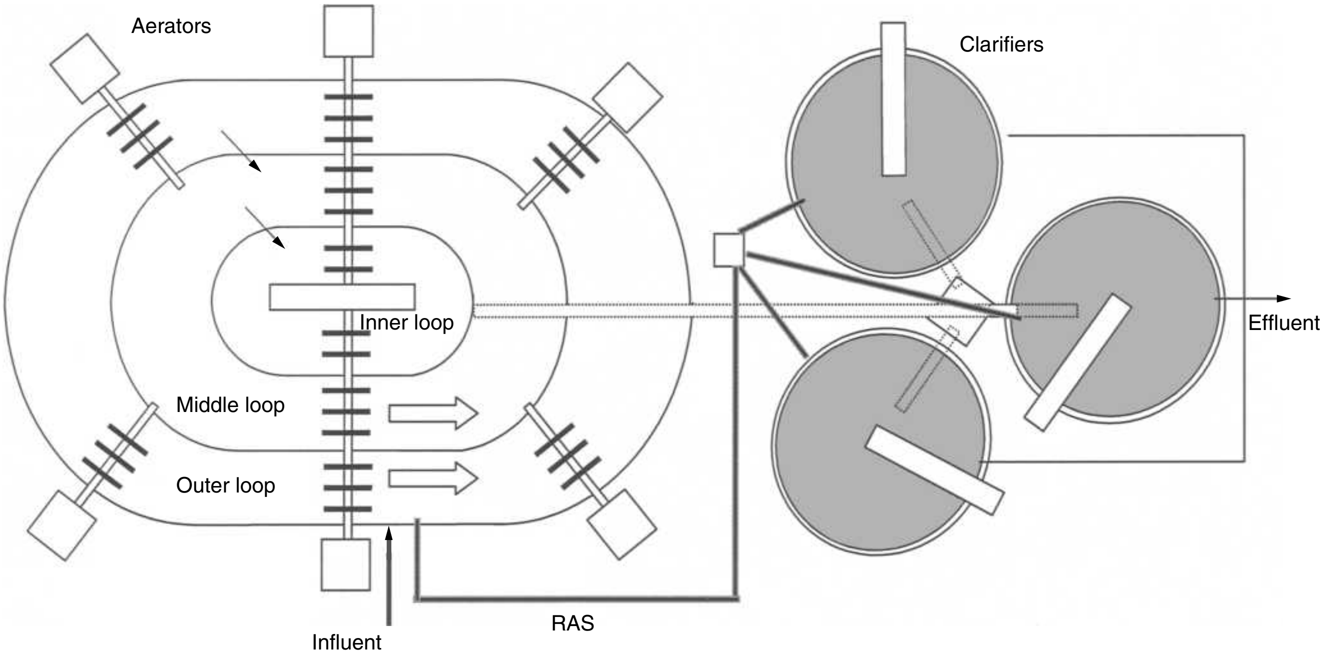

Figure 2. The general configuration of the ORBAL followed by configuration in WEST.

The relationship between the number of CSTRs in series and the concentration is shown in Fig. 1.

The difference between a true plug flow reactor and a true complete mix reactor is defined in terms of the axial turbulent diffusion coefficient, average flow velocity, length of the reactor, and the inverse of the Peclet number, or D/UL. The important thing to consider is that the higher the peak and the sharper the curve, the more the reactor acts like a plug flow reactor. (This also means that, for a greater number of tanks, one will have to do a lot more work in setting up the model.)

In Fig.1, the value for one tank is comparable with a complete mix reactor, whereas the value for 20 tanks approaches that of a plug flow reactor. There is a balance formula for this computation that is given by the following:

A correlation that relates the internal mixing characteristics (number of compartments or stages) to the physical properties (for diffused air systems) was used. The correlation, in SI units, is

$$N = 7.4\, Q_S\, (1 + R)\, L/WH$$

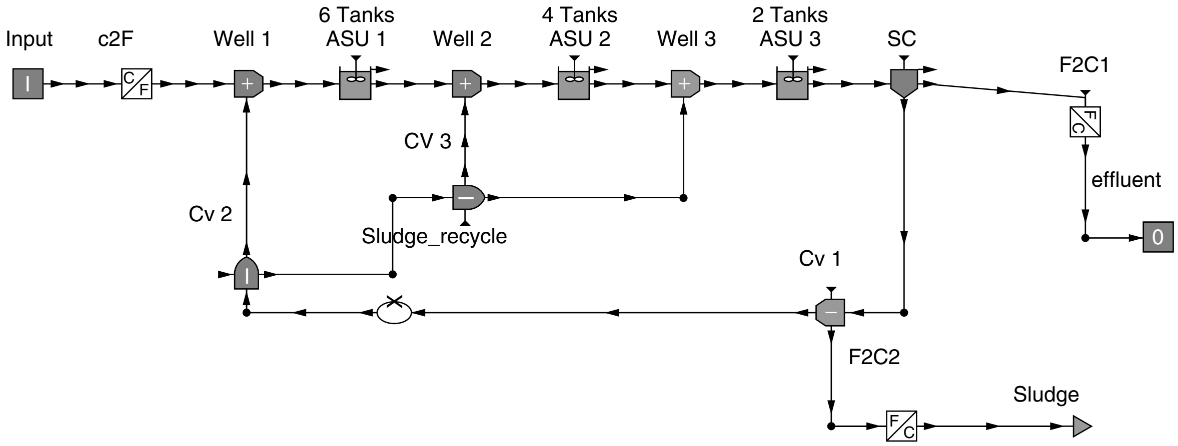

Figure 3. ORBAL plant configuration in WEST (*Source*: Dynamic calibration of the Orbal extended aeration plant by Peter A. VanRolleghem and H. Gucu Insel, Biomath Department, University of Ghent, October, 2002).

where N = number of compartments;
Q_S = flow, m^3/s;
L = length, m;
W = width, m; and
H = depth, m.
R = RAS ratio;

This formula was first published by Chambers (1). The units have to be in the overall range of the following:

$$28 < L < 500$$

$$2 < B < 20$$

$$2.4 < H < 6$$

$$0.7 < R < 1.5$$

$$1.3 \text{ hours} < t < 3 \text{ hours}$$

where $t = 3600\ Q\ (1 + R)$.

The following example may provide some guidance.

Recently, we had to model an ORBAL plant using WEST (Fig 2). The ORBAL has three concentric circles and a number of aerators with complex flow patterns because there is a submerged opening or, in some cases, a wall opening between the concentric tanks to allow the waste to pass from the outer tanks to the inner tanks.

The purpose of the figures is to introduce the reader to a practical application of the consideration of reactor hydraulics. In the ORBAL, there is a natural break point for each of the series of ORBAL channels, and those are the aerators (Fig. 3). The location of the aerators naturally divides the channels into logical units because of reaeration considerations. It can be argued that the channels could be divided into twice as many tanks for more accurate modeling, where the first tank would reflect the aeration input by the aerator and the second tank would reflect the lack of aeration input, which might be a better model, but it is definitely twice as complex and will require at least twice as long to compile and run. It may or may not be worth the effort.

Step 4: Laboratory and Other Data Organization

The objective is to gather enough data to be able to make an estimate of the magnitude and change in the flow sufficient to characterize the waste stream and its elements.

Depending on the model you are planning to use, you may have to go into the laboratory and obtain additional information. The number of samples and complexity of the sampling program is up to you and the budget you have available. We have observed everything from 12–15 samples run to establish some basic correlations, to a complete sampling campaign using automated equipment that will allow you to collect and analyze up to six sampling points and multiple analyses for each sampling location. This latter equipment program is described by Dr. Bruce Beck in his Environmental Process Control Laboratory or EPCL. The web address for the EPCL is http://hilbert.forestry.uga.edu/epcl/issues&info/flowchart.html.

It is difficult to provide specific guidance on the sample reliance for an unknown waste stream, but it would be nice if the laboratory data one obtained were reproducible to within about 10–20%. The entire discussion of precision and accuracy and the number of samples required therein is outside the scope of this paper. For a discussion of the issues involved in sampling and analysis, see Ref. 2.

Here are some suggestions for running the ASM1 testing and ASM2 and ASM2d testing from a proposal to a client. For additional guidance, you will want to see the descriptions of the models themselves.

> Any modeling or characterization effort requires a substantial amount of data. In this instance, we will probably need access to the plant analytical and operating records, chemical addition, and other records for at least 6 months, and perhaps a full year. The scope of the request is somewhat more extensive than the description might indicate, as it includes such routine operating data as the pump characteristics and rate, hours of operation, timing of the operations, aerator horsepower and hours of operation for each day, etc. The data should also include the quantity and type of chemicals used in various parts of the plant.

> Wastewater characteristics are divided into several elements. The principal elements include
>
> - Total and filterable COD
> - Total and filterable TKN
> - Total ammonia and nitrate
> - TSS & VSS
> - Total phosphate, filterable phosphate, and orthophosphate
> - Alkalinity
> - Volatile fatty acids (measured as acetate) (only for ASM2 and ASM2d)
>
> Analyses should be run in parallel with routine influent and effluent analyses for a period sufficient to determine reliable parameter variation and fractionation with routinely measured variables.
>
> A sampling campaign between 1 and 2 week long is suggested for the wastewater characterization study. The study should collect and analyze daily composite samples of influent and effluent. The study should be conducted in parallel with the routine sampling data being collected at the plant now.

Automatic sampling equipment that collects hourly grab samples of water and wastewater is often as good as can be obtained in a sampling campaign. Daily composite samples can be used but are often unreliable because the waste stream fluctuates with time and composite data will mask the diurnal and other variations.

Flowmeter readings are often unreliable, even when the flowmeter works. Calibration and inspection is suggested.

For internal calibration, you will need some data relating to TSS and VSS (filtered and unfiltered in various parts of the plant), along with DO measurements, and possibly some respirometry data, recycle rates, sludge levels in the clarifier, sludge wasting data, and just about everything you can imagine that an operator would need to run the plant properly. The trouble is that the data do not often exist or exist in the wrong form.

An example might be the notation in the plant operating log—“wasted sludge for two hours”. That tells you that the operator wasted sludge at between 1.5 and 2.5 hours, but nothing else unless you have either the valve settings and the MLSS at the time of the wasting.

If you are fortunate, you will find that he took an MLSS sample immediately before or after the wasting. If not, you may have to guess from the pump flow rate and talking to the operator. The key is that the operators almost always have a favorite method of operation that can often be recovered. They may know that if they turn the valve wide open, something will happen that will cause them work down the way, and so they leave the valve partially shut so that they do not have to clean up the floor of the sludge treatment facility.

The operation of the aeration equipment is often manual as well. It is safe to assume that about the only instrumentation you may find is the flowmeter, and that may not even work.

Generating the Flows When You Do Not Have the Data. When you have only BOD data or BOD, COD, and TSS data, WEST and some other programs have both a BOD transformer and/or a BOD/COD transformer that can be used to fractionate the flow into the necessary components. Remember the cautions expressed on letting a program fractionate the data for you.

If you have little data and have to generate dynamic and/or diurnal flow patterns from your source, you may want to use a sinusoidal pattern to generate the data. All good books on environmental engineering have some form of generic flow pattern for domestic wastewaters. The flows are often highest between 9 A.M. and 4 P.M. and lowest in the early morning hours when most people are asleep. Often there is a secondary peak in flow during the dinner and early evening hours when food preparation is the greatest.

You may want to look at your time data when it was collected from the influent and try to fit a time curve with each flow and concentration element to see if there is any variability in the data and determine whether you need to have the biosolids and chemical composition run counter or with the hydraulic basis. The following example may help to explain this point:

> Assume that a process discharges a uniform concentration of material and the flow varies. Then the concentration of contaminants would vary directly with the flow.
>
> If, however, the process discharged at a constant rate and contaminant level and if we add periodic boiler blowdown and filter backwash to the waste stream and some kitchen wastewater (which peaks from about 1–2 hours either side of midshift), then the flows and the concentration may vary inversely with each other or may spike at midshift. It may depend on the quantity of blowdown and backwash.

Getting the Hydraulics and the Tankage Correct. As part of the overall process and before you set up the flow sheet, you will need to address the issue of hydraulic similitude for the system, which really compares how well the model you are using models the hydraulic performance and hydraulic mixing of the system you are modeling. The best way to determine how well your system is performing is to conduct dye or tracer studies on the tank system. The purpose of the dye testing is to find out whether you are operating in a plug flow or complete mix or some other regimen. The differences among the types of reactors were discussed earlier in this article.

If you cannot perform dye testing to determine the mixing requirements, you should examine the system you are modeling carefully. There may be some logical divisions in the system that suggest that it should be modeled using a specific number of tanks. For example, an extended aeration system, such as an oxidation ditch, may have a number of aerators, and the physical positioning of the aerators may suggest a logical number of tanks to use for modeling the flow.

Each tank or tank division will have its own aeration capacity (*Kla*) that can be adjusted. Multiple aerators may suggest a configuration that needs more than one tank and an interlaced flow diagram to suggest the right type of flow connections, which is a matter that is settled by the judgment of the engineer.

At this point, it may be a good idea to rough out the flow sheet for your model, which is also a first

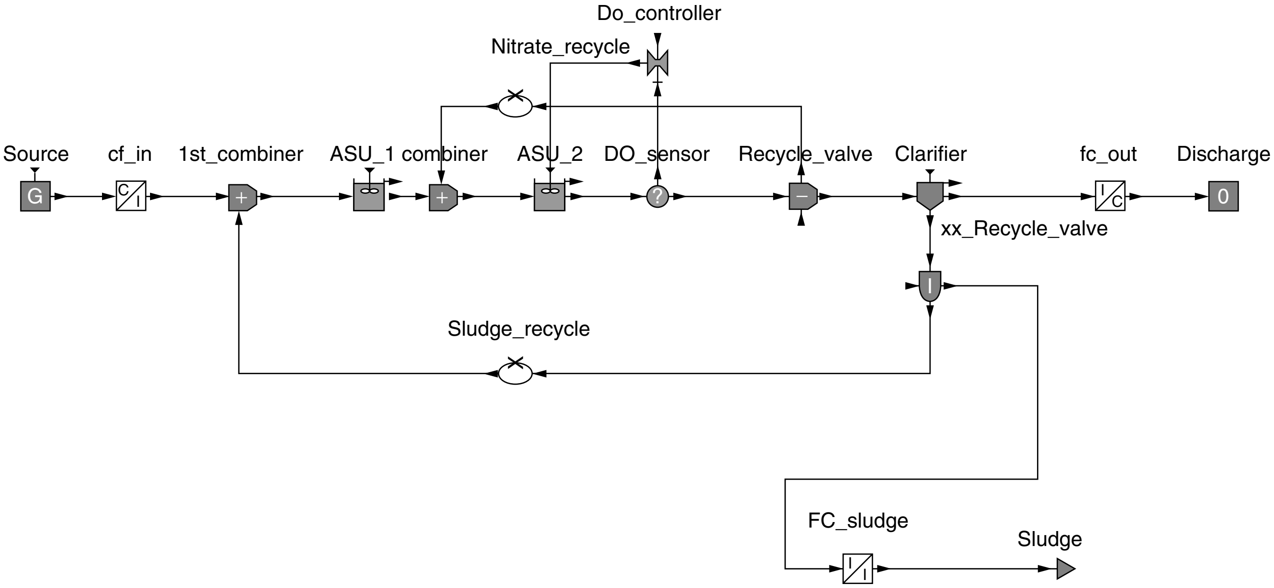

Figure 4. Labeled flow sheet in WEST.

draft of the process and instrumentation diagram (P & ID). It may not be detailed but rather simple. You can always fill in controls and details later when you set up the compositional model. Clarifier selection is also an important choice for both the model and the complexity of the models.

A simple flowsheet is shown in Fig. 4.

Start with an elementary drawing, and put the basic icons in place. Annotate it with the details you need to prepare the drawing of the plant, so that it reflects the P & ID as shown above. Then start your process simulator, and begin your work.

After you have completed the physical placement of the model elements and the selection of the model, you still have to several steps to go.

Step 5: Model Compilation and Setup

Setting up a model is a multipart process:

1. Initial definition of the model critical model parameters
2. Initialization of the variables
3. Setting up the integrator

Start by initializing the model. First, start with the parameters. Most of them are biological parameters that you will not have to adjust and probably should not adjust.

Concern yourself with the physical parameters first. You will want to look at the physical parameters and set things like tank volumes and initial guesses to determine the *Kla* (oxygen transfer and uptake rates), suspended solids levels in the tanks, and various physical parameters.

You will also have to go through and estimate the initial operating conditions for the reactors by going into the variables and filling them out.

One of the other types of errors that can be generated in ASM1, particularly, is *negative ammonia*. Negative ammonia is caused by an unbalanced waste in the model. The configuration of ASM1 is such that it does not have a “trap” for negative ammonia, and what the model is really saying is that the feed conditions are such that the ammonia is consumed at a faster rate than it is supplied by degradation of the organic material in the waste. Obviously it is an impossible condition, but the model does not know the difference. Sometimes, the autotrophs in the waste are too high, and a simple adjustment in the feed will correct that problem.

This is one reason why it is often more convenient to set up and run a steady-state model for the initial run. The steady-state system allows you to balance the model before you begin dynamic modeling.

After the steady-state model is balanced and running properly and after you have set the various values at the approximate levels you need for your initial conditions, then it is time to go back and recalibrate the model using your successful run data from the steady-state case. The purpose of this step is to bootstrap the model with the values you will be using rather than wait for it to reach equilibrium.

Integrator Settings and Data Collection. All equations in the IWA models are expressed as rate equations that need to be integrated. The simulator package you are using does this. In some packages, you have a choice of how fine you want your integration settings. On other simulators, you may not. Remember that if you use too large an increment, your program may be fast, but you sacrifice accuracy. Fine steps in the integrator provide nice smooth curves but take additional computation time and can produce very large effluent files.

Step 6: Input and Output File Preparation

The setup of the influent file is strongly dependent on which model is being used. Some models use comma delimited files, other tab delimited files, and some use an input and output from Excel files.

Step 7: Initialization of the Model Parameters and First Runs

The first run of a model may produce unexpected results. The unusual results are not unexpected, and to some extent, that is why one sets up a static model first. When the static model has been evaluated and balanced, then it is necessary to use the final values for variables and modify them to represent starting variables for the first runs.

What to Balance or Adjust. A limited number of things can be adjusted in most models:

- Primary clarifier underflow rate (removes solids).
- Oxygen transfer rates (*Kla* values) can be adjusted in each tank.
- Flow proportion in each tank (if flow sheet permits).
- Recycle rate on loops (can take almost infinite adjustment).
- Secondary clarifier underflow (increases sludge return and improves effluent solids).
- Sludge wasting rate (decreases solids in the system).
- *Adjustment of the rate coefficients and parameters is not recommended on initial runs!* (Adjusting these coefficients prematurely may mess up your results in later runs.)

What to Key in on During Your Modeling. Key in on the same things that the plant operator keys in on: suspended solids, oxygen levels, sludge wasting rates, hours of operation of certain processes, and flow rates. Look specifically at weekends because many plants are essentially unmanned on weekends.

These are the operator's only tools. The two or three hardest to measure are, frequently, the MLSS values in the tanks, the oxygen levels in the tanks when and where it is measured, and any other chemical parameters.

When you have the model balanced for steady-state flows, then start dynamic modeling. If you are fortunate enough to have good quality data on the plant, you may be able to get traces where peaks and valleys in the model results can be compared with the peaks and valleys in the performance data for the plant. It is almost like curve matching, but you are looking to see that any disturbances in the plant (and there will always be some) match disturbances in the model. The results may be very interesting; the peaks may not match in height, but they should be at about the same times and for the same duration as obtained from the plant data.

Step 8: Parameter Adjustment

Adjustment of the parameters is often as much art as science. It needs to be done only after a detailed analysis of the waste and the characteristics and after evaluating the modeling results compared with a case where there are sufficient data to enable comparison.

From the literature, the one case where parameter adjustment may be necessary is in phosphorous modeling. The sensitivity of the various coefficients and uptake rates can affect the storage of phosphate and the final results. The adjustment of parameters should be undertaken only after careful consideration and experience and probably substantial laboratory testing and/or a number of model runs to compare results with actual performance.

Unless you have specific chemical data or parametric data to indicate that a specific change in a model is desirable, do not plan on changing the given model parameters as it may cause problems later, which is especially true for dynamic modeling. If you do not have any good indication of what and where to change things, try leaving them alone and make adjustments only as a last resort after you have tried everything else and need to make those adjustments based on dynamic data or specific knowledge of the plant.

FINAL NOTES

Look carefully at your data and your modeling system. If you understand it and the way it is put together, fine! If you do not understand what is happening, and why, you are like the student who says, "Don't bother me with the theory, just show me where to plug in the numbers!". That is uncertain territory and can cause difficulties for the modeler. Unexpected results do occur and one has to understand both the results and how they relate to the physical model.

Acknowledgments
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BIBLIOGRAPHY

1. Chambers, B. (1992). Design methodology for optimization of aeration efficiencyin activated sludge plants. In: *Proc. 6th Fourm Appl. Biotechnol.*, Med. Fac. Ladnbouww, Univ. Ghent, 17, 1631–1642.
2. Russell, D.L. (1980). Monitoring and Sampling liquid effluents. *Chem. Eng.* October.

NEW YORK CITY HARBOR SURVEY

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The New York City Harbor Survey, begun in 1910 and conducted continuously since 1912, may have the longest operational history of any annual water quality monitoring program in the world. Initiated to document decaying water quality in New York Harbor and, therefore, cause changes in waste management practices, it now demonstrates the effectiveness of New York City's comprehensive wastewater treatment program. Data from the 53 stations of the Survey (some of which are monitored year-round using the dedicated Harbor Survey vessel) show general compliance throughout the Harbor with New York State water quality standards today, despite historical pollution problems.

INTRODUCTION

New York City is composed of islands and shorelines. The proximity of so much water to so many people has meant that much of the wastes produced by its residents during the past 300 years has been discarded into the waterways (1).

One impetus to understanding the impacts of water pollution has been to document damage to the environment (and associated threats to human health) from these releases. It is easier to provoke action when the magnitude of the problem is displayed. This concept was understood by the New York City Metropolitan Sewage Commission in 1909. To quantify conditions in the Harbor, parts of which were described as open sewers, where swimming was called a dangerous health hazard, and where a once unmatched oyster industry was soon to be abandoned, the Commission established the Harbor Survey (2).

The first New York Harbor Survey was undertaken in 1910; samples have been collected every year since 1912 (generating 91 years of data as of 2001). This appears to make it the longest continuously conducted water quality monitoring program in the world.

PHYSICAL SETTING

Water quality is determined by the amount of chemical contaminants present and by their fate and transport. New York Harbor (Fig. 1) has a complex physical oceanographic setting that must be understood to interpret sampling data.

Generally, the Harbor can be considered a drowned river valley (3), formed as the continental glaciation receded from Staten Island 20,000 years ago (4). The Hudson River is tidal to the Troy Dam, 150 miles north of Manhattan, and its flow is entirely freshwater only for the 90 miles north of Poughkeepsie. Flow over the Troy Dam (90% of the freshwater in the river) has an average annual peak of 40,000 cubic feet per second (cfs), usually in spring due to snowmelt and greater groundwater discharges. The other major rivers feeding the Harbor (the Passaic and Hackensack Rivers into Newark Bay and the Raritan River into Raritan Bay) contribute a quarter of the Hudson River flow (5,6).

Generally, the Harbor is a partially stratified estuary (the Hudson River, Upper Bay, Lower Bay, Raritan Bay, Newark Bay, the eastern portion of the Upper East River, and western Long Island Sound), where tidal currents mix salt water into riverine water. The earth's rotation causes concentration of less dense (fresher) water on the west side of each waterbody (7). Mixing of tidally advected salt water dilutes the freshwater, so that flows at The Battery often exceed 400,000 cfs (8). Strong tidal currents can break down the stratification caused by the Coriolis effect, especially in the Upper and Lower Bays (9).

However, this straight-forward depiction of water flows is complicated by the multiple ocean connections (most estuaries have only one), where the Upper Bay connects to the Atlantic Ocean through the Lower Bay and also through the East River into Long Island Sound and to the Ocean. In addition, minor, well-mixed tidal straits, including the Harlem River (connecting the East River to the Hudson River), the Kill van Kull (connecting Newark Bay to Upper Bay), and the Arthur Kill (connecting Newark Bay to Raritan Bay), are not partially stratified. Jamaica Bay, which tends to be well mixed, and although not contiguous with the other parts of the Harbor, is also considered part of the Harbor (8).

Flow patterns in the Lower East River are not simple. Flow is driven by the mismatch in tides between the Upper Bay and Long Island Sound. Velocities can reach 4.5 knots (still much less than 10 knot currents once measured before a large rock was removed) (10), and it tends to be well mixed. There are six water pollution control plants (WPCPs) along the East River, and they input 750 million gallons per day (MGD) of effluent [15% of the total flow of 6 billion gallons per day (BGD)] (11).

Jamaica Bay also contains an abundance of sewage effluent; its natural tributaries were captured by sewers during urbanization. Up to half of its water can be sewage effluents (12), partially because water residence time is more than a month (up from 11 days due to dredging, which increased the depth of the Bay from 3 feet to 16 feet) (13). The Bay is generally shallow enough that stratification caused by summer insolation is of short duration due to mixing by winds (12).

New York Harbor was once famed for its natural beauty and seafood resources (14). The physical changes in the Harbor have caused impacts which in many cases cannot be differentiated from those from pollution. The predredged Harbor was 18–20 feet deep (9). Ships sailed Long Island Sound to avoid the shoals of the Lower Bay (10). Channels criss-cross the harbor, at depths as great as 45 feet, and plans are to increase some to more than 50 feet (15). The Harbor used to hold gently sloping coastal marshes and mudflats but now has hardened, steep-sided, deepened channels. Losses include 61,000 acres of tidal marsh (17), and fills have created 7,000 acres in the City (18). The islands in the Harbor have been removed, expanded, connected to other islands, and otherwise altered (19).

SOCIOLOGICAL SETTING

New York was attractive to immigrants in colonial days because of its natural resources. Its location made it (and the Hudson Valley) the key site of the Revolutionary War. The construction of the Erie Canal made New York City the economic capital of the United States (20). New York Harbor and water power available in New Jersey made the region a center of the Industrial Revolution and, ultimately, the country's economic engine (21).

Thus, New York City and its environs grew with time. It had 25,000 residents at the turn of the nineteenth

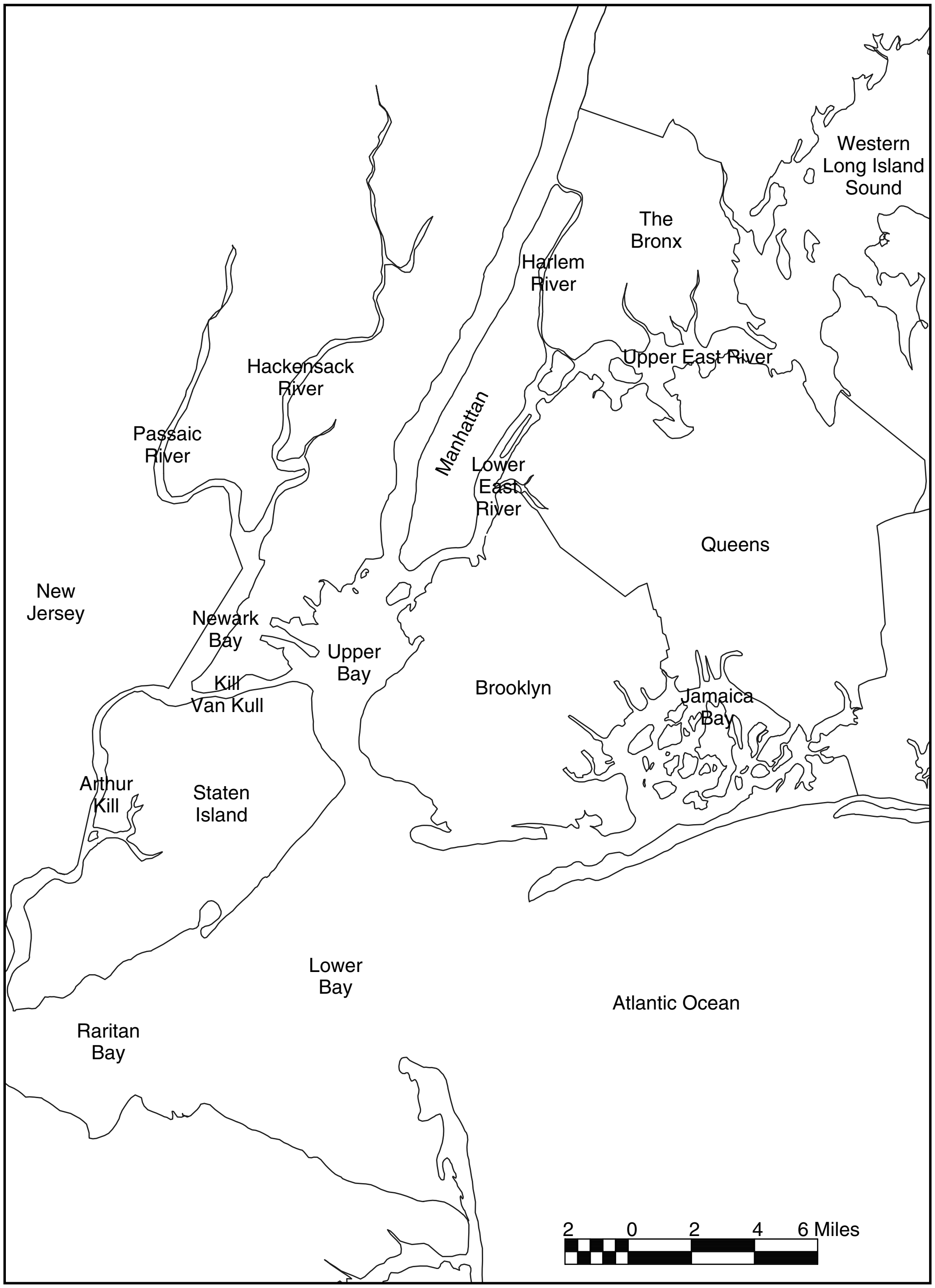

Figure 1. New York Harbor.

century (1). Population in the Harbor drainage area exceeded four million by the twentieth century (22) and more than 20 million at the turn of the twenty-first century (23). These multitudes produced solid and septic wastes, and the Harbor was the local disposal point since the 1600s. City solid waste was deposited into the Harbor or nearby waters until the early 1900s (24). Untreated sewage, likewise, was sent to the Harbor for dilution and transport away from land. As of 1905, 5.3 million people in New York and New Jersey sent sewage to the Harbor (25), augmented by industrial effluents (26).

In 1910, seven small WPCPs in New York City processed approximately 19 MGD, but the "process of purification has not materially reduced either the suspended matter or matters in solution." Typhoid outbreaks occurred in 1904 and 1918. In 1925, oyster fishing was banned. The result was construction of a sewage system for the City in the 1930s (25), although complete waste treatment was not achieved until 1989 (27).

CURRENT NEW YORK CITY SEWAGE TREATMENT INFRASTRUCTURE AND PROGRAMS

The 8.0 million residents of New York City are served by 14 WPCPs that generate 1.3 BGD of effluent (Table 1). All of these plants achieve secondary treatment (defined as 85% removal of BOD and TSS) (28).

New York City uses a combined stormwater–wastewater collection system of 1930s' design (1). Its engineers were not anticipating modern pollution controls for stormwater but intended to conduct as much water management as possible using the least amount of piping (which nonetheless totals 6344 miles) (28).

The combined system is stressed in the rain. To prevent volume overloads at the WPCPs, wastewater bypasses the plants. The combined sewer overflows (CSOs) that result remain a serious pollution concern. Water conservation measures led to City-wide decreases in consumption from 1.4 BGD in 1990 to 1.24 BGD in 1999, despite a population increase of 400,000. The reductions mean that dry weather flows to the WPCPs use only 70% of the system's capacity. Thus, the WPCPs can now manage more than 50% of the runoff (annually), and CSOs have decreased (29). The City has further committed to a $1.5 billion program to build CSO abatement facilities (28).

In the 1970s and 1980s, CSOs were the source of a local problem: floatables—washup of medical wastes on local beaches. Close examination of the wastes and transport calculations showed they were washed off City streets into CSOs (30). The problem has diminished due to the capture of materials in the Harbor and at catchbasins and an emphasis on street-cleaning (28).

The NYCDEP has decreased the toxicity of its sewage effluent through source control—700 sewer users have decreased metals loadings from 3000 pounds per day (1974) to 205 pounds per day. The Shoreline Survey Program monitors storm sewers for dry weather flows and then tracks down illegal discharges. The Sentinel Monitoring Program uses coliform to identify contaminated outfalls for investigation and remediation (28).

Table 1. NYC Water Pollution Control Plants

WPCP	Primary Treatment	Secondary Treatment	Last Upgrade	Current Capacity (MGD)
Coney Island	1936	1995	1995	100
Wards Island	1937	1937	1997[a]	275
Bowery Bay	1939	1942	1973	150
Tallman Island	1939	1939	1976	80
Jamaica	1943	1943	1971	100
26th Ward	1944	1951	1990	85
Hunts Point	1952	1952	1979	200
Owls Head	1952	1952	1995	120
Rockaway	1952	1962	1971	45
Port Richmond	1953	1978	1979	60
Oakwood Beach	1956	1956	1978	40
Newtown Creek	1967	1967[b]	1967[b]	310
North River	1986	1991	1991	170
Red Hook	1987	1989	1990	60

[a] Additional tanks installed in 1998 increased capacity by 25 MGD.
[b] Currently operated as modified aeration. Upgrade to full secondary operation planned for 2007.

THE HARBOR SURVEY

Six stations were sampled in 1910. Sampling was continued in 1912 and has been conducted each year since. A special section of the NYCDEP, the Marine Science Section, conducts the Survey. It has its own 55-foot, aluminum-hulled, twin-engine diesel research vessel, the HSV OSPREY. The OSPREY has an onboard laboratory and is crewed by six to eight. It sails 5 days per week from June to September, when all 53 stations (Fig. 2) are sampled biweekly (a subsection of stations is sampled monthly, year-round) (28).

The Survey aims to determine the impacts of sewage treatment on the Harbor. Therefore, the parameters keenly tracked are coliform, dissolved oxygen (DO), and nutrients, especially nitrogen compounds. Temperature and salinity data are collected and used to determine the physical structure of the Harbor waters, placing laboratory results in context. Ecological data (chlorophyll *a* concentrations and some phytoplankton identification) are also collected. Beginning in 1985, samples were collected from the water surface (within 1 meter of the surface) and from the bottom of the water column (1 meter from the bottom). Statistical analyses of the data showed strong correlations between top and bottom data; beginning in 2001, the Survey collected field parameters (temperature, pH, turbidity, salinity, and DO) from top and bottom waters and water quality samples of surface water only (28). Before 1985, nearly all lab data were generated from composite samples (27).

DOCUMENTED WATER QUALITY TRENDS

Harbor Survey data have been used to address two basic questions:

- How bad was water quality? and
- Has a resolution of sewage-related pollution been reached now?

Suszkowski (25) analyzed the first 60 years of Survey data, using basinwide averages of summer data (ie., all summer sample results from the Hudson River were summed and averaged to generate one "Hudson River" value) and Harbor-wide averages (the mean of all basins). The findings were that the mean DO, measured by saturation percent, decreased from approximately 80% of saturation in 1910 to 40% in the late 1930s. In the 1960s, the DO slowly increased to 70%. The lowest values were found in the inner areas of the Harbor. The DO trends were linked to biological oxygen demand loadings from raw sewage and WPCP effluents. The correlation indicated that organic loading from raw and treated sewage was the prime factor in decreased DO levels.

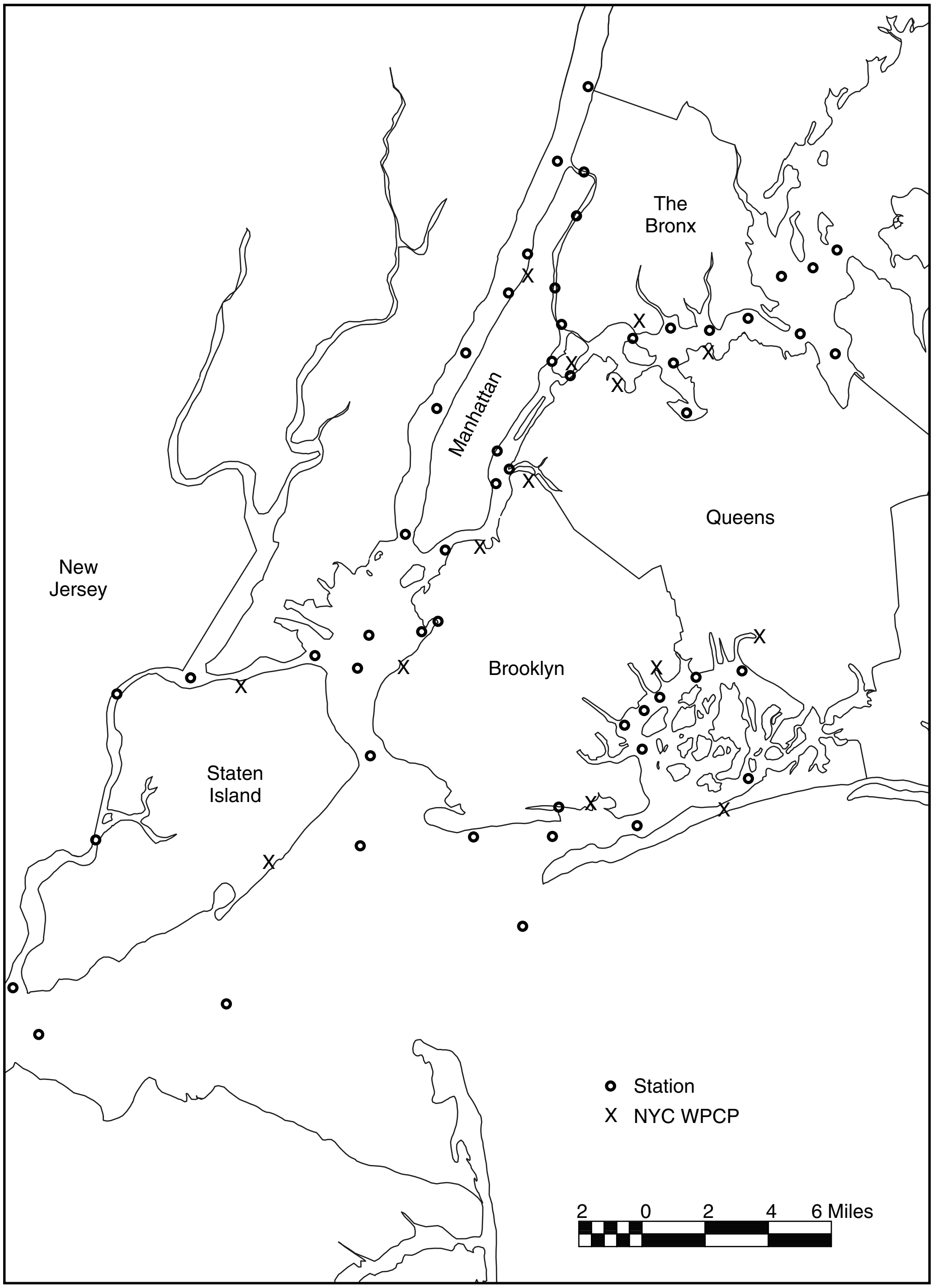

Figure 2. Harbor survey stations.

Beginning in 1989, NYCDEP began to self-report the results of the Survey; that year also marked the end of routine disposal of untreated sewage. NYCDEP had confidence that the Survey would show improvements in water quality, and so these reports could serve as public outreach to tout City environmental programs (27). Beginning in 1999, academic institutions prepared the longer of the two annual reports; the intent was an increase in rigor and a broadened perspective.

The NYCDEP summary reports show improving trends for all analytes nearly harborwide. The improvements have been so great that New York State water quality goals are being met routinely, as measured by DO and fecal coliform summer means, reported both as waterbody means and individual sample results (31).

SUNY at Stony Brook used a more sophisticated statistical analysis to identify trends. Its methodology also resulted in determinations of improved water quality since

1985. Order of magnitude reductions in fecal coliform and striking increases in the DO for nearly every station were found, and most of the linear trends were statistically significant at $p < .05$. The improvements were greatest in the late 1980s, probably from large reductions in raw sewage inputs as the entire City was connected to sewage treatment (28).

THE HARBOR SURVEY AND PUBLIC POLICY

One region where improvements in water quality are not apparent is western Long Island Sound. Long term trends for bottom DO do not show any improvements since the 1940s and may exhibit a declining trend (28). The Long Island Sound Study has identified hypoxia (low bottom DO) as the most serious problem in the Sound. A policy was set to reduce nitrogen inputs to the Sound by nearly 60%, intending to force higher bottom DO by reducing the impact of eutrophication (32).

The New York City East River WPCPs export most of their effluent (and associated nutrient loads) to the Sound. The Sound Study management plan requires multibillion dollar upgrades of the WPCPs to achieve tertiary treatment levels to reach agreed-upon nutrient reductions (33). Data from plant operations and the Harbor Survey show that 30% reductions in nitrogen loadings during the period 1992 to 2000 (caused by operational changes) concur with statistically significant declines in nitrogen concentrations in western Long Island Sound. However, the pattern of water column nitrogen concentrations does not correlate with changes in WPCP nitrogen releases, even using time lags of several months—in addition to the absence of increases in bottom DO in western Long Island Sound (28). The simple conceptual model, used by the Sound Study, that elevated wastewater nutrient concentrations in the East River cause increased phytoplankton concentrations in western Long Island Sound, leading to reductions in bottom DO due to microbial consumption of the deceased plankton (32), appears to be inadequate to explain the data. Cleorn (34), in an analysis of estuarine responses to eutrophication, showed that local physical conditions and biological community structures determine the particular reaction of waterbodies to elevated nutrient inputs. NYCDEP remains hopeful that its monitoring data may allow the City to find another way of addressing this complicated problem of low bottom DO [a situation that affects 25% of all estuarine waters in the northeast United States each summer (35)].

CONCLUSIONS

New York Harbor, a complex estuary, has been polluted by waste disposal for more than three centuries. For nearly 100 years, New York City has conducted a water quality monitoring program to measure impacts from sewage and WPCP effluent. This program, the Harbor Survey, documented the impacted water quality found in the Harbor before the City's wastewater treatment system was completed. Monitoring since 1985 has measured impressive improvements in parameters of concern. The program documents the effectiveness of the City's sewage treatment program, and it also serves as a public outreach and education tool and a means of helping to determine root causes of serious environmental problems in the Harbor.

BIBLIOGRAPHY

1. Melosi, M.V. (2000). *The Sanitary City*. The Johns Hopkins University Press, Baltimore, MD.
2. Metropolitan Sewerage Commission. (1912). *Present Sanitary Conditions of New York Harbor and the Degree of Cleanness which is Necessary and Sufficient for the Water*. Report of the Metropolitan Sewerage Commission, Wyncoop Halenbeck Crawford, Co., New York.
3. Pritchard, D.W. (1967). What is an estuary: physical viewpoints. *Estuaries*. AAAS Pub. 87, pp. 3–5.
4. Sanders, J.E. (1974). Geomorphology of the Hudson Estuary. In: *Hudson River Colloquium. Ann. NY Acad. Sci.* O.A. Roels (Ed.). V. 250, New York, pp. 5–38.
5. Moran, M.A. and Limburg, K.E. (1985). The Hudson River ecosystem. In: *The Hudson River Ecosystem*. K.E. Limburg, M.A. Moran, and W.H. McDowell (Eds.). Springer-Verlag, New York, pp. 7–39.
6. USGS Water Resources of New Jersey website. http//:nj.usgs.gov.
7. Oey, L.Y., Mellor, G.L., and Hires, R.I. (1985). Tidal modeling of the Hudson-Raritan estuary. *Estuarine Coastal Shelf Sci.* **20**: 511–527.
8. Abood, K.A. (1974). Circulation in the hudson river estuary. In: *Hudson River Colloquium. Ann. NY Acad Sci.* O.A. Roels (Ed.). V. 250, New York, pp. 39–111.
9. Duedall, I.W., O'Connors, H.B., Wilson, R.E., and Parker, J.H. (1979). *The Lower Bay Complex. MESA New York Bight Atlas Monograph 29*. New York Sea Grant Institute, Albany, NY.
10. Swanson, R.L, Parker, C.A., Meyer, M.C., and Champ, M.A. (1982). *Is the East River, New York, a River or Long Island an Island?* NOAA Technical Report, NOS 93, National Oceanic and Atmospheric Administration, Rockville, MD.
11. Blumberg, A.F. and Pritchard, D.W. (1997). Estimates of transport through the East River, New York. *J. Geophys Res.* **102**(C3): 5685–5703.
12. HydroQual, Inc. (1998). *A Water Quality Model for Jamaica Bay: Calibration of the Jamaica Bay Eutrophication Model (JEM)*. HydroQual, Inc., Mahwah, NJ.
13. Swanson, R.L., West-Valle, A.S., and Decker, C.J. (1992). Recreation vs. waste disposal: the use and management of Jamaica Bay. *Long Island Hist. J.* **5**(1): 21–41.
14. Juet, R. (1609). The third voyage of Master Henry Hudson. In: *Collections of the New York Historical Society in the Year 1809*. V. 1. 1811. I. Riley, New York, pp. 102–145.
15. US Army Corps of Engineers New York District website. http://www.nan.usace.army.mil/harbor.
16. Squires, D.F. (1990). A historical review of changes in near-shore habitats in the Sound-Harbor-Bight system. In: *Cleaning Up Our Coastal Waters: An Unfinished Agenda*. M.T. Southerland and K. Swetlow (Eds.). Dynamac Corp., Rockville, MD, pp. 403–428.
17. Waldman, J. (1999). *Heartbeats in the Muck*. The Lyons Press, New York.
18. Squires, D.F. and Bone, K. (1997). The beautiful lake: the promise of the natural systems. In: *The New York Waterfront:*

Evolution and Building Culture of the Port and Harbor. K. Bone (Ed.). Monacelli Press, New York, pp. 16–33.

19. Swanson, R.L. and Squires, D.F. (2002). Ellis Island, New York and New Jersey. *New York Hist.* **83**(3): 248–270.
20. Adams, A.G. (1996). *The Hudson Through the Years*, 3rd Edn. Fordham University Press, New York.
21. Cunningham, J.T. (1978). *This is New Jersey*, 3rd Edn. Rutgers University Press, New Brunswick, NJ.
22. Suszkowski, D.J. (1990). Conditions in the New York/New Jersey harbor estuary. In: *Cleaning Up Our Coastal Waters: An Unfinished Agenda*. M.T. Southerland and K. Swetlow (Eds.). Dynamac Corp., Rockville, MD, pp. 105–132.
23. US Census Bureau website. http//:www.census.gov.main/www/cen2000.
24. Miller, B. (2000). *Fat of the Land*. Four Walls Eight Windows, New York.
25. Suszkowski, D.J. (1973). *Sewage Pollution in New York Harbor: A Historical Perspective*. Masters Thesis, SUNY at Stony Brook, Stony Brook, NY.
26. Mueller, J.A. (1990). Toxic inputs and fate in the New York-New Jersey Harbor, Bight, and Long Island Sound. In: *Cleaning Up Our Coastal Waters: An Unfinished Agenda*. M.T. Southerland and K. Swetlow (Eds.). Dynamac Corp., Rockville, MD, pp. 317–354.
27. Brosnan, T.M. and O'Shea, M.L. (1996). Long-term improvements in water quality due to sewage abatement in the lower Hudson River. *Estuaries* **19**(4): 890–900.
28. Swanson, R.L. and Tonjes, D.J. (2001). *The New York City 2000 Regional Harbor Survey*. P. Heckler, B. Ranheim, N-J. Yao, and B.W. Stephens (Eds.). New York City Department of Environmental Protection, New York.
29. Swanson, R.L. and Tonjes, D.J. (2001). Water conservation cleans Long Island Sound. *Clearwaters* **31**(2): 8.
30. Bell, T.M., Schubel, J.R., and Swanson, R.L. (1989). *Floatable Wastes and the Region's Beaches: Answers to Some Common Questions*. Marine Sciences Research Center Special Report 85, SUNY at Stony Brook, Stony Brook, NY.
31. NYCDEP. (2001). *2000 New York Harbor Water Quality Regional Report*. New York City Department of Environmental Protection, New York.
32. LISS. (1994). *The Comprehensive Conservation and Management Plan*. The Long Island Sound Study, Stamford, CT.
33. LISS. (1997). *Proposal for Phase III Actions for Hypoxia Management*. EPA 840-R-97-001. The Long Island Sound Study, Stamford, CT.
34. Cleorn, J.E. (2001). Our evolving conceptual model of the coastal eutrophication problem. *Mar. Ecol. Prog. Ser.* **210**: 223–253.
35. USEPA. (2000). *Ambient Water Quality Criteria for Dissolved Oxygen (Saltwater): Cape Cod to Cape Hatteras*. United States Environmental Protection Agency, Washington, DC.

NITRIFICATION IN THE ACTIVATED SLUDGE PROCESS

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There are two reduced forms of nitrogen that are of concern to wastewater treatment plant operators and state and federal regulatory agencies. These forms contain hydrogen and consist of nonionized ammonia or ammonia (NH_3) and ionized ammonia or ammonium ion (NH_4^+). Although ammonia and ammonium ions are both present in wastewater, the amount of each is dependent on the pH of the wastewater (Fig. 1).

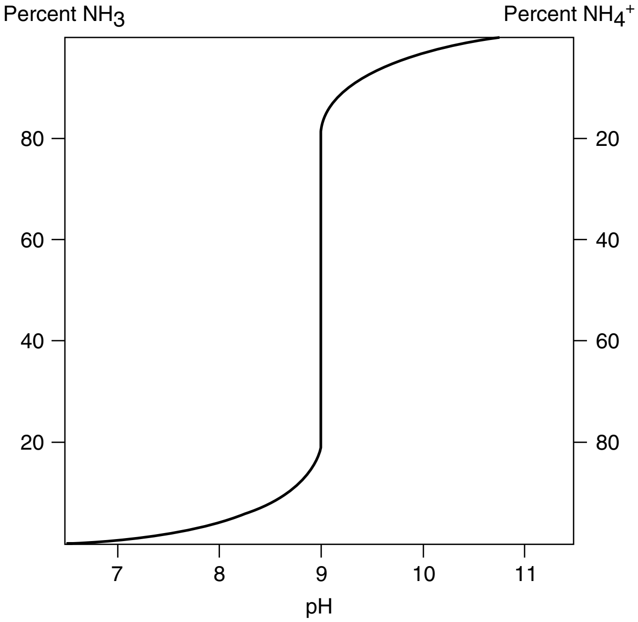

Figure 1. Relative distribution of ammonia and ammonium ions as determined by pH.

Wastewater nitrification is the biological oxidation of ammonium ions to nitrite ions (NO_2^-) (Eq. 1) or the biological oxidation of nitrite ions to nitrate ions (NO_3^-) (Eq. 2).

$$NH_4^+ + 1.5\ O_2 \xrightarrow{\textit{Nitrosomonas}} NO_2^- + 2\ H^+ + H_2O + \text{energy} \tag{1}$$

$$NO_2^- + 0.5\ O_2 \xrightarrow{\textit{Nitrobacter}} NO_3^- + \text{energy} \tag{2}$$

Nitrification occurs because nitrifying bacteria oxidize ammonium ions and nitrite ions in order to obtain cellular energy. There are two principal genera of nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*. Although both genera of bacteria are strict aerobic organisms, *Nitrosomonas* can oxidize only ammonium ions, and *Nitrobacter* can oxidize only nitrite ions.

There are four nitrogen-containing molecules that are involved in wastewater nitrification. These molecules include ammonia, ammonium ions, nitrite ions, and nitrate ions. Because nitrite ions are highly unstable, they usually do not accumulate in wastewater and are considered to be a short-lived intermediate molecules that are quickly converted to nitrate ions. However, there are operation conditions that do permit the accumulation of nitrite ions (Table 1).

Ammonium ions enter activated sludge processes from nitrogenous compounds that are found in domestic and industrial wastewater. Domestic wastewater contains urea, amino acids, and proteins. Urea and simple amino acids degrade in the sewer system through hydrolysis

Table 1. Operational Conditions that Permit the Production and Accumulation of Nitrite Ions

Operational Condition	Description
Depressed temperature	$\leq$15 °C
Limiting process conditions	Change in pH Inhibition Low dissolved oxygen level Slug discharge of soluble cBOD

and deamination, respectively. Once degraded, these compounds release ammonium ions. Due to the hydrolysis of urea and deamination of simple amino acids, most municipal activated sludge processes contain 25–30 mg/L of influent ammonium ions.

Stable amino acids and proteins degrade in the aeration tank and release ammonium ions. Urea, amino acids, and proteins are organo-nitrogen compounds. Additional organo-nitrogen compounds that are found and degraded in aeration tanks include surfactants and polymers. Ammonium ions and organo-nitrogen compounds that release ammonium ions can be found in many industrial wastewaters that are discharged to activated sludge processes (Table 2). Nitrite ions and nitrate ions that are found in activated sludge processes usually are produced in the aeration tank. However, there are some industrial dischargers of nitrite ions and nitrate ions (Table 2).

Activated sludge processes that are required to satisfy an ammonia discharge limit or total nitrogen discharge limit must nitrify. Although many activated sludge processes are not required to nitrify, operators of these processes may promote nitrification to ensure process control or use the nitrate ions produced through nitrification during controlled anoxic (denitrification) periods to obtain improved floc particle structure and decrease operational costs (Table 3). Finally, many activated sludge processes that are not required to nitrify may "slip" into nitrification. Regardless of permit requirements, activated sludge processes may enter an undesired form of nitrification that results in increased operational costs, process upsets, and permit violations.

Regardless of the presence or absence of a nitrification requirement, nitrogenous compounds are of concern to operators of activated sludge processes (Table 4) and regulatory agencies (Table 5) due to their undesired impacts on the activated sludge process and receiving body of water, respectively. The nitrogenous compounds of concern consist of inorganic compounds (NH_3, NH_4^+, NO_2^-, and NO_3^-) and organic-nitrogen compounds (total kjeldahl nitrogen or TKN).

There are several forms of nitrification that can occur in activated sludge processes (Table 6). These include one complete and four incomplete forms. The identification of the form of nitrification that occurs in the activated sludge process is of value to an operator to ensure acceptable nitrification and correct undesired incomplete nitrification.

If nitrification occurs as incomplete #3 or incomplete #4, nitrite ions are produced. The accumulation of these

Table 2. Industrial Discharges of Ammonium Ions, Nitrite Ions, and Nitrate Ions

	Nitrogenous Compound		
Industrial Discharge	NH_4^+	NO_2^-	NO_3^-
Automotive	X		
Chemical	X		
Coal	X		
Corrosion inhibitor		X	
Fertilizer	X		
Food	X		
Leachate	X		
Leachate (pretreated)		X	X
Livestock	X		
Meat	X		
Meat (flavoring)			X
Meat (preservative)		X	
Meat (pretreated)		X	X
Ordnance	X		
Petrochemical	X		
Pharmaceutical			X
Primary metal	X		
Refineries	X		
Steel	X	X	X
Tanneries	X		

Table 3. Benefits Obtained Through the Use of Controlled Anoxic Periods (Denitrification)

- Decrease sludge production
- Destroy undesired filamentous organism growth
- Improve process control: ensure adequate cBOD removal
- Improve process control: ensure the presence of a "healthy" biomass
- Return alkalinity to the treatment process
- Strengthen floc particles

Table 4. Nitrogenous Compounds of Concern to Operators of Activated Sludge Processes

Compound	Formula	Impact
Ammonia	NH_3	Toxicity
Ammonium ion	NH_4^+	Oxygen demand upon nitrification to NO_2^- Primary nitrogen nutrient for bacterial growth Toxicity upon conversion to NH_3
Nitrite ion	NO_2^-	Denitrification ("clumping") in the secondary clarifier Increased chlorine demand (chlorine "sponge") Oxygen demand upon nitrification to NO_3^- Toxicity
Nitrate ion	NO_3^-	Denitrification ("clumping") in the secondary clarifier Secondary nitrogen nutrient for bacterial growth Toxicity upon reduction to NO_2^- by *E. coli*
Organic-nitrogen	(TKN)	Oxygen demand upon degradation Release of cBOD upon degradation Release of nBOD (NH_4^+) upon degradation

Table 5. Nitrogenous Compounds of Concern to Regulatory Agencies

Compound	Formula	Impact
Ammonia	NH_3	Toxicity
Ammonium ion	NH_4^+	Oxygen demand upon nitrification to NO_2^- Toxicity upon conversion to NH_3
Nitrite ion	NO_2^-	Oxygen demand upon nitrification to NO_3^- Toxicity
Nitrate ion	NO_3^-	Causative agent for methemoglobinemia Primary nitrogen nutrient for aquatic plants Undesired growth of aquatic plants, especially algae
Organic-nitrogen(TKN)		Oxygen demand upon degradation Release of cBOD upon degradation Release of nBOD (NH_4^+) upon degradation

Table 6. Forms of Nitrification

Form of Nitrification	Mixed Liquor Effluent Filtrate Concentration, mg/L		
	NH_4^+	NO_2^-	NO_3^-
Complete	<1	<1	As great as possible
Incomplete #1	<1	As great as possible	<1
Incomplete #2	>1	<1	>1
Incomplete #3	<1	>1	>1
Incomplete #4	>1	>1	>1

ions in the activated sludge process is known as the chlorine "sponge," nitrite "kick," and nitrite "lock," because nitrite ions react quickly with chlorine and consume large quantities of chlorine. Approximately 13 pounds of chlorine are consumed per mg/L NO_2^- produced and accumulated per million gallons of flow. Nitrite ions in the activated sludge process interfere with the destruction of filamentous organisms in the mixed liquor or return activated sludge (RAS) via chlorination. Nitrite ions also interfere with the destruction of indicator organisms and pathogens in the final effluent via chlorination. To correct for the chlorine sponge, appropriate operational measures should be used to compensate for depressed temperature or correct for the responsible limiting factor.

Forms of incomplete nitrification occur as a result of depressed wastewater temperature (<15 °C) and limiting process conditions. Limiting process conditions include (1) change in pH, (2) a slug discharge of soluble cBOD, (3) temporary low dissolved oxygen level, and (4) toxicity. Additional factors that influence nitrification include alkalinity deficiency, decreased hydraulic retention time (HRT), and phosphorus deficiency. By identifying and correcting the condition responsible for incomplete nitrification, the return of acceptable nitrification should occur within 2–3 d.

The adverse impact of depressed wastewater temperature upon nitrification can be overcome through the use of appropriate changes in operational conditions. These changes include increasing the HRT of the aeration tanks, removing more colloidal and particulate BOD in the primary clarifiers, increasing dissolved oxygen concentration in the aeration tanks, and using bioaugmentation products. These products consist of commercially prepared cultures of nitrifying bacteria and organotrophic (saprophytic) bacteria that remove carbonaceous BOD quickly.

There are several significant operational conditions that impact nitrification in the activated sludge process. These conditions include temperature, mean cell residence time (MCRT), dissolved oxygen concentration, inhibition, alkalinity, and pH. Of these conditions temperature and MCRT are the most critical.

Due to the relatively small quantity of energy obtained from the oxidation of nitrogenous compounds, nitrifying bacteria reproduce very slowly. The generation times for *Nitrosomonas* and *Nitrobacter* under optimal laboratory conditions are approximately 8 and 10 h, respectively. In the activated sludge process the generation time of these organisms is estimated to be approximately 2–3 days. Therefore, high MCRTs are required at activated sludge processes to permit the growth of large numbers of nitrifying bacteria. However, warm wastewater temperatures provide for increased bacterial activity. Therefore, the number of nitrifying bacteria and the MCRT can be reduced. However, cold wastewater temperatures provide for decreased bacterial activity, and the number of nitrifying bacteria and the MCRT must be increased (Table 7).

Because nitrifying bacteria are strict aerobes, nitrification in the activated sludge process is influenced by dissolved oxygen concentration in the aeration tank. Nitrification is considered to proceed efficiently within the dissolved oxygen range of 2–3 mg/L. At dissolved oxygen concentration above 3 mg/L, nitrification may become more efficient, if carbonaceous BOD is more quickly removed from the aeration tank. If carbonaceous BOD is more quickly removed, then more hydraulic retention time is provided for nitrification. Approximately 4.6 pounds of dissolved oxygen are consumed for each pound of ammonium ions oxidized to nitrate ions (Table 8).

Generally, whatever is inhibitory to the organotrophic bacteria (cBOD-removing bacteria) also is toxic to nitrifying bacteria and is toxic to nitrifying bacteria at lower values. The more sensitive nature of nitrifying bacteria to inhibition is due to the relatively small quantity of energy obtained by nitrifying bacteria from the oxidation of nitrogenous compounds as compared to the quantity of energy obtained by organotrophic bacteria from the oxidation of carbonaceous compounds. The relatively small quantity of energy available to nitrifying bacteria

Table 7. Temperature and MCRT Recommended for Nitrification

Temperature, °C	MCRT, days
10	30
15	20
20	15
25	10
30	7

Table 8. Approximate Quantity of Oxygen Consumed During Nitrification

Biochemical Reaction	O_2, lb	O_2, kg
1 kg NH_4^+ to 1 kg NO_2^-		1.6
1 lb NH_4^+ to 1 lb NO_2^-	3.4	
1 kg NO_2^- to 1 kg NO_2^-		0.5
1 lb NO_2^- to 1 lb NO_2^-	1.2	
1 kg NH_4^+ to 1 kg NO_3^-		2.1
1 lb NH_4^+ to 1 lb NO_3^-	4.6	

limits their ability to repair cellular damage caused by inhibitory conditions.

There are several forms of inhibition that can damage nitrifying bacteria and adversely affect nitrification in the activated sludge process (Table 9). Those that commonly occur include inorganic (Table 10), organic (Table 11), and substrate inhibition. A unique form of inhibition that affects nitrifying bacteria is “recognizable,” soluble carbonaceous BOD inhibition.

Substrate inhibition occurs through the production of free ammonia (NH_3) at elevated pH values and nitrous acid (NNO_2) at depressed pH values. Free ammonia and free nitrous acid are toxic to nitrifying bacteria. In the presence of relatively high ammonium ion concentrations (>500 mg/L) in the aeration tank, either free ammonia is produced with increasing pH or free nitrous acid is produced with decreasing pH. Therefore, the discharge of high concentrations of ammonium ions to the aeration tank or the release of high concentrations of ammonium ions in the aeration tank should be prevented.

Table 9. Forms of Inhibition that Affect Nitrifying Bacteria and Nitrification

Form of Inhibition	Description or Example
Free chlorine residual	Chlorination of the mixed liquor
Inorganic	Cyanide or heavy metals
Organic	Phenols or recognizable, soluble carbonaceous BOD
pH	<5
Substrate	Free ammonia or free nitrous acid
Sunlight	Ultraviolet radiation
Temperature	<5 °C

Table 10. Inhibitory Threshold Concentrations of Some Inorganic Wastes that Affect Nitrifying Bacteria and Nitrification

Inorganic Waste	Concentration, mg/L
Chromium (hexavalent)	0.25
Chromium (trivalent)	0.05
Copper	0.35
Cyanide	0.5
Mercury	0.25
Nickel	0.25
Silver	0.25
Sulfate	500
Zinc	0.3

Table 11. Inhibitory Threshold Concentrations of Some Organic Wastes that Affect Nitrifying Bacteria and Nitrification

Organic Waste	Concentration, mg/L
Allyl alcohol	20
Aniline	8
Chloroform	18
Mecaptobenzothiazole	3
Phenol	6
Skatol	7
Thioacetamide	0.5
Thiourea	0.1

Recognizable, soluble carbonaceous BOD inhibition occurs in the presence of simplistic organic compounds (Table 12). These compounds are capable of inhibiting enzymatic activity within the nitrifying bacterial cell. This inhibitory effect is not resolved until the organic compounds are either reduced in concentration or removed completely from the waste stream. Many of these inhibitory organic compounds are produced through fermentative reactions that occur in the biofilm and sediment within sewer systems and help to prevent nitrification in the sewer system. Additional factors that prevent nitrification in the sewer system include lack of an adequate population of nitrifying bacteria, short retention time, and absence of dissolved oxygen or a relatively small quantity of dissolved oxygen.

Alkalinity is removed and destroyed during nitrification. Alkalinity is removed from the wastewater by nitrifying bacteria as a source of carbon for growth, repair, and, most importantly, reproduction. Alkalinity is destroyed in the wastewater through the production of nitrous acid by *Nitrosomonas* during the first biochemical reaction of nitrification. As alkalinity is removed and destroyed, the pH of the aeration tank decreases.

Approximately 7.14 mg of alkalinity are consumed for each mg of ammonium ion oxidized to nitrate ion. To ensure adequate alkalinity for proper nitrification, the mixed liquor effluent of the aeration tank should contain at least 50 mg/L of alkalinity after complete nitrification. If an alkalinity deficiency exits for proper nitrification, alkalinity can be added to the mixed liquor with the use of an appropriate chemical (Table 13).

The pH of the aeration time affects enzymatic activity of the nitrifying bacteria. Activated sludge processes

Table 12. Examples of Recognizable, Soluble Carbonaceous BOD

Organic Compound	Formula
Aminoethanol	$CH_3NH_2CH_2OH$
Ethanol	CH_3CH_2OH
Ethyl acetate	$CH_3COC_2H_5$
i-Propanol	$(CH_3)_2CHOH$
Methanol	CH_3OH
Methylamine	CH_3NH_2
n-Butanol	$CH_3(CH_2)_2CHOH$
n-Propanol	$CH_3CH_2CH_2OH$
t-Propanol	$(CH_3)_3COH$

Table 13. Chemicals Suitable for Alkalinity Addition

Chemical Name	Formula	Common Name
Sodium bicarbonate	$NaHCO_3$	Baking soda
Calcium carbonate	$CaCO_3$	Calcite, limestone, whiting, chalk
Sodium carbonate	Na_2CO_3	Soda ash
Calcium hydroxide	$Ca(OH)_2$	Lime
Magnesium hydroxide	$Mg(OH)_2$	Magnesia
Sodium hydroxide	NaOH	Caustic soda

that nitrify efficiently do so at near neutral pH values (6.8–7.2). Nitrification at pH values greater than 7.2 are used, but nitrifying bacteria adjust slowly to significant swings in pH.

Nitrification can be achieved in one-stage systems or two-stage systems. One-stage systems consist of one aeration tank or a series of aeration tanks that remove carbonaceous BOD and also nitrify. Two-stage systems consist of a series of tanks. The first tanks in the series remove carbonaceous BOD only. The last tanks in the series nitrify only. Two-stage systems provide better process control than one-stage systems, and with increasing regulatory requirements to nitrify more and more activated sludge processes, especially in the temperate regions of North America, may need to nitrify using two-stage systems. Regardless of the nitrification requirements placed upon activated sludge processes, a knowledge of the biology of nitrification and its application to activated sludge processes are of value in achieving and maintaining cost-effective nitrification in compliance with permitted discharge limits.

EFFLUENT LIMITATIONS AND THE NPDES PERMIT

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THE CLEAN WATER ACT AND INDUSTRIAL DISCHARGES

The Federal Water Pollution Control Act of 1972 was enacted by Congress with the stated objective “to restore and maintain the chemical, physical, and biological integrity of the Nation’s waters” (1). The act acquired its common name, the Clean Water Act (CWA), in its first reauthorization by Congress in 1977. CWA in its essence can be considered in three conceptual parts: funding for local agencies to construct wastewater treatment plants; requirement for the states to develop water quality standards, using a set of criteria developed under CWA as goals for the chemical constituent conditions of waters of the United States; and creation of a series of regulations for permitting wastewater discharges from industrial facilities and from treatment plants. The CWA enacted a permit requirement for wastewater discharges, prohibiting discharges in the absence of a permit, and developed a permit system with roles for federal, state, and local agencies. CWA requirements have teeth: substantial financial and criminal penalties are authorized for discharging without a permit as well as for violation of the permits, with enforcing agencies directed to apply a sliding scale related to the severity of a violation, up to $25,000 per day during which the discharge is in violation, and higher fines plus jail time for violations found to be negligent, intentional, and/or to cause injury to humans (2).

The three parts are designed to work together to drive toward protection and improvement of water quality nationwide. The first, funding (and associated regulation) for locally-operated wastewater treatment plants, created an extensive physical and institutional infrastructure over time that implements controls on household, municipal, and industrial wastewater discharges to waters of the United States. The Publicly Owned Treatment Works (POTW) became an instrument of the Clean Water Act, accountable to federal requirements but operated by local agencies and exercising local control over a local network of dischargers.

The second conceptual part of CWA initiated a system of ambient standards for waters of the United States or conditions in which any given water body can be documented to attain those uses the public chooses for that water body. A standard is defined to consist of two parts: a designated beneficial use for the water body and the physical conditions under which that use is supported. The embodied concept of protecting waters for particular, specified uses continues to drive water quality goals in the United States. The conditions determined to meet those uses typically are derived from the federally-developed criteria—logically avoiding conducting the same research multiple times when each state chooses conditions for specified designated uses. As of 1999, water quality criteria had been developed for some 115 pollutants, including 65 named classes or categories of priority (toxic) pollutants (2). In this way, standard development incorporates the federal role of providing scientific information on satisfactory conditions for attaining a given use (e.g., chemical, temperature, and flow requirements to support particular species of sports fisheries) and states’ preferences in selecting designated uses for each water body within their borders (although this is limited by a CWA stricture against allowing degradation, which effectively precludes failure to protect designated uses in place as of 1975, without extensive review and justification).

The third conceptual part of CWA is a system of permits for wastewater discharges, applicable to POTWs; industrial wastewater discharges; and other miscellaneous discharges. The controls take a form known as “uniform numeric limitations,” and as such are designed to require facilities of a given type nationwide to attain a common standard, recognizing wastewater quality as an equal goal, and equal burden, for discharges in all parts of the United States. The uniform limit has a powerful theoretical basis in the scheme of regulatory systems, which is that by specifying a numeric target rather than a selected technology, dischargers are encouraged to identify the least-cost approach that would attain that target for their own industrial facility, which might be substantially different from the treatment method that serves best for other facilities. This structure provides an incentive to promote research and development of improved, lower cost treatment technologies that would attain the same target in a more effective manner. That incentive is imperfect, as long as the limit remains greater than zero, because research and development is encouraged only to the extent of identifying less costly means to attain the specified limit. In contrast, economic approaches, such as emission trading or charges-and-standards, also encourage research and development on the most cost-effective ways to reduce discharges of pollutants extending below the specified standard, in principal also encouraging research into low-emission or zero-discharge technologies that are not equally encouraged by the numeric limit approach. The uniform numeric limitation approach also foregoes the advantages of a competing system, one that could attain greater economic efficiency by allowing trading pollutants among different dischargers with different attainment costs, of the kind employed by certain Clean Air Act regulations. An extensive body of environmental economics literature addresses these concepts; see, for example, Tietenberg (3).

CWA engendered an interwoven system of regulations and policy goals spanning federal, state, and local agencies across the United States. The Act was envisioned as dynamic, to be revised and refined over time, taking advantage of research advances and the expected water quality improvements; and to some extent, that has occurred. Two major reauthorizations, in 1977 and 1987, encompassed substantial changes, and periodic rulemaking has introduced new directions, such as the emphasis on watershed management in the early 1990s. However, since that time, little of substance has changed (4). Annual updates on CWA and related issues can be found in the Congressional Research Service's Issue Brief series [e.g., (5)]. A legislative and conceptual overview of CWA, its history and intent, can be found in (4) and in a 25-year summary prepared by the Water Environment Federation (1). The entire Clean Water Act may be seen in the Code of Federal Regulations (CFR) under Title 40, Protection of the Environment; Chapter I, Environmental Protection Agency; sections 401–499, Clean Water Act. A searchable version of the CFR is maintained online by the National Archives and Records Administration, updated quarterly as regulations are modified or expanded. The website for CFR Title 40 is http://www.gpoaccess.gov/topics/environment.html.

NPDES: CWA'S NUMERIC EFFLUENT SYSTEM

The National Pollutant Discharge Elimination System (NPDES) is the mechanism developed in the CWA to specify numeric limitations for effluent from both industrial facilities and POTWs. In the 1972 CWA, Congress authorized the newly-organized Environmental Protection Agency (EPA) to develop, promulgate, and enforce NPDES requirements.

Uniform numeric limitations for industry are specified in two forms. The first is by substance: EPA is directed to develop a list of allowable limitations for both "conventional pollutants," which were widely recognized as of 1972, and "priority pollutants," consisting largely of toxic substances about which information was and is still emerging. The second is by industrial category: numeric limitations are listed for each of a range of industry groups (categories) selected by EPA according to facility types likely to have similar wastewater characteristics and problems, and similarity of the treatment technologies likely to be successful in removing pollutants from wastewater typical of that industry's characteristics. These categorical standards within a given industry recognize two types of discharges: direct discharges into waters of the United States and indirect discharges into municipal wastewater systems, known as "pretreatment" standards, because after onsite treatment, the discharges are intermingled and treated again by the receiving POTW. For some substances in some industry categories, the specified numeric limitations are somewhat different for direct and for indirect discharges.

In order to be uniform across the United States, logically it is not possible to select numeric effluent limitations based on water quality. No uniform standard could address the wide variation of water bodies' assimilative capacities, mixing properties, biological communities, and other considerations or the wide variation of discharges' volumes, timing, intermingled substances, and similar characteristics. The NPDES rules were expected to attain water quality improvement simply by specifying a uniform target for all discharges that would require industrial facilities, and POTWs, to provide some treatment to remove pollutants recognized as potentially harmful to the environment. Therefore, the NPDES limitations were of the type we can term "technology based": the numeric limitations were selected by EPA after a thorough review of the kinds of wastewater treatment technologies available, those known to have been constructed and operated by at least some facilities in the United States. The operating characteristics of the technologies provided knowledge of the attainable chemical characteristics of wastewater after treatment and some information about the cost to treat wastewater to achieve a specified standard. EPA was directed to use that information to specify a numeric limit, not a technology that all dischargers must adopt, but a number that all discharges must attain, based on the conclusion that available technologies could successfully attain the number.

Both the substance-specific and the category-specific limitations achieve the same conceptual advantages of any numeric limitation, i.e., the discharger (and the entity responsible for wastewater treatment) may select the most cost-effective technology for his own situation, encouraging innovative research and development to develop lower cost processes if possible. This concept today remains central to the goals of EPA and NPDES: "A facility's drive to identify cheaper, more effective ways to achieve compliance is consistent with EPA's mission of clarifying and simplifying environmental regulatory control" [Sector Notebook series, (6)]. The structure of NPDES regulations does not permit EPA to specify treatment technologies, instead requiring EPA to specify a numeric target (although EPA is allowed to justify its selection of a limitation by documenting that a cost-effective treatment exists that would attain the limitation).

The technology-based structure does, however, generate another conceptual weakness in the NPDES numeric limitation scheme: Limitations based on current technology have the effect of “freezing” the technology at that level. Research and development on lower cost ways to attain the specified limitation are strongly encouraged, but no incentive exists to invest in developing or implementing improved technology that would attain any greater pollutant removal than specified in the limitation. It may be inferred that Congress’ intent under CWA was to routinely revise the limitations as more information becomes available through continuing research on the effects and treatability of toxic materials. (In fact, as the term “elimination” in the title suggests, Congress envisioned that industry and POTWs would attain effectively zero discharge of substances found to cause water quality problems in receiving waters.) The history of CWA reauthorizations does not show a robust program of routinely revisiting and revising the limitations for most substances once they have been initially selected.

EFFLUENT LIMITATIONS BY SUBSTANCE

EPA developed the numerical limitations for its NPDES requirements using information about technologies available during the 1970s, when the requirements were written, as well as the best information at the time about technological capabilities expected in the future. The initial set of limitations focused on the “conventional” pollutants and on the kinds of treatment technologies then well known and proven to be economically feasible for typical industrial facilities; these were known as “best practicable control technologies” (BPT). CWA specified a timeframe by which dischargers needed to meet the BPT requirements, which were, of course, specified in the form of a numeric limit, not a specified technology. Conventional pollutants subject to BPT were:

—Suspended solids
—Biochemical oxygen demanding substances (BOD)
—Fecal coliform
—Acidity (pH)

A second set of limits was promulgated that were to be attained on a later timeframe and were termed “best available technology” found to be economically achievable (BAT). These BAT requirements also included more stringent regulations for conventional pollutants. That feature places NPDES into the subcategory of technology-based rules known as “technology forcing,” because the increasingly stringent requirements as a rule tended to drive dischargers to develop increasingly effective treatment technologies. The BAT requirements focused on limitations for nonconventional pollutants (heavy metals, pesticides, and other organic chemicals), including a list of 125 “priority” or toxic pollutants. Priority toxic pollutants and their effluent limitations appear in the Clean Water Act section 307(a).

EFFLUENT LIMITATIONS BY INDUSTRIAL CATEGORY

Further BPT and BAT point-source limitations are written for certain substances in discharges from certain industries, specified separately for each of a number of industrial categories. These are uniform within the industry, but may differ from the broader uniform limitations in any of a number of ways: some are more stringent requirements for the same substance; some impose mass-based limitations in addition to the uniform concentration-based limitations; and others specify requirements for different substances, common to the industry category but not included in the broader uniform requirements. These requirements, in general, encompass limitations for both direct and indirect point-source discharges.

Table 1 lists the categories of industrial wastewater discharges subject to NPDES categorical effluent limitations, along with the CFR section where those limitations can be found (for instance at the website given above). Using that information, the searchable CWA referenced above is a good way to locate current categorical standards. The industry categories of NPDES are not grouped according to the familiar Standard Industrial Classification (SIC) system, but instead use the groups developed by EPA in its CWA analyses.

For many of these industry categories, a number of useful descriptive and advisory documents have been prepared by EPA, other government agencies, and a range of private sector and industry-association groups. Two useful sets of documents from EPA are the Sector Notebooks and the Compliance Assurance documents, developed by EPA in the mid- to late-1990s. The last column in Table 1 includes the Federal report number of those documents that address particular NPDES categories, where such documents have been developed. Those guides do not contain the full text of the regulations and are not to be understood as the complete list of actions required by the regulated community, so the reader should refer to complete regulations to ensure compliance. Instead, they summarize the totality of regulatory requirements of which an operator should be aware. These are perhaps at their most useful in summarizing the range of environmental regulations that apply to a particular sector, including placing CWA requirements in the context of other regulations and listing the kinds of measuring, reporting, and documenting that can fulfill one or several of these requirements singly or jointly. Counter to the NPDES approach, many of those useful documents do follow the traditional SIC categorization, so the facility operator needs to find his or her own activities using a broad and flexible definition of his own processes.

Information about other industries, not named as CWA point-source categories, includes:

Dry cleaning	EPA/310-R-95-001
Wood furniture and fixtures	EPA/310-R-95-003
Motor vehicle assembly	EPA/310-R-95-009
Printing	EPA/310-R-95-014
Air transportation	EPA/310-R-97-001
Ground transportation	EPA/310-R-97-002
Water transportation	EPA/310-R-97-003
Shipbuilding and repair	EPA/310-R-97-008
Agricultural crop production	EPA/310-R-00-001
Agricultural livestock production	EPA/310-R-00-002
Aerospace	EPA/310-R-98-001

Table 1. Industry Sectors Subject to Category Numeric Limitations for Wastewater Discharges; Sources of Information

Industry Sector (Point Source Category)	CFR Section (Effluent Limitations Listed)	Additional Information*
Dairy products processing	405	
Grain mills	406	
Canned and preserved fruits and vegetables processing	407	
Canned and preserved seafood processing	408	
Sugar processing	409	
Textile mills	410	EPA/310-R-97-009
Cement manufacturing	411	EPA/310-R-95-017 (stone, clay, glass, and concrete)
Concentrated animal feeding operations (CAFO)	412	EPA/310-R-00-002017 (agricultural livestock production)
Electroplating	413	
Organic chemicals, plastics, and synthetic fibers	414	EPA/310-R-95-012 (organic chemicals); EPA/310-R-97-006 (plastic resin, manmade fibers); EPA/310-R-95-016 (rubber and plastic)
Inorganic chemicals manufacturing	415	EPA/310-R-95-006 (lumber and wood products)
Soap and detergent manufacturing	417	
Fertilizer manufacturing	418	EPA/310-R-00-003 (agricultural chemical, pesticide, and fertilizer industry)
Petroleum refining	419	EPA/310-R-95-013
Iron and steel manufacturing	420	EPA/310-R-95-005
Nonferrous metals manufacturing	421	EPA/310-R-95-010
Phosphate manufacturing	422	
Steam electric power generating	423	EPA/310-R-97-007
Ferroalloy manufacturing	424	
Leather tanning and finishing	425	
Glass manufacturing	426	EPA/310-R-95-017 (stone, clay, glass, and concrete)
Asbestos manufacturing	427	EPA/310-R-95-017 (stone, clay, glass, and concrete)
Rubber manufacturing	428	EPA/310-R-95-016 (rubber and plastic)
Timber products processing	429	EPA/310-R-95-006 (lumber and wood products)
Pulp, paper, and paperboard	430	EPA/310-R-95-015
Meat products	432	
Metal finishing	433	
Coal mining	434	
Oil and gas extraction	435	EPA/310-R-99-006
Mineral mining and processing	436	EPA/310-R-95-011 (non-fuel, non-metal mining)
Centralized waste treatment	437	
Metal products and machinery	438	EPA/310-R-95-007 (fabricated metal products)
Pharmaceutical manufacturing	439	EPA/310-R-97-005
Ore mining and dressing	440	EPA/310-R-95-008 (metal mining)
Transportation equipment cleaning	442	EPA/310-R-95-018
Paving and roofing materials	443	EPA/310-R-95-017 (stone, clay, glass, and concrete)
Waste combustors	444	
Landfills	445	
Paint formulating	446	EPA-305-S-97-005 (paint, . . ., and allied products manufacturing)
Ink formulating	447	
Gum and wood chemicals	454	
Pesticide chemicals	455	EPA/310-R-00-003 (agricultural chemical, pesticide, and fertilizer industry)
Explosives manufacturing	457	
Carbon black manufacturing	458	
Photographic	459	
Hospitals	460	
Battery manufacturing	461	
Plastics molding and forming	463	
Metal molding and casting	464	EPA/310-R-97-004
Coil coating	465	
Porcelain enameling	466	
Aluminum forming	467	
Copper forming	468	
Electrical and electronic components	469	EPA/310-R-95-002
Nonferrous metals forming and metal powders	471	

*Sector Notebook Project, developed by EPA's Office of Compliance, maintained online at http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/.

NPDES AND WATER QUALITY-BASED LIMITATIONS

Since its inception, CWA has included the stated intent that water quality considerations would overlay the uniform effluent limitations and, where necessary to attain ambient standards, would justify more stringent requirements for particular discharges, which was to be done by the states' routinely assessing the attainment of water quality standards in receiving waters. In cases where uniform limitations had been fully attained, and the water quality continued to fall short of state-specified standards, the states were to develop plans that would lead to attaining the specified ambient standards in all waters. NPDES is envisioned as a tool to attain the standards: states and/or POTWs may issue more restrictive NPDES limitations than the uniform effluent limits. This condition is identified as water quality-based effluent limitations.

For a variety of institutional reasons, this approach was applied only to a limited extent over roughly the first 20 years of CWA implementation. Since the mid-1990s, largely driven by court findings that the states should be held to water quality-based protections, EPA and the states have been busily developing programs to attain ambient standards, in large part within the Total Maximum Daily Load (TMDL) program of watershed-based planning and water quality protection. That program is addressed more fully in other parts of this encyclopedia. From the standpoint of effluent limitations on industrial wastewater discharges, the key aspect of this program is that specified limitations under NPDES permits may be made more stringent than the uniform limitations specified under CWA regulations. Selection of those limitations is guided not by economic considerations, but wholly by the requirement to attain water quality standards of the effluent's receiving waters and of systems connected to those waters.

STORM WATER EFFLUENT LIMITATIONS

The discharge of storm water runoff appears as a separate category of effluent limitation under CWA, except for a small number of industry categories (petroleum refining, for example) where storm water is included in wastewater to be collected, treated, and discharged under the wastewater NPDES permits. For most industry categories, storm water runoff requirements are a separate set of rules promulgated pursuant to the 1987 reauthorization of CWA, effective in 1992. Storm water runoff was identified in the original CWA as a nonpoint source, separate from the NPDES regulations designed for point sources, and set aside for regulation under future rulemaking. After a court finding in the 1980s that storm water can be considered a point source—in many cases, it does, after all, enter waters of the United States from a discrete channel or pipe leaving a municipal system or an industrial facility—EPA was required to include discharges of storm water runoff under NPDES.

The approach EPA has adopted for storm water runoff is substantially different from that of other industrial point sources in at least two respects. One is that EPA does not specify or require numeric effluent limitations on storm water discharges; instead, storm water discharges both by industrial facilities and by local agencies (through municipal separate storm sewer systems, MS4s) are subject to narrative standards, such as that the discharge not cause or contribute to water quality problems in waters of the United States. The second key difference is the use by EPA and the states of the general permit approach. NPDES permits for storm water discharges associated with industrial activities have been promulgated as permits encompassing rules for the entire regulated community, rather than written specifically for each discharger. That is, the permits identify by type the facilities, and the discharges, that are subject to the permit; specify a series of actions required of facilities subject to the permit; and require dischargers that fit that type to identify themselves and complete the specified requirements (7). Failure to comply carries the same penalties as other discharges without an NPDES permit, and EPA and the states are expected to implement compliance and enforcement actions to promote and require compliance; but facilities do not hold site-specific permits, and in almost no cases are they held to numeric effluent limitations. As a result of these major differences from the overall structure of numeric effluent limitations in other NPDES requirements, industrial discharge of storm water runoff is not treated within this section.

BIBLIOGRAPHY

1. Water Environment Federation. (1997). The Clean Water Act 25th Anniversary Edition. Water Environment Federation, Alexandria, VA.
2. Copeland, C. (1999).
3. Tietenberg, T. (2001). *Environmental Economics and Policy*. Addison Wesley Longman Inc., New York.
4. Copeland, C. (2003). *CRS Issues Brief for Congress: Water Quality: Implementing the Clean Water Act.* The Library of Congress: Congressional Research Service, Resources Science and Industry Division, Order Code IB89102, Washington, DC.
5. Copeland, C. (2004). *CRS Issues Brief for Congress: Clean Water Act Issues in the 108th Congress*. The Library of Congress: Congressional Research Service, Resources Science and Industry Division, Order Code IB10108, Washington, DC.
6. U.S. Environmental Protection Agency. (2002). Laws & Regulations: Clean Water Act History; A Brief Introduction to the Clean Water Act; and Finding Clean Water Act Updates. Available at http://www.epa.gov/region5/water/cwa.htm.
7. U.S. Environmental Protection Agency. (1995). Final National Pollutant Discharge Elimination System Storm Water Multi-Sector General Permit for Industrial Activities. *Federal Register* **60**(189): 50803–51319.

READING LIST

U.S. Government Printing Office National Archives and Records Administration. (2004). *Code of Federal Regulations*. Title 40, Protection of the Environment; Chapter I, Environmental Protection Agency; Parts 401–499, Clean Water Act.

U.S. Environmental Protection Agency. (2000). National Pollution Discharge Elimination System Permitting Program. Available at http://www.epa.gov/owm/npdes.htm.

U.S. Environmental Protection Agency. (1997). Office of Compliance, Office of Enforcement Compliance and Assurance. EPA Sector Notebook Project, 1995 through 2002. Available at www.epa.gov/compliance/resources/publications/assistance/sectors/.

ODOR ABATEMENT IN WASTEWATER TREATMENT PLANTS

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INTRODUCTION

Odorous emissions from sewer systems and wastewater treatment plants are produced generally by hydrogen sulfide (H_2S) and volatile or semivolatile organic compounds at very low concentrations; they are present in the liquid phase and are emitted into ambient air at the liquid–gaseous interface (1). These odors cause serious complaints in the vicinity of wastewater treatment plants. As a result, odor control has become a key issue facing wastewater treatment plant management (2). Developments are under way to improve techniques for assessing odor and producing new technologies for destroying odor.

Volatile organic compounds (VOCs) are often amenable to biological treatment through a variety of reactor formats. However, several other technologies exist that could be used in treating them to abate odor. The eventual choice of a technology largely depends on the efficiency of treatment and capital and operating costs. The advent of the "triple bottom line" now considers sustainability of the technique also, although this concept is in its infancy. Biological treatment undoubtedly represents a sustainable green option, but it must also be proven economically viable and efficient.

HOW IS ODOR MEASURED?

Olfactometry is the most widely used method for measuring odor concentrations (3). Odor is "measured" by diluting the odor-bearing gas in a dynamic system where it is presented to groups of volunteers at various dilutions. The threshold odor number (TON) is the concentration at which half of the panel of volunteers can detect the smell (4) or fail to distinguish it from odor-free air. Although far from perfect at present (5), a quantitative approach to the development of standards in olfactometry is being developed successfully in Europe (6).

Electronic sensing systems—the so-called "electronic nose"—are being researched as a replacement for, or complement to, olfactory measurements. Arrays of nonspecific sensors can respond to many thousands of chemical species due to the broad selectivity of the sensor surfaces (7). This technique can be used to produce a unique odor profile or fingerprint, which can be further interrogated by pattern recognition techniques or neural networks. Although this is far from a complete technology, results have shown that a nonspecific sensor array can measure odor concentration from a specific wastewater treatment works (2).

WHAT CAUSES ODOR AT WASTEWATER TREATMENT PLANTS?

Odor-producing substances created during wastewater treatment are small, relatively volatile molecules whose molecular weight is about 30–150. The odor is composed of a large number of different chemicals. Many of these substances develop from the anaerobic decomposition of organic matter containing sulfur and nitrogen. Inorganic gases produced during wastewater treatment include hydrogen sulfide (H_2S), ammonia (NH_3), carbon dioxide (CO_2), and methane (CH_4), of which only hydrogen sulfide and ammonia create odor problems.

Many of the causal molecules contain sulfur and are produced in trace concentrations during anaerobic decomposition. For example, mercaptans (Table 1) are highly offensive at very low threshold concentrations and are common in wastewater treatment. They are reduced compounds, analogous to alcohols with a substitution of sulfur for oxygen in the OH radical (8). Hydrogen sulfide is the predominant odorant from sewage, and it results from bacterial sulfate reduction, a dissimilatory, anaerobic process using sulfate as a terminal electron acceptor.

Anaerobic decomposition of proteins, amino acids, and urine results in a variety of odorous, nitrogen-containing compounds (Table 1). The resulting amines

Table 1. Odorous Chemicals from Wastewater Treatment[a]

Compound	Formula	Odor Character
Hydrogen sulfide	H_2S	Rotten eggs
Diallyl sulfide	$(CH_2CHCH_2)_2S$	Garlic
Diethyl sulfide	$(C_2H_5)_2S$	Nauseating
Dimethyl disulfide	$(CH_3)_2S_2$	Putrification
Allyl mercaptan	CH_2CHCH_2SH	Garlic
Butyl mercaptan	C_4H_9SH	Unpleasant
Crotyl mercaptan	$CH_3CHCHCH_2SH$	Skunk, rancid
Methyl mercaptan	CH_3SH	Decayed cabbage, garlic
Thiocresol	$CH_3C_6H_4SH$	Skunk, rancid
Thiophenol	C_6H_5SH	Putrid, nauseating, decay
Ammonia	NH_3	Sharp, pungent
Methylamine	$CH_3\ NH_2$	Fishy
Trimethylamine	$(CH_3)_3N$	Fishy, ammoniacal
Cadaverine	$NH_2(CH_2)_5\ NH_2$	Decomposing meat
Indole	$C_8H_6\ NH$	Fecal, nauseating
Skatole	$C_9H_8\ NH$	Fecal, nauseating
Acetic acid	CH_3COOH	Vinegar
Butyric acid	C_3H_7COOH	Rancid, sweaty
Valeric acid	C_4H_9COOH	Sweaty
Formaldehyde	$HCHO$	Acrid, suffocating
Butyraldehyde	C_3H_7CHO	Rancid, sweaty
Acetone	CH_3COCH_3	Fruit, sweet
Butanone	$C_2H_5COCH_3$	Green apple

[a] (Adapted from References 8 and 9)

have an offensive, fishy smell, and indole and skatole smell strongly of feces. Anaerobic fermentation end products include a range of short-chain volatile fatty acids that have a rancid, disagreeable odor. Aldehydes, alcohols, and ketones are byproducts of carbohydrate fermentation. Although many of these compounds have an odor described as sweet or fruity, their contribution with the other components leads to odors characteristic of wastewater treatment plants. Thus, it is hardly surprising that over 40% of respondents in a study of 100 German wastewater treatment plants (10) identified sludge treatment processes as sources of odor.

VOLATILITY

VOCs can be defined as those compounds whose vapor pressure is 0.01 kPa or more. The volatility of a compound is a function of its vapor pressure. Vapor pressure may be thought of as the pressure exerted by a chemical on the atmosphere. Compounds that have high vapor pressure exert higher pressure on the atmosphere and therefore have an increasing driving force to volatilize. High water solubilities and low vapor pressures tend to decrease the potential for volatilization of dilute species from water. However, compounds that have a low vapor pressure may still have a high tendency to escape if their water solubility is low. For example, methanol as a pure compound is highly volatile but has a low tendency to evaporate from aqueous solution as it has infinite water solubility. So vapor pressure alone is not the best guide to volatility.

Henry's law constant is the best indicator of the tendency of a compound to volatilize from water. It can be expressed in two forms; one has units and one has a dimensionless form. Henry's law in the dimensionless form (H_D) can be expressed as

$$H_D = C_A/C_W \tag{1}$$

where C_A = the concentration in air (mol/m^3)
C_W = the concentration in water (mol/m^3).

Henry's law is the ratio of the partial pressure of a compound in the atmosphere to its concentration in water. Henry's law constant H_D has units of atm-m^3/mole and can be converted to its dimensionless form by

$$H = H_D(RT)^{-1}$$

where R = the universal gas constant [8.2×10^{-5} m^3-atm (mole-K)$^{-1}$]
T = the temperature on the Kelvin scale (K)

Thus, high values for Henry's constant indicate that the compound is volatile and low values indicate low volatility. Figure 1 is a working guide to the volatility of compounds based on Henry's law constants.

BIODEGRADABILITY

The ability of microorganisms to degrade environmental pollutants depends on the chemical functional groups present; some are more easily attacked than others. Although there is a well-accepted order of biodegradability of functional groups, the predictability of biodegradation is not yet an exact science:

$$\begin{aligned}&\text{Ester} \rightarrow \text{anhydride} \rightarrow \text{carbonyl} \rightarrow \text{sites of unsaturation}\\&\quad\rightarrow \text{methyl} \rightarrow \text{amide} \rightarrow \text{hydroxyl}\\&\quad\rightarrow \text{epoxide} \rightarrow \text{benzene} \rightarrow \text{methylene}\end{aligned}$$

$$\xrightarrow{\hspace{12em}}$$

Decreasing biodegradability

As the knowledge of biodegradability is woefully incomplete (less than 0.01% of known organic compounds have been tested) at present, there has been an initiative started to gather the information available and organize it systematically (12).

AQUEOUS PHASE PARTITION

When dealing with VOCs, a rate-determining step is likely to be aqueous solubility. Convincing evidence now exists that microbial biodegradation happens only in the aqueous phase, and therefore the overall rate of biodegradation of hydrophobic pollutants may be mass transfer limited. Of relevance to VOCs is the concept of threshold (13). If a chemical is so volatile that only a very low concentration exists in aqueous solution, then this may limit microbial growth. At some lower value, all the energy available from the carbon entering the cell may be used to keep the cell alive, and none is used for growth. The substrate (the VOC in this instance) is being metabolized, but the population size and biomass are not increasing. This concentration represents the threshold.

Hydrophobicity is the final key determinant of bioavailability and thus biodegradability. As a general rule, polar,

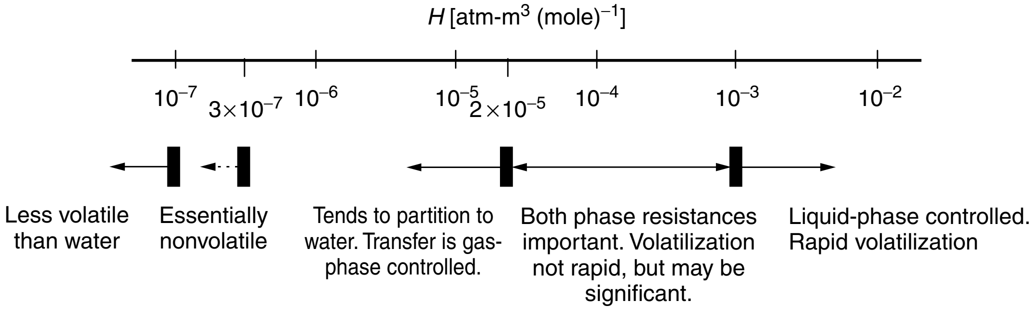

Figure 1. Ranges and relative values of Henry's law constants (adapted from Reference 11).

water-soluble, hydrophilic chemicals are more readily available to organisms than nonpolar, water-insoluble, hydrophobic ones. The polarity of a chemical has a strong negative correlation with its log octanol–water partition coefficient (log K_{ow}). K_{ow} is the ratio of a chemical's concentration in octanol to its concentration in water at equilibrium. K_{ow} was developed by the pharmaceutical industry as an index to predict the behavior of a drug in the body because partitioning between octanol and water roughly mimics partitioning between body fat and water. It is used as a convenient measure of hydrophobicity.

The above highlights the fact that the biodegradability of individual VOCs depends on the interplay of several factors. But it is also used to stress that VOCs have to be made available to an aqueous phase before biodegradation is feasible.

COMPETING TECHNOLOGIES

There are several noteworthy technologies for treating VOCs to abate odor.

Recovery/Removal

Recovery/removal treatments extract the VOC from the air stream for recycling. Whereas recovery has obvious benefits in industries using solvents, there is no benefit in the animal rendering business.

Adsorption. This is the physical adhesion of molecules to the surfaces of an adsorbent without chemical reaction. The adsorbent is usually present as a finely powdered material to maximize the surface area for contact. For activated carbon, the surface area available is very high, of the order of 1000 m^2/g. Where both the VOC concentration and the flow rate are low, activated carbon is the normal absorbent of choice. In such instances, the carbon is removed periodically and sent for regeneration or disposal. When the VOC concentrations or the flow rates are high, an *in situ* regeneration system is usually used.

Scrubbing. Water is the most common scrubbing liquid. Alkaline solutions are used for acidic components and acid solutions for alkaline compounds such as ammonia (14).

Condensation. At high VOC concentrations, an air stream may be cooled sufficiently to allow condensing the VOC as a liquid. Cryogenic condensation may be required to achieve sufficiently low concentrations. Such techniques are relatively energy-intensive, which contributes to high running costs (See Fig. 7).

Destruction

Destructive technologies aim to break down VOCs to carbon dioxide and water.

Oxidation. Oxidation can destroy most organic compounds. It is currently the most widely used technology for VOC treatment, but both thermal and catalytic oxidation systems have very high capital and running costs. Thermal oxidation requires raising the exhaust gas temperature to over 800 °C; heat recovery is employed to improve cost-effectiveness. Catalytic incineration operates at around 350 °C.

A summary of the available technologies for treating VOCs is shown in Fig. 2.

BIOLOGICAL TREATMENT TECHNOLOGIES

The biotreatment plants available for VOC treatment are adaptations of traditional, highly successful fixed film

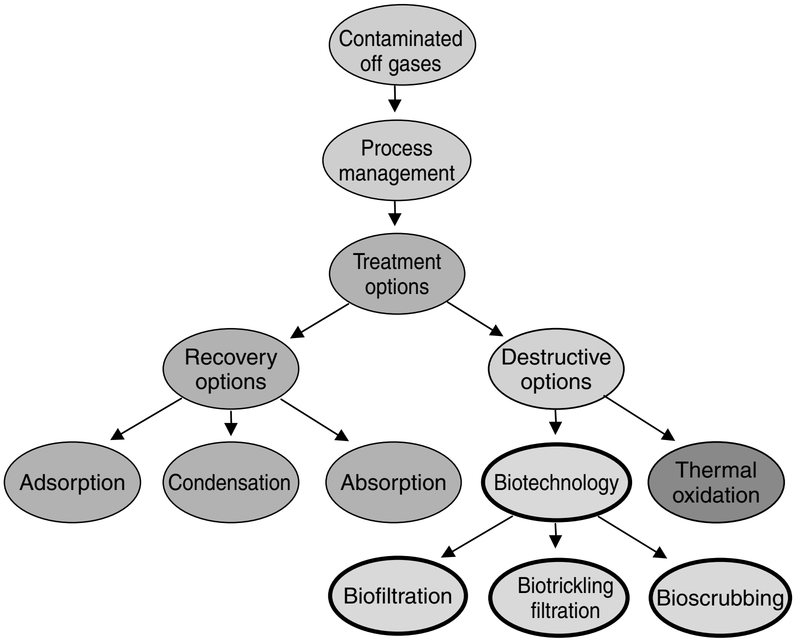

Figure 2. Available options for treating VOCs.

technologies used for wastewater treatment. The most crucial modification is the means of dissolving the VOC in the aqueous phase. They are simple mechanically, which means that maintenance and operation are simple and inexpensive. Expected life spans are of the order of 20 years. The most frequent maintenance required is periodic cleaning of the filter support material and sludge disposal.

Biofilters

VOC-containing stream(s) are humidified and discharged to the top of a reactor filled with an inert support medium to which the appropriate microorganisms attach and form a treating biofilm. Treatment is in the down-flow mode (Fig. 3); thus treatment is only effected by biofilm organisms and not by freely suspended biomass. Natural supports (e.g., bark, peat, compost, heather) improve the sustainability of the operation. Plastic supports can be used, but those available for wastewater trickling filters are probably too large; the void volume is so large that short-circuiting may be possible.

Biotrickling filter. The VOC-laden airstream enters at the bottom of the reactor and passes upward through the biofilm immobilized on a high surface area synthetic support (Fig. 4). Water downflow ensures the delivery of inorganic nutrients and keeps the biomass moist. The VOCs dissolved in the aqueous phase are mineralized in the process. Note that filter is a misnomer—filtration plays only a small part in the operation; the major contribution comes from biological oxidation.

Bioscrubber. VOCs are first absorbed in a liquid phase (usually water) in a tower packed with an inert biomass support (A, Fig. 5). The solution is then pumped to an aerated tank containing a suspended flocculating biomass in an activated sludge process (B) where biodegradation takes place. The treated water is settled to return biomass to the process, and the wastewater discharged.

CHOICE OF OPTIONS

A wide range of factors other than costs govern the technology choice. The principal factors are concentration and flow rate. Figure 6 gives a technology selection based on these two factors. However, bear in mind that plants are application-specific. For example, biofilters appear to be the best option (of the biological and other treatments) for dealing with animal carcass disposal VOCs (14).

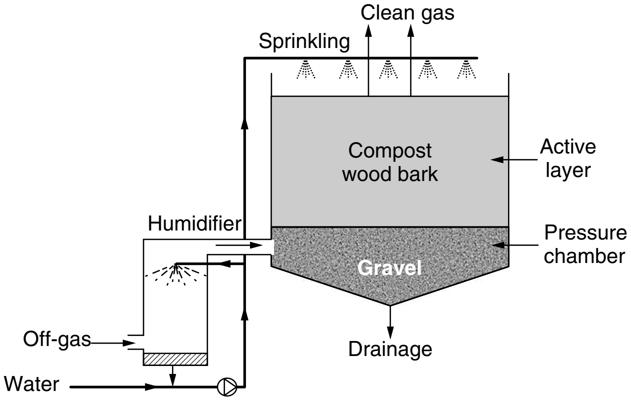

Figure 3. Biofilter characteristics.

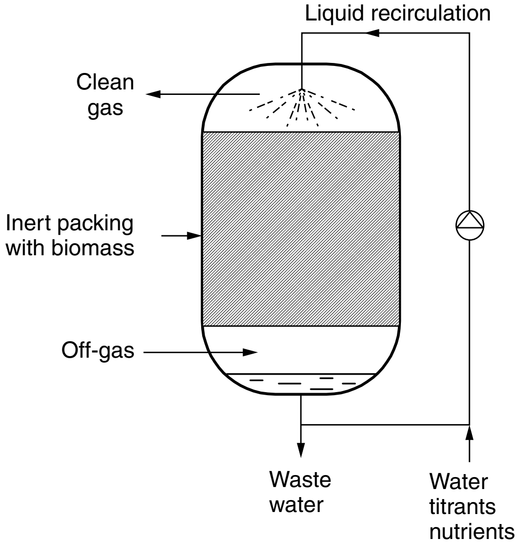

Figure 4. Biotrickling filter characteristics.

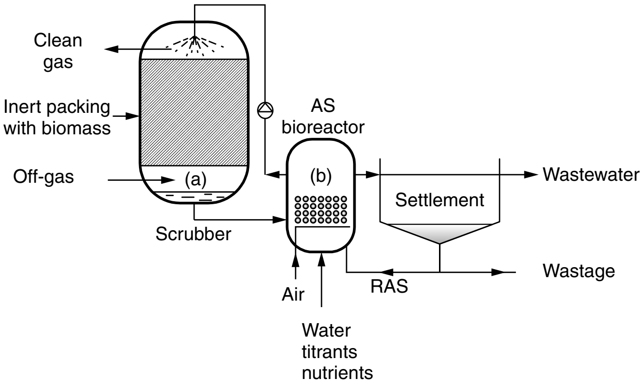

Figure 5. Bioscrubber characteristics.

THE BOTTOM LINE

Biological treatments for VOC degradation must compete with the other available technologies in treatment efficiency and also cost. The ambient conditions for treatment, low maintenance, and reasonable capital costs mean that biological methods compare very favorably with other competing technologies (Fig. 7). The size and the complexity of the plant are the determining factors that affect treatment cost. Plant size is a function of the volume of off-air to be treated daily and how well the VOCs dissolve in water.

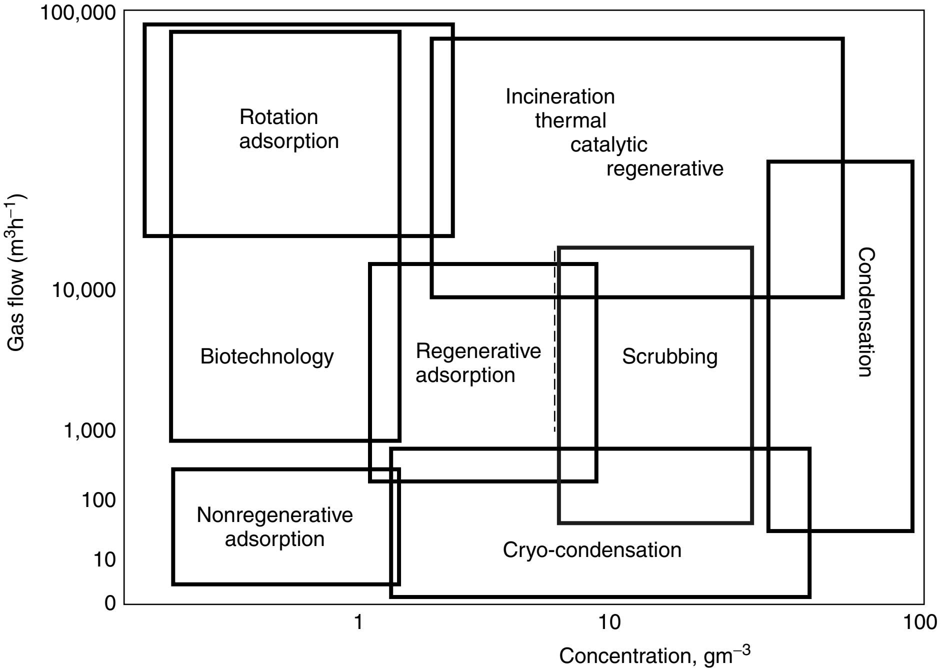

Figure 6. Effect of concentration and flow rate on choice of abatement option.

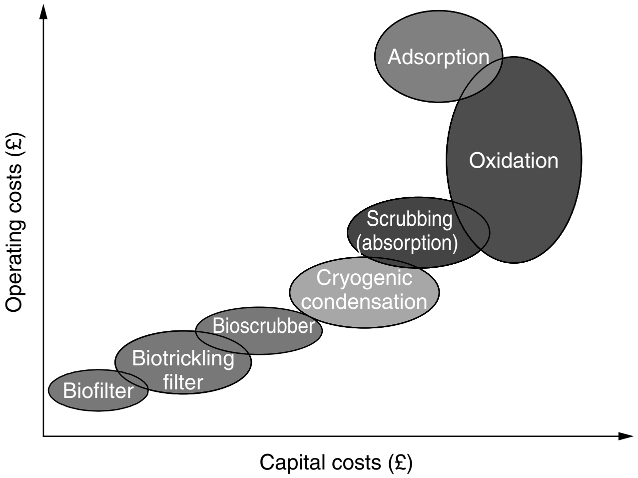

Figure 7. Relative costs of biological treatment versus other systems for VOCs.

BIBLIOGRAPHY

1. Frechen, F-B. and Köster, W. (1998). Odour emission capacity of wastewaters—standardization of measurement method and application. *Water Sci. Technol.* **38**: 61–69.
2. Stuetz, R.M., Fenner, R.A., and Engin, G. (1999). Assessment of odours from sewage treatment works by an electronic nose, H_2S analysis and olfactometry. *Water Res.* **33**: 453–461.
3. Defoer, N., De Bo, I., Van Langenhove, H., Dewulf, J., and Van Elst, T. (2002). Gas chromatography-mass spectrometry as a tool for estimating odour concentrations of biofilter effluents at aerobic composting and rendering plants. *J. Chromatogr. A* **970**: 259–273.
4. Porteous, A. (2000). *Dictionary of Environmental Science and Technology*, 3rd Edn. John Wiley, Chichester, UK.
5. Bliss, P.J., Schulz, T.J., Senger, T., and Kaye, R.B. (1996). Odour measurement—factors affecting olfactometry performance. *Water Sci. Technol.* **34**: 549–556.
6. Schulz, T.J. and van Harreveld, A.P. (1996). International moves towards standardisation of odour measurement using olfactometry. *Water Sci. Technol.* **34**: 541–547.
7. Persaud, K.C., Khaffaf, S.M., Hobbs, P.J., and Sneath, R.W. (1996). Assessment of conducting polymer odour sensors for agricultural malodours measurement. *Chem. Sci.* **21**: 495–505.
8. EPA/625/1-85/018. (1985). *Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants*. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH.
9. Gostelow, P., Parsons, S.A., and Stuetz, R.M. (2001). Odour measurements for sewage treatment works. *Water Res.* **35**: 579–597.
10. Frechen, F-B. (1988). Odour emissions and odour control at wastewater treatment plants in West Germany. *Water Sci. Technol.* **20**: 261–266.
11. Watts, R.J. (1997). *Hazardous Wastes: Sources, Pathways, Receptors*. John Wiley & Sons, New York.
12. Wackett, L.P. and Ellis, L.B.M. (1999). Predicting biodegradation. *Environ. Microbiol.* **1**: 119–124.
13. Alexander, M. (1999). *Biodegradation and Bioremediation*. Academic Press, San Diego, CA.
14. Bio-Wise. (2000). *VOC and Odor Abatement. A Review of Biological Abatement Technology*. Lewis, Boca Raton, FL.

READING LIST

Gostelow, P., Longhurst, P.J., Parsons, S.A., and Stuetz, R.M. (2003). *Sampling for Measurement of Odours*. IWA, Colchester, UK.

Stuetz, R.M. and Frechen, F-B. (2001). *Odours in Wastewater Treatment*. IWA, Colchester, UK.

AQUEOUS REACTIONS OF SPECIFIC ORGANIC COMPOUNDS WITH OZONE

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Ozone is an allotropic form of oxygen and exists as a pale-blue gas (O_3) with a pungent odor. It is very reactive chemically and decomposes without difficulty ($2O_3 \rightarrow 3O_2$). Within the arena of water treatment, it is used for disinfection and for taste and odor control. Ozone is 13 times more soluble in water than in oxygen, with a half-life of approximately 40 minutes at 14.6 °C at pH = 7.6. The density of ozone ranges from 1.09 kg/m at 0 °C to 0.14 kg/m^3 at 60 °C (1). From the table presented by Ullmann, the data fit a polynomial regression of Eq. 1.

$$y = -1.66\text{E-}06x^3 + 3.9\text{E-}04x^2 - 3.3\text{E-}02x + 1.086 \qquad R = 0.9998 \tag{1}$$

where y = O_3, kg/m^3 and x = temperature, °C.

At higher temperatures and pH, the half-life decreases significantly. Although an excellent disinfectant, ozone oxidizes ammonia in a negligible amount in water treatment operations and ozone has little to no residue within a water distribution system. In addition to the above-mentioned aspects of ozone use, the other uses of ozone are:

- Control of excessive color
- Oxidation of iron and manganese
- Oxidation of organics
- Flocculation aid
- Does not form trihalomethanes (THMs); ozone has the ability to remove precursors to THM formation (2)

To analytically determine the amount of ozone residual in water, the 1995 edition of *Standard Methods, Method 4500-O_3 B.*, calls out the Indigo Colorimetric Method as the approved method (3).

Ozone-induced oxidations in aqueous environments can generally be described in the sequence of reactions as depicted in Fig. 1 (4,5). An amount of the ozone dissolved in an aqueous environment reacts directly with solutes (M). Usually these reactions are highly selective and demonstrate slow kinetics, on the order of minutes. Part of the ozone will decompose before reaction with solutes leading to free radicals. Among the free radicals, the hydroxyl radical is one of the most reactive oxidants. The hydroxyl radical can easily oxidize all types of organic contaminants along with several inorganic solutes. The hydroxyl radicals demonstrate rapid kinetics and are consumed in microseconds while demonstrating little substrate selectivity. In measured oxidations in model solutions, the indication is that up to 0.5 mole of hydroxyl radical ($OH^\bullet$) is formed per mole of ozone decomposed. As the pH increases, so does the decomposition of ozone, which is catalyzed by the hydroxyl ion (OH^-). Ozone decomposition may be accelerated by an autocatalyzed sequence of reactions in which radicals formed from decomposed ozone act as chain carriers. Some solutes will react with the hydroxyl radicals and from secondary radicals ($R^\bullet$), which may still act as chain carriers. Other species, such as bicarbonates, will inhibit chain reactions, which transform the primary radicals to terminal species (Φ). The rate of ozone decomposition is a function of the ozone concentration and pH as well as the solutes present (6,7).

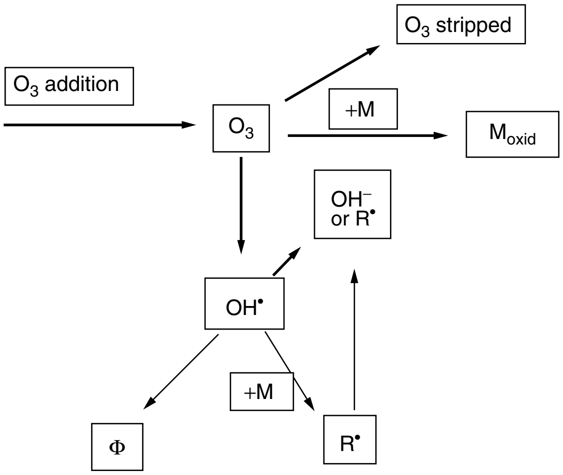

Figure 1. Ozone-induced oxidation.

When ozone attacks an organic carbon–carbon double bond (alkene), it first forms a molozonide, which quickly rearranges itself to an ozonide before the release of product (8) (see Fig. 2). Likewise, ozone will attack an alkyne bond in the following manner (8) (see Fig. 3). In an aqueous environment, ozone has different reactions because of its electronic configuration and may directly oxidize organic compounds. The reactivity of ozone is strongly influenced by electron density at sites of attack. Reactions of ozone with aromatics substituted with electron donor groups (OH, CH3, and NH_2) are exacerbated. However, aromatics substituted with electron withdrawing groups (COOH and NO_2) are retarded. The direct reactions can be divided into two categories: (1) the cyclo addition (Criegee mechanism) and an electrophilic reaction. The Criegee mechanism is selective to carbon–carbon double bonds, which then forms carbonyl compounds. An excellent review of the above-mentioned reactions may be found in Refs. 4 and 9. Rice reported on the following organic groups open to reactions with ozone (10) (see Fig. 4).

Discussions of ozone reactions with aliphatic compounds are found in Refs. 6 and 11–14. References 15–19

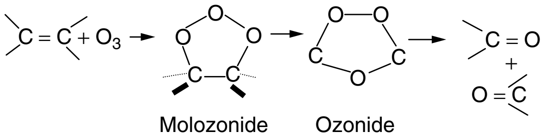

Figure 2. Molecular alternation.

Internal alkyne $R{-}C{\equiv}C{-}R' + O_3 \longrightarrow RCOOH + R'COOH$

Terminal alkyne $R{-}C{\equiv}C{-}H + O_3 \longrightarrow RCOOH + CO_2$

Figure 3. Ozone/alkyne relationship.

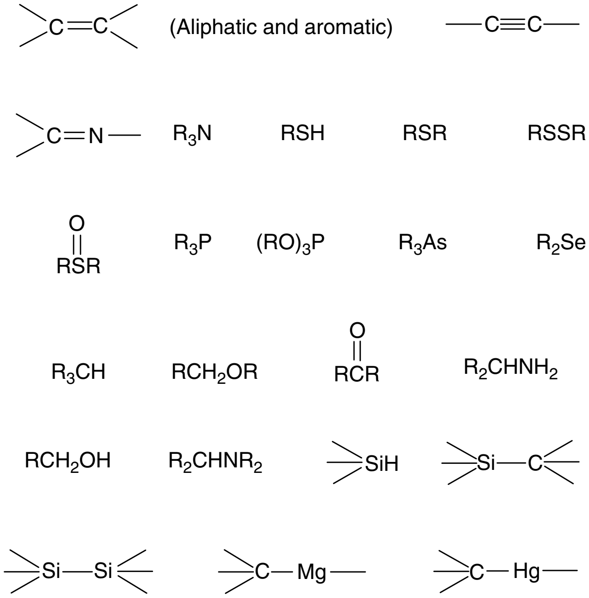

Figure 4. Organic groups reacting with ozone.

discuss reactions with aromatics with nonelectron withdrawing groups. For reactions with aromatics such as phenol, see Refs. 20–23.

BIBLIOGRAPHY

1. (1991). *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Edn. VCH Verlagsgesellschaft, Germany, pp. 415–419.
2. De Zuane, J. (1997). *Handbook of Drinking Water Quality*, 2nd Edn. John Wiley & Sons, New York, pp. 138, 463.
3. APHA, AWWA, WEF. (1996). *Standard Methods, Method 4500-O_3 B., Indigo Colorimetric Method*, 19th Edn. American Public Health Association, Washington, DC, pp. 4–104–4-106.
4. Strumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry*, 3rd Edn. John Wiley & Sons, New York, p. 692.
5. Hoigne, J. and Bader, H. (1978). *Prog. Wat. Technol.* **10**: 657.
6. Langlais, B., Reckhow, D.A., and Brink, D.R. (1991). *Ozone in Water Treatment*. Applicatiion and Engineering. Lewis Publishers, Chelsea, MI.
7. Staehelin, J. and Hoigne, J. (1985). *Environ. Sci. Technol.* **19**(12): 1206–1213.
8. McMurray, J. (1992). *Organic Chemistry*, 3rd Edn. Brooks/Cole Publishing Company, Pacific Grove, CA, p. 239.
9. Beltran, F.J. (2004). *Ozone Reaction Kinetics for Water and Wastewater Systems*. Lewis Publishers, CRC Press Company, New York, pp. 7–13.
10. Rice, R.G., (1997). *Ozone Sci. & Eng.* **18**(6): 477–515.
11. Decoret, C., Royer, J., Legube, B. and Dore, M. (1984). *Environ. Technol. Lett.* **5**: 207–208.
12. Hoigne, J. and Bader, H. (1983) *Water Res.* **17**: 185–194.
13. Hoigne, J. and Bader, H. (1983). *Water Res.* **17**: 173–183.
14. Fronk, C.A. (1987). *Ozone-Science Engineering* **9**: 265–287.
15. Dore, M., Langlais, B., and Legube, B. (1980). *Ozone-Science Engineering* **2**: 39–54.
16. Legube, B., Langlais, B., Sohm, B., and Dore, M. (1981). *Ozone-Science Engineering* **3**: 33–48.
17. Legube, B., Langlais, B., and Dore, M. (1981). *Water Sci. Technol.* **13**: 553–570.
18. Legube, B., Guyon, S., Sugimitsu, H., and Dore, M. (1983). *Ozone-Science Engineering* **5**: 151–170.
19. Schalekamp, M., Dietlicher, K., Valenta, J., and Gould, J.P. (1982). *Water Sci. Technol.* **14**: 1042–1043.
20. Gurol, M.D. and Singer, P.C. (1983). *Water Res.* **17**: 1173–1181.
21. Gurol, M.D. and Vatistas, R. (1987). *Water Sci. Technol.* **19**: 1177–1181.
22. Singer, P.C. and Gurol, M.D. (1983). *Water Res.* **17**: 1163–1171.
23. Gould, J.P. (1987). *Ozone-Science Engineering* **9**: 207–216.

THE FATE OF PERSISTENT ORGANIC POLLUTANTS (POPs) IN THE WASTEWATER TREATMENT PROCESS

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INTRODUCTION

Municipal wastewaters may contain a wide range of organic compounds deriving as components of domestic sewage, the urban runoff, including wet and dry deposition from the atmosphere, and industrial discharges (1,2). Among them are chlorinated biphenyls, dioxins and furans, polycyclic aromatic hydrocarbons, pesticides, pharmaceutical and personal care products, detergents, dyes, and solvents (3–7). Modern wastewater treatment plants (WWTPs) can effectively accomplish carbon and nitrogen removal, as well as microbial pollution control. However, conventional treatment technologies have not been specifically designed for the different organic contaminants of wastewater (natural or synthetic). The removal efficiencies of these compounds are influenced, apart from their physicochemical properties, by microbial activity and environmental conditions (2,8). Several studies have shown that the elimination of organic contaminants is often incomplete (2,7,9), rendering WWTPs important sources of toxic chemicals to the receiving environment (10–15).

Persistent organic pollutants (POPs) are a class of chemicals with pronounced persistence to biological/chemical degradation and, as such, are expected to be less efficiently eliminated in the conventional biological treatment of wastewater. Included in this class are the intended industrial products organochlorine pesticides (OPs), among them Dieldrin, Aldrin, Endrin, DDT, Toxaphene, Mirex, Chlordane, hexachlorobenzene, hexachlorocyclohexanes (HCHs), chlorinated biphenyls, and PCBs and the unintended polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). In addition to their

Table 1. Selected Physicochemical Properties[a] of POPs

	$\log K_{\mathrm{ow}}$	H_c (atm·m^3· mol^{-1})	WS
PCDD/Fs	4.8–8.2 (Ref. 24)	$10^{-4.8}$–10^{-7} (Ref. 26)	10^{-4}–10^{-9} mol/L (Ref. 28)
PCBs	4.3–8.2	$3–5 \times 10^{-4}$ (Ref. 27)	0.1–160 ppb (Ref. 29)
OPs	3.6–6.2 (Ref. 25)	4.6×10^{-7}–5×10^{-4} Ref. 27	0.7–8000 ppb

[a] K_{ow}, *n*-octanol–water partition coefficient; H_c, Henry's law constant; WS, water solubility.

persistence, POPs are hydrophobic compounds with a strong tendency for bioaccumulation. They have toxic effects on animal reproduction, development, and immunological function. POPs span a large range of volatility and condensation temperatures, and some may present high mobility through the global distillation process (16). Several actions have been taken by environmental organizations and governments to restrict the inputs of POPs to the environment. The emissions of PCDD/Fs from their major sources—waste incinerators—have been strictly regulated. The production of PCBs and OPs has been banned in the United States and in Europe since the mid-1970s, although some of them were still being used until lately in developing countries, and in 2001 the Stockholm Convention for POPs banned the manufacture and use of these chemicals worldwide.

Several studies worldwide have indicated the presence of POPs in wastewaters treated in WWTPs (2,6,12,15, 17–23). Their influent concentration levels depend on the origin of the wastewater, and mainly on the contribution of industrial discharges. The fate of POPs in WWTPs is influenced by several factors: the physicochemical properties (Table 1) of the compounds, their biodegradability potency, and the composition of treated wastewater and the operational characteristics of the plant.

THE ACTIVATED SLUDGE TREATMENT PROCESS

Conventional WWTPs include two reactors—the primary reactor (primary sedimentation tank) and the biological reactor (aeration and secondary sedimentation tanks)—and, finally, a disinfection stage. The sludge that is produced during the primary and secondary sedimentation also undergoes treatment comprising digestion (usually anaerobic), thickening, homogenization, and dewatering (Fig. 1).

Behavior of POPs in the Primary Reactor

POPs entering the primary treatment stage of a WWTP are likely to be removed through sorption onto suspended solids and subsequent sedimentation, advection out of the tank to the biological reactor (either in the dissolved or the adsorbed phase), volatilization to the atmosphere through diffusional exchange at the air–water interface, and biotransformation (30). Given the hydrophobic character of most POPs and their resistance to biodegradation, the principal removal mechanisms from this stage are sorption, advection, and possibly volatilization, whereas biotransformation is considered to have only a minor influence. Sorption to the sludge has been shown to remove considerable fractions of POPs, in general between 18% and 90% for individual compounds (2,31–33). The physicochemical parameter that best describes the tendency of POPs to be sorbed onto suspended particles is the *n*-octanol–water partition coefficient (K_{ow}). The tendency of POPs to be sorbed could be generalized as follows (34):

$\log K_{\mathrm{ow}} < 2.5$	Low sorption potential
$\log K_{\mathrm{ow}} > 2.5$ and < 4.0	Medium sorption potential
$\log K_{\mathrm{ow}} > 4.0$	High sorption potential

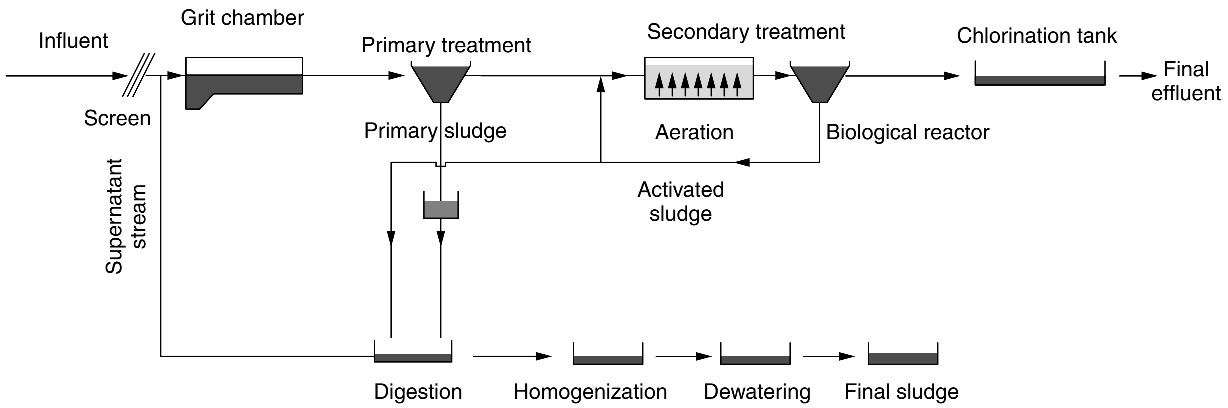

Figure 1. Flowchart of a conventional wastewater treatment plant.

The log K_{ow} values of individual POPs vary between 3.8 for HCHs and 8.2 for highly chlorinated dioxins and furans (Table 1), suggesting different sorption rates for different compounds within this class of chemicals.

Katsoyiannis and Samara (35), investigating the distribution of 20 POPs (13 OPs and 7 PCBs) between the sorbed and the aqueous phase of untreated and treated wastewater and sludge in a conventional WWTP, found that phase partitioning, expressed by the distribution coefficient K_d is influenced by two parameters: the concentration of solids, either suspended or settling (SS), and the concentration of dissolved organic carbon (DOC). For both parameters, an inverse relationship with log K_d was observed, suggesting that DOC and nonsettling microparticles can be an important carrier of POPs in the dissolved phase of treated effluents. Morris and Lester (32) also suggested that the existence of miscible organic solvents and nonsettling fine particles (<100 μm) in the wastewater can increase the percentage of hydrophobic chemicals that remain in the effluent of the primary sedimentation tank.

The removal efficiency of POPs in the primary stage due to sorption can also be affected by the operational characteristics of the plant. According to Byrns (30), the removal of POPs due to sorption in settled sludge from the primary sedimentation stage might be influenced (decreased) following a reduction in sedimentation efficiency resulting, for instance, from an increased influent flow rate.

Volatilization and biodegradation/biotransformation are not expected to have significant contribution to the removal of POPs in the primary sedimentation tank. However, remarkable losses have been observed in the mass balance of DDT around the primary reactor, which were attributed to biodegradation under aerobic conditions (35,36).

Behavior of POPs in the Biological Reactor

In the activated sludge stage, a similar array of mechanisms controls the fate and intermedia transport of POPs. In this stage, air stripping due to the forced injection of air into the mixed liquor is considered as opposed to the diffusional exchange under the quiescent conditions characterizing the primary stage.

Sorption on activated sludge has been shown to remove up to 65% of Heptachlor, 18% of Lindane, and 60% of Aroclor 1254 entering the biological reactor (22,37). Byrns (30) suggested that almost 96% of DDT and 2,3,7,8-TCDD but only 34% of Dieldrin are likely to be adsorbed to surplus sludge. The secondary sorption rates are usually lower than the primary ones.

Data for the biodegradation/biotransformation of POPs in biological treatment plants are sparse and relatively few studies have been undertaken to determine rate coefficients (rate coefficients as low as 0.0001 have been reported in Ref. 38 for DDT, Dieldrin, and 2,3,7,8-TCDD). Biotransformation of a chemical in the dissolved phase is governed by the hydraulic retention time of the mixed liquor in the biological reactor, whereas for chemicals strongly sorbed to the biomass solids, the average reaction time for biodecay will be governed by the operating solids retention time as a result of the biosorption phenomenon (30). Biodegradation/biotransformation in the secondary treatment has been suggested for certain POPs, such as for Lindane (33,39), for Aldrin to Dieldrin, for Isodrin to Endrin, for Heptachlor to Heptachlorepoxide (37), and for DDT to DDE and DDD (21,35). Highly chlorinated compounds such as PCBs and PCDD/Fs are considered as resistant to degradation under aerobic conditions and would only degrade under anaerobic conditions (34).

Volatilization of POPs during the secondary treatment is facilitated by the forced injection of air in the aeration tank, which is important for some POPs. Volatilization occurs from the dissolved fraction since the fraction sorbed to the solid phase is not directly available, under equilibrium conditions, for mass transfer across the water–air interface. The significance of volatilization losses of specific organic compounds during sewage treatment can be estimated using the following empirically defined categories based on Henry's law constant (H_c, in atm·m^3·mol^{-1}) (34):

$H_c > 1 \times 10^{-4}$	High volatilization potential
$H_c < 1 \times 10^{-4}$	Low volatilization potential

The H_c values of POPs vary between 3×10^{-4} for PCBs to 5×10^{-7} for Endrin (Table 1), suggesting that removal due to volatilization is also a compound-specific mechanism. Bamford et al. (40), studying the air–water exchange of PCBs, suggested that approximately 10% of the dissolved PCB content in a water column exchanges with the atmosphere each day. In their study, Petrasek et al. (37) showed that Heptachlor and Aroclor 1254 might be removed up to 50% by volatilization, whereas Lindane would hardly be volatilized. Finally, Byrns (30), modeling the fate of organic xenobiotics in conventional WWTPs, predicted very low removal percentages ($<0.1\%$) for DDT, Dieldrin, and 2,3,7,8-TCDDs due to volatilization in the activated sludge stage.

Behavior of POPs in the Disinfection Stage

Disinfection is the final treatment step in a WWTP before the discharge of the effluent wastewater. Disinfection is usually done by use of free chlorine, which is followed by formation of chlorinated disinfection by-products, especially when the wastewater contains high concentrations of natural organic matter. These chlorinated by-products are basically trihalogenated methanes (THMs), but it has been suggested that formation of some POPs might also occur (41). No formation of POPs has been reported when other disinfection reagents are used (e.g., ClO_2).

The Fate of POPs in the Sludge Treatment Stream

The amounts of POPs that are removed primarily and secondarily by sorption/sedimentation are transported to the sludge treatment stream. It has been estimated that compounds with log $K_{ow} > 3.5$ will concentrate in sewage sludge in concentrations more than 200 times higher than the ones found in the raw wastewater, while for compounds with log $K_{ow} > 5$, the concentration factor may be even 1000 (30).

The persistence of POPs during the digestion of sludge under anaerobic conditions has not been completely clarified and many controversial studies have been published on this issue. Hill and McCarty (42) investigated the effect of anaerobic conditions during sludge digestion on the degradation of DDT, Aldrin, Dieldrin, Endrin, Heptachlor, and γ-HCH. They noticed enhanced degradation in comparison to the aerobic conditions for all the compounds except Dieldrin. The resistance to degradation followed the order Dieldrin > Aldrin > DDD > DDT > Endrin > Heptachlor > γ-HCH. Zitomer and Speece (43) reported that reductive dehalogenation takes place under anaerobic conditions, reducing the level of chlorination of organochlorine pesticides, thus making them more amenable to further degradation and in general rendering residues less toxic. Dechlorination of OPs is facilitated by the presence of suitable microorganisms in sewage sludge; for instance, the anaerobic bacterium *Clostridium rectum* is capable of degrading γ-HCH (44). In the case of PCDD/Fs, the dechlorination pathway is from the higher chlorinated 2,3,7,8-subtituted PCDD/Fs to the lower ones, which, in antithesis to PCBs and pesticides, have a higher toxic equivalence factor (TEF) rating, something that increases the overall toxicity of sewage sludge (45,46). Fu et al. (47) reported that abiotic dechlorination of PCDD/Fs in sludge leads to DiCDD/Fs as end products. This suggestion was also prompted by Stevens et al. (48), who found that DiCDFs were the predominant congeners in U.K. sewage sludges. However, this suggestion was not confirmed by Klimm et al. (49) and by Disse et al. (50), who under strictly anaerobic conditions did not observe any formation or destruction of PCDD/Fs. On the contrary, Klimm et al. (49) observed formation of hepta- and octa-CDDs under semianaerobic conditions, something that led to a twofold increase in the concentration of these congeners. Under the same conditions, there was no formation of other PCDD/Fs or PCBs congeners.

From the above-mentioned, it is difficult to decide if the POPs degrade or do not degrade during the anaerobic digestion of sewage sludge. The fact that POPs can be detected in almost all sewage sludges after treatment (46) suggests that they are rather resistant to this process.

The concentration of POPs, especially of PCBs and of PCDD/Fs, in sewage sludges is of great importance, since sewage sludge is often used in agriculture for soil amendment. The European Union (51), in order to improve the long-term protection of soils, is working on a new directive, which includes maximum permissible concentrations for use of sludge in agriculture. According to this upcoming directive (51), the sum concentration of 7 PCB congeners (IUPAC −28, −52, −101, −118, −138, −153, −180) should not exceed 800 μg/kg (dry matter, dm), the concentration of PCDD/Fs should not exceed 100 ng TEQ/kg (dm), and the sum of organochlorine compounds should not exceed 500 mg/kg (dm). In studies dealing with the occurrence of POPs in sewage sludges, ΣPCB levels have been found to vary dramatically from 22.7 to 8000 μg/kg (dm) (1,2,52–62). The reported PCDD/Fs concentrations are also greatly variable ranging between 0.7 and 4100 ng TEQ/kg (dm) (52,63–67).

The Fate of POPs Throughout the Overall Treatment Process

Studies have shown that POPs are recalcitrant to the conditions prevailing in typical biological WWTPs and persist in one or more phases within the treatment plant. Reported removal efficiencies throughout the overall treatment process range within 18–100% for PCBs and 75–90% for several OPs (2,6,31). There are no available data concerning the removal of PCDD/Fs in WWTPs. The distribution of POPs within the WWTP is dependent on the physicochemical properties of the chemicals and the operating conditions within the plant. The principal removal mechanism for the most hydrophobic POPs is through sorption to sludge particles and transfer to the sludge processing system. Advective transport into the final effluent, in association with suspended solids or in the dissolved phase, is also important for less hydrophobic compounds. It has been reported that from the 50 kg of all PCBs annually entering a WWTP, 60% is removed through the wasted sludge, 26% is discharged into the recipient with the final effluent, while 14% is lost due to volatilization or biotransformation (35). Therefore, the long-term ecotoxicological effects on both terrestrial and aquatic organisms need to be assessed for safe disposal of the products of the wastewater treatment process.

BIBLIOGRAPHY

1. Blanchard, M. et al. (2001). Origin and distribution of polyaromatic hydrocarbons and polychlorobiphenyls in the urban effluents to wastewater treatment plants of the Paris area (France). *Water Res.* **35**(15): 3679–3687.
2. Katsoyiannis, A. and Samara, C. (2004). Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: occurrence and removal. *Water Res.* **38**(11): 2685–2698.
3. Bedding, N.D., McIntyre, A.E., Perry, R., and Lester, J.N. (1982). Organic contaminants in the aquatic environment. I sources and occurrence. *Sci. Total Environ.* **25**: 143–167.
4. Valls, M., Fernandez, P., and Albaiges, J. (1989). Broad spectrum analysis of organic contaminants in urban wastewaters and coastal receiving systems. In: *Organic Contaminants in Wastewater, Sludge and Sediment: Occurrence, Fate and Disposal*. D. Quagherbeur, I. Temmerman, and G. Angeletti (Eds.). Elsevier Applied Science, New York, pp. 19–34.
5. Paxeus, N., Robinson, P., and Balmer, P. (1992). Study of organic pollutants in municipal wastewater in Goeterborg, Sweden. *Water. Sci. Technol.* **25**: 249–256.
6. Pham, T.T. and Proulx, S. (1997). PCBs and PAHs in the Montreal urban community (Quebec, Canada) wastewater treatment plant and in the effluent plume in the St. Lawrence River. *Water Res.* **31**(8): 1887–1896.
7. Carballa, M. et al. (2004). Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Res.* **38**: 2918–2926.
8. Johnson, A.C. and Sumpter, J.P. (2002). Removal of endocrine disrupting chemicals in activated sludge treatment works. *Environ. Sci. Technol.* **256**: 163–173.
9. Manoli, E. and Samara, C. (1999). Occurrence and mass balance of polycyclic aromatic hydrocarbons in the Thessaloniki sewage treatment plant. *J. Environ. Qual.* **28**: 176–187.
10. Bergh, A. and Peoples, R. (1977). Distribution of polychlorinated biphenyls in a municipal wastewater treatment plant and environs. *Sci. Total Environ.* **8**(3): 197–204.

11. Shannon, E., Ludwig, F., and Waldmanis, I. (1977). Polychlorinated biphenyls (PCBs) in municipal waste waters. An assessment of the problem in the Canadian lower Great Lakes. *Environmental Canada Research Report*, No 49.
12. McIntyre, A., Perry, R., and Lester, J. (1981). The behaviour of polychlorinated biphenyls and organochlorine insecticides in primary mechanical waste water treatment. *Environ. Poll. Ser. B* **2**: 223–233.
13. Barrick, R. (1982). Flux of aliphatic and polycyclic aromatic hydrocarbons to central Puget Sound from Seattle (Westpoint) primary sewage treatment effluent. *Environ. Sci. Technol.* **16**: 682–692.
14. Eganhouse, R. and Kaplan, I. (1982). Extractable organic matter in municipal wastewater. 1. Petroleum hydrocarbons: temporal variations and mass emission rates to ocean. *Environ. Sci. Technol.* **16**: 180–186.
15. Granier, L., Chesterikoff, A., Chevreuil, M., and Letolle, R. (1988). Essai de bilan des polychlorobiphenyles (PCB) a la station d'epuration de l'agglomeration parisienne (Acheres). *C.R. Acad. Sci. Paris* **306**(Ser. II): 1175–1178.
16. Wania, F. and Mackay, D. (1996). Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol. News* **30**(9): 390–396.
17. Pujadas, E. et al. (2001). Application of the new C18 speedisks™ to the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in water and effluent samples. *Chemosphere* **43**: 449–454.
18. Peters, T., Nestrick, T., and Lamparski, L. (1984). The determination of 2,3,7,8-tetrachlorodibenzo-*para*-dioxin in treated wastewater. *Water Res.* **18**(8): 1021–1024.
19. De Alencastro, L.F. and Taradellas, J. (1983). Study of the concentration of PCBs in used water from a wastewater treatment plant. *Gaz Eaux Eaux Usees* **3**: 113–122.
20. Van Luin, A.B. and Van Starkenburg, W. (1985). Hazardous substances in wastewater. *Water Sci. Technol.* **17**: 843–853.
21. Saleh, F.Y., Lee, G.F., and Wolf, H.W. (1980). Selected organic pesticides, occurrence, transformation, and removal from domestic wastewater. *JWPCF* **52**: 19–28.
22. Hannah, S.A., Austern, B.M., Eralp, A.E., and Wise, R.H. (1986). Comparative removal of toxic pollutants by six wastewater treatment processes. *JWPCF* **58**: 27–34.
23. Nicoud, S., Humbert, B., De Alencastro, L.F., and Taradellas, J. (1988). Organic micropollutants at the effluents of the wastewater treatment plant, at the water of Rhone and the water of Leman-Campagne 1987. *Rapport sur les études et recherches entreprises dans le basin Lemanique*, pp. 225–234.
24. Lorber, M., Barton, R., Winters, D., Bauer, K., Davis, M., and Palausky, J. (2002). Investigation of the potential release of polychlorinated dioxins and furans from PCP-treated utility poles. *Sci. Total Environ.* **290**(1–3): 15–39.
25. Huckins, J.N., Petty, J.D., Prest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., and Johnson, B.T. (2000). *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samples of Waterborne Hydrophobic Contaminants*. Columbia Environmental Research Center, USGS, USDI and California Analytical Division, Agilent Technologies, Inc., Palo Alto, CA.
26. Eitzer, B. and Hitte, R. (1989). Atmospheric transport and deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* **23**: 1396–1401.
27. U.S. EPA. (1982). *Fate of Priority Pollutants in Publicly Owned Treatment Works*. Final Report, Vol. I. EPA 440/1-82/303. Effluent guidelines division WH-552. U.S. EPA, Washington, DC.
28. Wang, Y. and Wong, P. (2002). Mathematical relationships between vapor pressure, water solubility, Henry's law constant, *n*-octanol–water partition coefficient and gas chromatographic retention index of polychlorinated-dibenzo-dioxins. *Water Res.* **36**: 350–355.
29. Anonymous (www.es.lancs.ac.uk/ecerg/kcjgroup/11.pdf).
30. Byrns, G. (2001). The fate of xenobiotic organic compounds in wastewater treatment plants. *Water Res.* **35**(10): 2523–2533.
31. Chevreuil, M., Granier, L., Chesterikoff, A., and Letolle, R. (1990). Polychlorinated biphenyls partitioning in waters from river, filtration and wastewater plant: the case for Paris (France). *Water Res.* **24**(11): 1325–1333.
32. Morris, S. and Lester, N. (1994). Behaviour and fate of polychlorinated biphenyls in a pilot wastewater treatment plant. *Water Res.* **28**(7): 1553–1561.
33. Kipopoulou, A.M., Zouboulis, A., Samara, C., and Kouimtzis, Th. (2004). The fate of Lindane in the conventional activated sludge treatment process. *Chemosphere* **55**: 81–91.
34. Rogers, H.R. (1996). Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Sci. Total Environ.* **185**: 3–26.
35. Katsoyiannis, A. and Samara, C. (2004). Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance. *Environ. Res.* in press.
36. Pereira, W.E., Hostettler, F.D., and Rapp, J.B. (1996). Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. *Mar. Pollut. Bull.* **41**(3): 299–314.
37. Petrasek, A.C. et al. (1983). Fate of toxic organic compounds in wastewater treatment plants. *JWPCF* **55**(10): 1286–1296.
38. Howard, P., Boethling, R., Jarvis, W., Meylan, W., and Michalenko, E. (1991). *Handbook of Environmental Degradation Rates*. Lewis Publishers, Chelsea, MI.
39. Dorussen, H.L. and Wassenberg, W.B.A. (1997). Feasibility of treatment of low polluted waste water in municipal waste water treatment plants. *Water Sci. Technol.* **35**(10): 73–78.
40. Bamford, H.A., Ko, F.C., and Baker, J.E. (2002). Seasonal and annual air–water exchange of polychlorinated biphenyls across Baltimore harbor and the northern Chesapeake Bay. *Environ. Sci. Technol.* **36**: 4245–4252.
41. Ahmed, F.E. (2003). Analysis of polychlorinated biphenyls in food products. *TRAC–Trends Anal Chem.* **22**: 170–185.
42. Hill, D. and McCarty, P. (1967). Anaerobic degradation of selected chlorinated hydrocarbon pesticides. *J. Water Pollut. Cont. Fed.* **39**(8): 1259–1277.
43. Zitomer, D. and Speece, R. (1993). Sequential environments for enhanced biotransformation of aqueous contaminants. *Environ. Sci. Technol.* **27**(2): 227–244.
44. Mogilevich, N. (1982). Microbial destruction of organohalogen compounds. *Sov. J. Water Chem. Technol.* **43**(3): 98–109.
45. Barkowskii, A.L. and Adriaens, P. (1996). Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. *Appl. Environ. Microbiol.* **62**: 675–681.
46. Stevens, J., Green, N., and Jones, K.C. (2003). Fate of 1,2,3,4,6,7,8-heptachlorodibenzofuran and pentachlorophenol during laboratory-scale anaerobic mesophilic sewage sludge digestion. *Chemosphere* **50**: 1227–1233.

47. Fu, Q.S., Barkowskii, A.L., and Adriaens, P. (1999). Reductive transformation of dioxins: an assessment of the contribution of dissolved organic matter to dechlorination reactions. *Environ. Sci. Technol.* **33**: 3837–3842.
48. Stevens, J., Green, N.J.L., and Jones, K.C. (2001). Survey of PCDD/Fs and non-ortho PCBs in UK sewage sludges. *Chemosphere* **44**: 1455–1462.
49. Klimm, C., Schramm, K.W., Henkelmann, B., Martens, D., and Kettrup, A. (1998). Formation of octa- and heptachlorodibenzo-*p*-dioxins during semi anaerobic digestion of sewage sludge. *Chemosphere* **37**: 2003–2011.
50. Disse, G., Weber, H., Hamann, R., and Haupt, H.J. (1995). Comparison of PCDD and PCDF concentrations after aerobic and anaerobic digestion of sewage sludge. *Chemosphere* **31**: 3617–3625.
51. EU. (2000). *Working Document on Sludge*. 3rd draft—unpublished.
52. Eljarrat, E., Caixach, J., and Rivera, J. (2003). A comparison of TEQ contributions from PCDDs, PCDFs and dioxin-like PCBs in sewage sludges from Catalonia, Spain. *Chemosphere* **51**: 595–601.
53. Stevens, J., Northcott, G., Stern, G., Tomy, G., and Jones, K.C. (2003). PAHs, PCBs, PCNs, organochlorine pesticides, synthetic muscs, and polychlorinated *n*-alkanes in UK sewage sludge: survey results and implications. *Environ. Sci. Technol.* **37**: 462–467.
54. Ottaviani, M., Crebelli, R., Fusselli, S., La Rocca, C., and Baldassari, L.T. (1993). Chemical and mutagenic evaluation of sludge from a large wastewater treatment plant. *Ecotox. Environ. Safety* **26**: 18–32.
55. Sulkowski, W. and Rosinka, A. (1999). Comparison of the efficiency of extraction methods for polychlorinated biphenyls from environmental wastes. *J. Chromatogr. A* **845**: 349–355.
56. Paulsrud, B., Wien, A., and Nedland, K.T. (2000). *A Survey of Toxic Organics in Norwegian sewage Sludge, Compost and Manure*. Aquateam, Norwegian Water Technology Centre, Oslo, Norway.
57. Alcock, R. and Jones, K.C. (1993). Polychlorinated biphenyls in digested UK sewage sludge. *Chemosphere* **25**(12): 2199–2207.
58. Kedding, M., Langenohl, T., and Witte, H. (1989). PCB, Dioxine und Furane im Klarschlamm und deren Auswirkungen bei der landwirtschaftlichen Klarschlammverwertung. *Korrespondenz Abwasser.* **35**: 19–26.
59. Lazzari, L., Sperni, L., Bertin, P., and Pavoni, B. (2000). Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micropollutant concentrations during sewage sludge composting processes. *Chemosphere* **41**: 427–435.
60. Taradellas, J., Muntau, H., and Beck, H. (1985). Abundance and analysis of PCBs in sewage sludge. In: *COST 681 Symposium on Processing and Use of Organic Sludge and Liquid Agricultural Wastes*. October 8–11, Rome, Italy.
61. Blanchard, M., Teil, M.J., Ollivon, D., Legenti, L., and Chevreuil, M. (2003). Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environ. Res.* **95**(2): 184–197.
62. McGrath, D., Postma, L., McCormack, R.J., and Dowdall, C. (2000). Analysis of Irish sewage sludges: suitability of sludge for use in agriculture. *Irish J. Agric. Food Res.* **39**(1): 73–78.
63. Fabrellas, B., Sanz, P., Abad, E., Rivera, J., and Larrazabal, D. (2004). Analysis of dioxins and furans in environmental samples by GC-ion-trap MS/MS. *Chemosphere* **55**(11): 1469–1475.
64. Eljarrat, E., Caixach, J., and Rivera, J. (1999). Decline in PCDD and PCDF levels in sewage sludges from Catalonia (Spain). *Environ. Sci. Technol.* **33**(15): 2493–2498.
65. Langenkamp, H., Part, P., Erhardt, W., and Pruess, A. (2001). *Organic Contaminants in Sewage Sludge for Agricultural Use*. A publication of the European Union. Available at http://europa.eu.int/comm/environment/waste/sludge/organics_in_sludge.pdf.
66. Rappe, C., Andersson, R., Studer, C., and Karlaganis, G. (1997). Decrease in the concentrations of PCDDs and PCDFs in sewage sludge from Switzerland. *Organohal. Comp.* **33**.
67. Rappe, C., Andersson, R., Karlaganis, G., and Bonjour, R. (1994). PCDDs and PCDFs in samples from various areas in Switzerland. *Organohal. Comp.* **20**: 79–84.

THE ROLE OF ORGANOCLAY IN WATER CLEANUP

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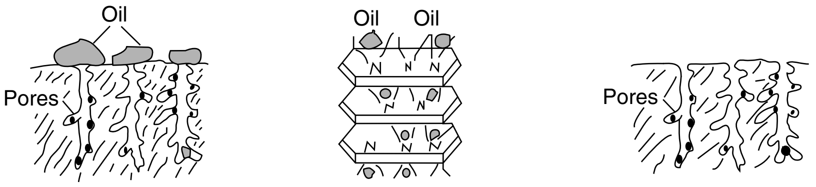
Organically modified clays, also called organoclays, have been used to clean up water since 1985. Their prime function is as a prepolisher for activated carbon, ion exchange resins, and membranes. They are also used in a stand-alone mode after dissolved air flotation (DAF) and oil/water separation units. Their main use is to remove oils, greases, and other large hydrocarbons of low solubility from water. They are very adept at removing chlorinated hydrocarbons. In this application, organoclays are usually blended with anthracite in a ratio of 30% organoclay and 70% anthracite. The reason is that the organoclay, in its pure form, would collect so much oil in its interstitial pore spaces, and due to swelling of the clay, that it would last no longer than activated carbon, which removes 8–10% of oil based on its weight, before its pores are blinded. The organoclay blend, on the other hand, removes 50–70% of oil based on its weight, some seven times as much as activated carbon. The economic benefit for the end user, the one who pays for the cleanup, is a savings of 50% or more of operating costs.

Organoclays can be called prepolishers to carbon, but it can also be said that carbon is a postpolisher to organoclay. The reason is that the organoclay also removes other compounds, such as PNAHs, BTEX, PCBs, and other hydrocarbons of low solubility, with extreme efficiency. This has been shown in many publications through the last 15 years (1–5).

Organoclays are bentonites modified with quaternary amines. Bentonite is a volcanic, chemically altered rock that consists primarily of the clay mineral montmorillonite. Montmorillonite contains inorganic exchange ions, particularly sodium, calcium, and magnesium that hydrate in the presence of water and produce a hydrophilic environment on the surface of the clay. Mixing a cationic quaternary alkyl ammonium chloride or bromide compound with the bentonite makes the clay organophilic. Bentonite, which is hydrophilic in its natural state, becomes hydrophobic and organophilic when modified with



Activated carbon granule pore spaces of activated carbon, blinded by emulsified oil.

Clay platelets, modified with quaternary amine, removal of emulsified oil on the clay surface.

Activated carbon downstream of organoclay, ready to remove more soluble compounds.

Figure 1. How activated carbon and organoclay remove oil from water.

quaternary amines (6,7). The positively charged end of the amine chain, which consists of a carboxylic head that includes a nitrogen ion, exchanges for a sodium or calcium ion on the surface of the bentonite. The cationic amine now becomes neutral, and the thus formed organoclay has turned into a nonionic surfactant that has a solid phase. The swelling capacity of sodium bentonite in water is up to 15 times its volume, but nearly zero in hydrocarbon fuels and solutions (8). After the organic modification, the organoclay swells some 15 times in a fuel such as gasoline and by some 20% when placed into a column and exposed to fuels such as gasoline (9–11). Its swelling capacity in water is very low. If alcohol is added to a fuel, the organoclay will swell even more and turn the system into a gel, or even grease. For this reason, organoclays have been used as thickeners for paints, drilling muds, greases, printing inks, and many other systems since the 1950s.

Figure 1 shows how the two media differ in removing oil from water. The organoclay removes it by partition, whereas the activated carbon removes oil and other hydrocarbons by adsorption. Partition takes place outside the clay particle; adsorption takes place inside the pores, which is the reason that they become blinded by organic compounds equal to or exceeding the diameter of the pores.

During the late 1950s, it was discovered that organoclays remove organic compounds from water, including benzene (12). It was found that organoclays can remove chlorinated organic hydrocarbons of low solubility efficiently (13,14). Excellent descriptions of the mechanisms of organoclay interactions with organic compounds are also given by Lagaly (15,16).

The removal of these compounds from water by organoclays is the result of a partition mechanism similar to the process when immiscible organic compounds such as octanol are added to water contaminated with organic compounds (16,17–19). The interlayer phase of the organoclay acts as a partition medium for oils, greases, and other hydrocarbons (1,20–24). A portion of these organic compounds moves out of the water and into the organic compound where it is more soluble; like dissolves into like. The relative solubility of the contaminant determines the amount retained in each phase. The terminology can be extended to contaminants partitioning from the water phase into a solid phase such as organic cations sorbed to a clay surface. The higher the solution concentration of a compound and the lower its solubility, the larger the quantity removed by the organoclay by partitioning. The organic compounds are held closely by the quaternary amine by coulombic forces (25), and the contaminant is not easily leached off. If an amount of amine is exchanged into the bentonite that exceeds its stoichiometric capacity, the amine chains will still attach to the organoclay in a tail-to-tail interaction. The result is that this organoclay now has a positive charge and will remove organic and inorganic anions from water, such as humic acids and hexavalent chromium (Fig. 2) (26).

Only part of the clay surfaces is covered with the quaternary amines, so a portion remains free, available for cation exchange with heavy metals such as lead, zinc, nickel, cadmium, and iron. The cation exchange capacity of bentonite ranges from 70–95 meq/100 gram. Column studies were conducted with pure organoclay and an organoclay/anthracite blend, testing for a number of metals simultaneously, and then testing for the removal capacity for single metals (27).

The main application of organoclays has been in groundwater remediation. Removal of oil from water is the organoclay's main function. Figure 3 shows a column test with organoclay/anthracite to determine the sorptive capacity of this medium for a vegetable oil. A 30-inch long (76.2 cm) by 3-inch diameter (7.62 cm) column was constructed from polyvinyl chloride (PVC) and filled with about 6 pounds of sorbent material to be studied. A peristaltic pump forced an aqueous solution containing 680 mg/L of vegetable oil through the column, after the column was backwashed with water to displace any air pockets. Samples were collected periodically at the outflow of the column and analyzed for their organic content using chemical oxygen demand (COD) analysis. The results are shown in Table 1 and Fig. 3.

The percent removal capacity for a mineral oil such as Bunker C would be much higher because it is less soluble than vegetable oil. Figure 3 is a graphic description of these data.

Figure 4 shows the results of a column study comparing the removal capacity for oil between organoclay/anthracite and bituminous activated carbon. To gain some background data, the ability of powdered, nonionic organoclay to remove a variety of oils from water was tested in jar tests (26,28). The results displayed in Figs. 5–8 show that organoclay removes all oils from water exceptionally well, as long as they are refined. It is far superior to activated carbon, which is why it is used as a prepolisher. If oil is not refined, which means its composition includes polar compounds, either a cationic organoclay has to be used, or the oil, which is now partially chemically emulsified, must be deemulsified (1,21,23,28–30). Figure 9 shows

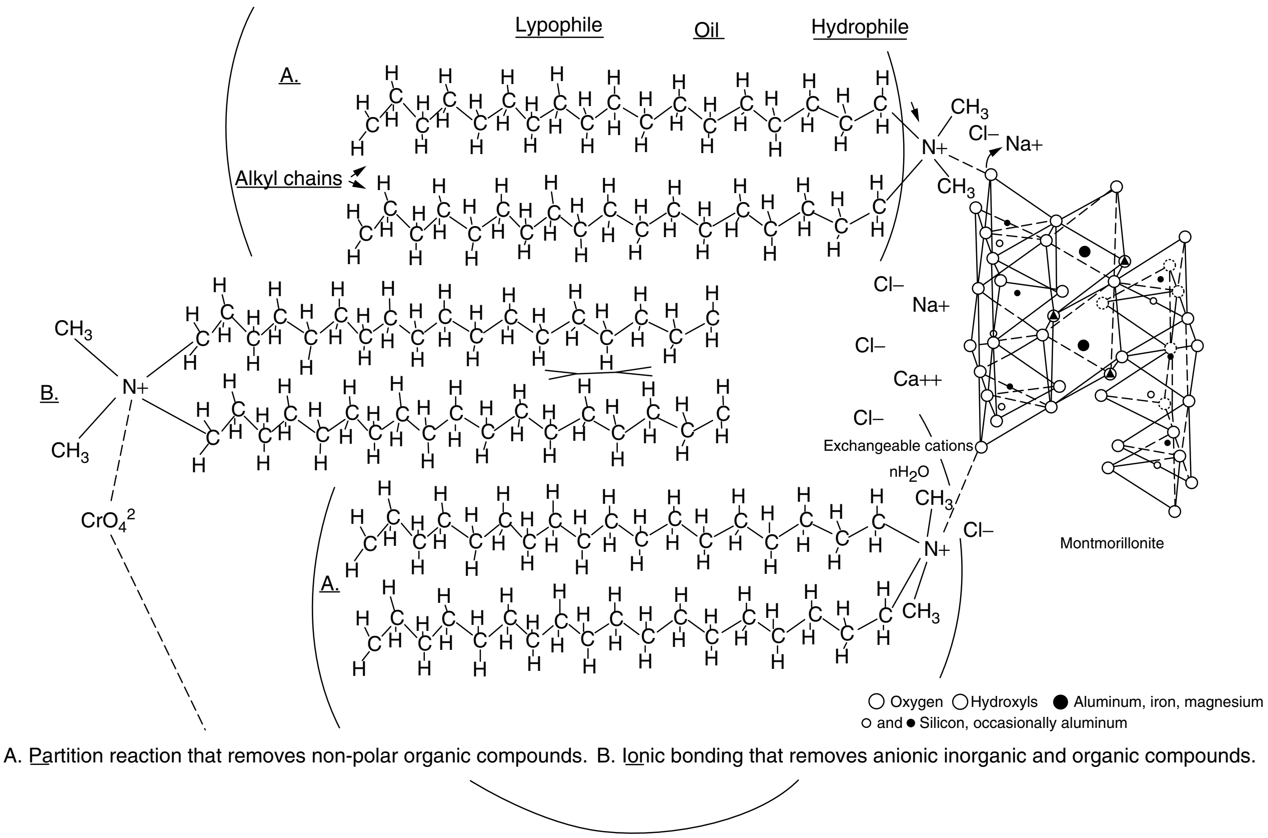


Figure 2. Model of an organoclay indicating partition and ion exchange adsorption mechanisms.

the effect of surfactants, which act as emulsifiers for oil, on the performance of organoclay. The effects are the same as on activated carbon; as solubility increases due to emulsification, the sorptive capacity decreases. Only the nonionic surfactant shows little effect on organoclay performance; probably it does not polarize the oils to any significant extent. Tests have shown that organoclay is just as effective in the removing surfactants from water as activated carbon (30). However, organoclay always prefers oil to any other compound; thus once the emulsion is split, the organoclay is used to remove the oil, followed by carbon which removes the surfactants.

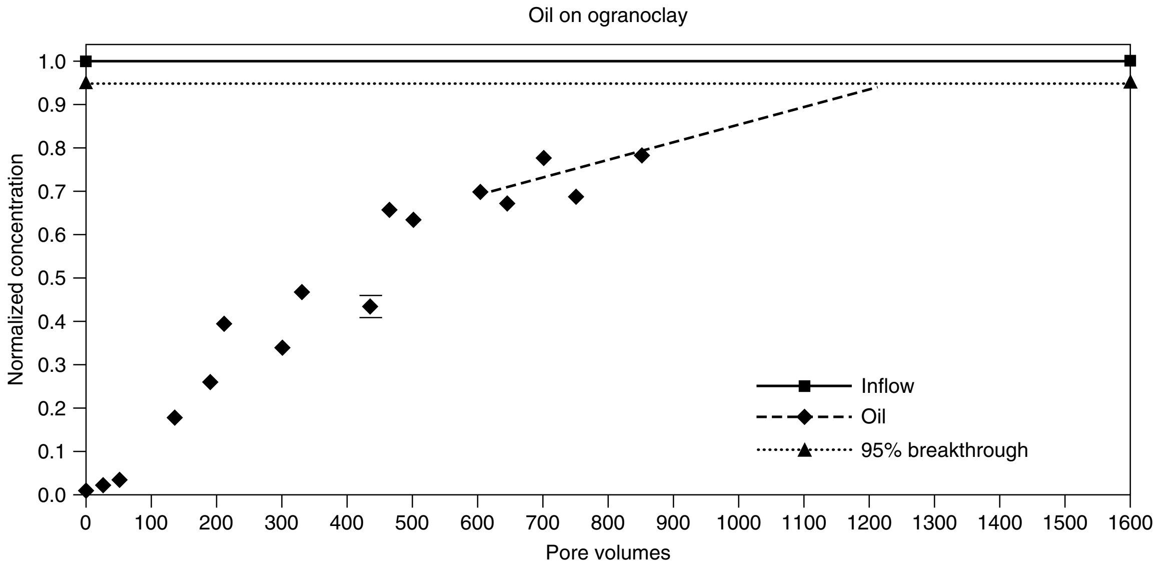


Figure 3. Breakthrough curve of oil on organoclay.

Table 1a. Sorbent Mass, Porosity, Flow Rate, and Residence Time

Mass Sorbent,		Porosity	Flow Rate,		Residence Time
kg	lb	%	mL/min	gal/h	min
0.141	0.31	0.3	15.45	0.23	8

Table 1b. 95% Breakthrough for Organoclay/Anthracite Given in Pore Volumes and Minutes Along with Estimated Mass of Oil Sorbed Per Mass of Sorbent in mg/kg, lb/lb, and On a Percent Basis

Breakthrough		Mass Sorbed		Mass Sorbed per Mass Sorbent		
PV	min	g/lb		g/kg	lb/lb	% by sorbent
1150	9,200	65.8	0.14	475	0.475	47.5

A minicolumn test was used to determine the ability of organoclay to remove such compounds as benzene, toluene, xylene, naphthalene, and PCB, and to be able to compare the data with those of bituminous activated carbon. The minicolumn method consists of spiking water with the compound to be evaluated and pumping that water through 1 gram of sorbent powder, which is tightly packed into a very small column. Pumping is performed until the influent concentration equals that of the effluent concentration (26). The sorbents are of 200 U.S. mesh size. This method is more comparable to large-scale, real situations than isotherms.

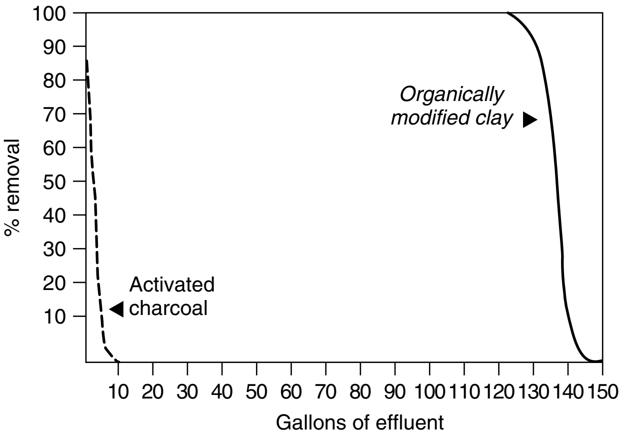


Figure 4. Removal of oil from water.

RESULTS

Figure 10 is a graphical illustration of minicolumn tests. When testing the removal capacity of the sorbents for benzene, toluene, *o*-xylene, and naphthalene, the organoclay performs similarly to carbon and performance improves as the solubility of the compounds decreases. Nonionic organoclay outperforms activated carbon with PCB 1260, as well as with motor oil, which is nearly insoluble in water. Surprisingly, organoclay removes methylene chloride much more effectively than activated carbon. The reasons are unclear, except that organoclay has an affinity for chlorinated compounds. Earlier results for vinyl chloride proved similar. It is theorized

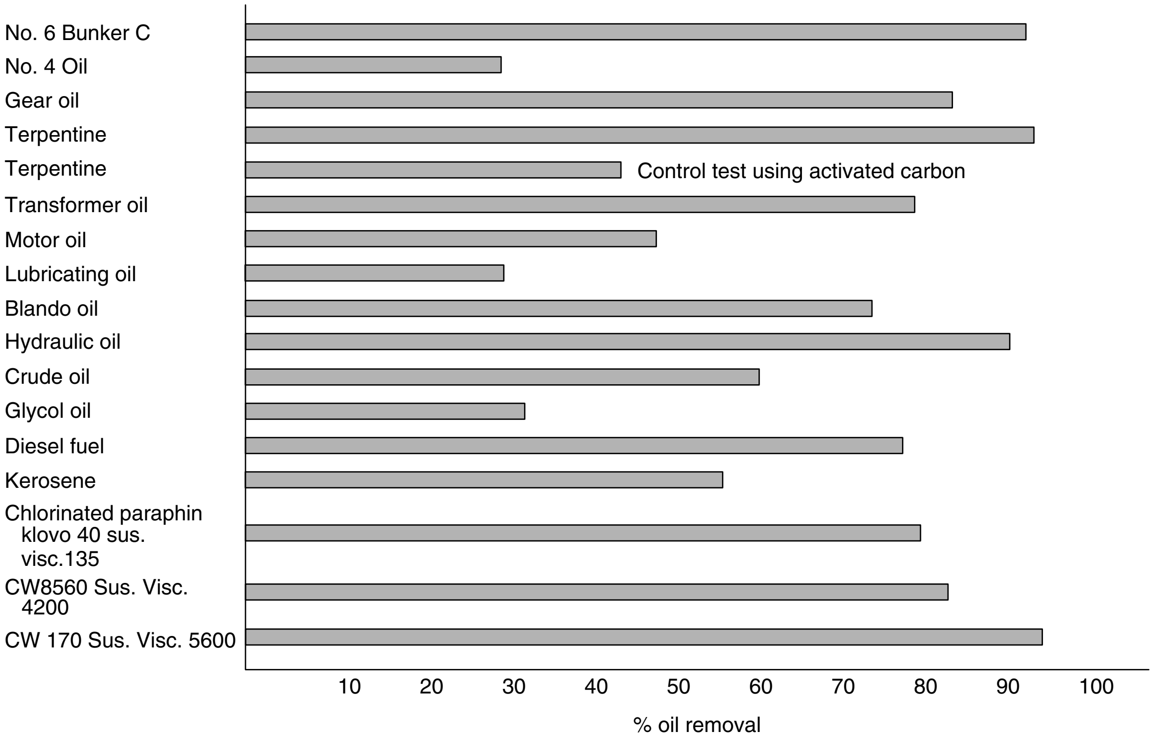


Figure 5. Removal of mineral oils from water by organoclay.

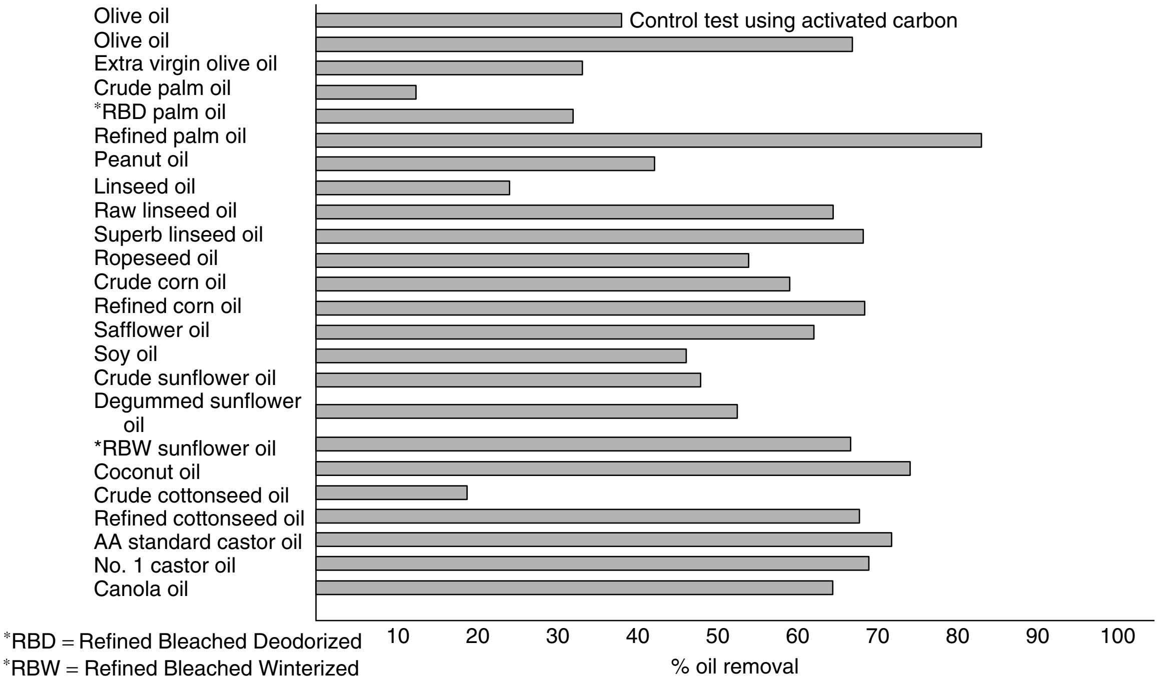


Figure 6. Removal of plant oils from water by organoclay.

that compounds such as methylene chloride have high electronegativity due to the presence of large amounts of halogens such as chlorides. The organoclay possesses positive charges on the surface due to the presence of inverted quaternary amine chains, so methylene chloride could chemically bond to these charges via their electronegativity. Therefore, two removal mechanisms, partitioning and ionic bonding, account for organoclay removal capacity for these compounds.

These tests were followed by a set of tests using a ternary effluent, which is a wastewater containing three different organic hydrocarbons, naphthalene, benzene, and toluene. This allowed the observation of competition among these compounds for adsorption sites. Of each compound, 900 mL/gram were added to water. It was possible to add that much naphthalene because benzene and toluene helped dissolve it. Usually, its solubility is only 10 mg/L. This concentrate was pumped separately through a column of organoclay, powdered activated carbon, and organoclay/carbon combined. In that case, the bottom of the minicolumn contained 0.5 grams of activated carbon, and the upper half contained 0.5 grams of organoclay. This was done to determine if the organoclay/carbon combination is more effective than each sorbent alone.

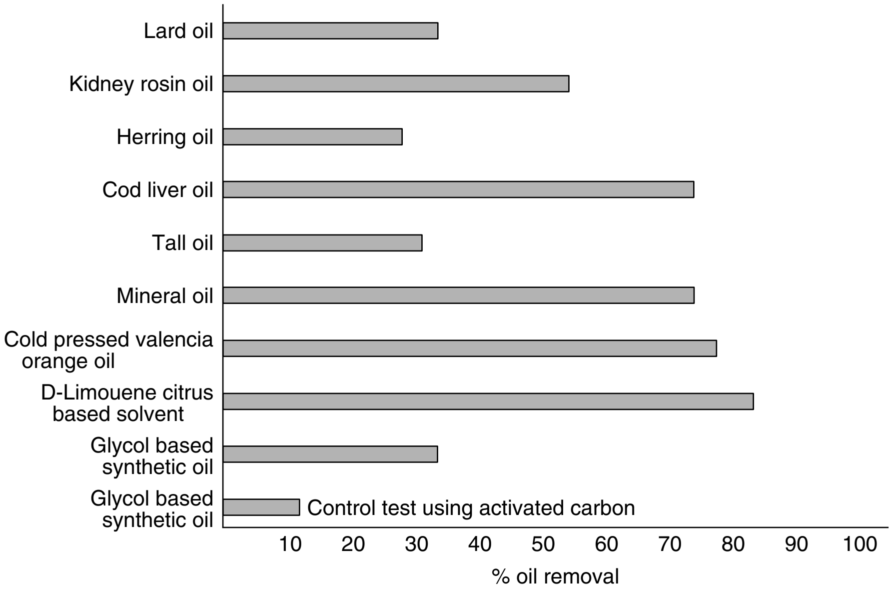


Figure 7. Removal of miscellaneous oils from water.

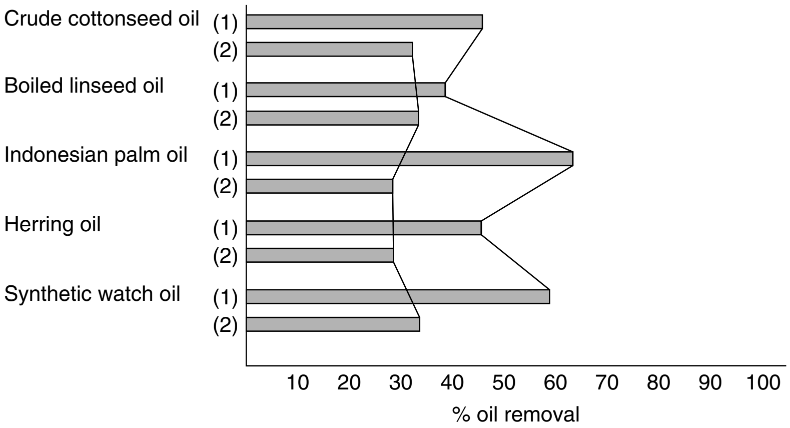


Figure 8. Removal of miscellaneous oils from water by different organoclays.

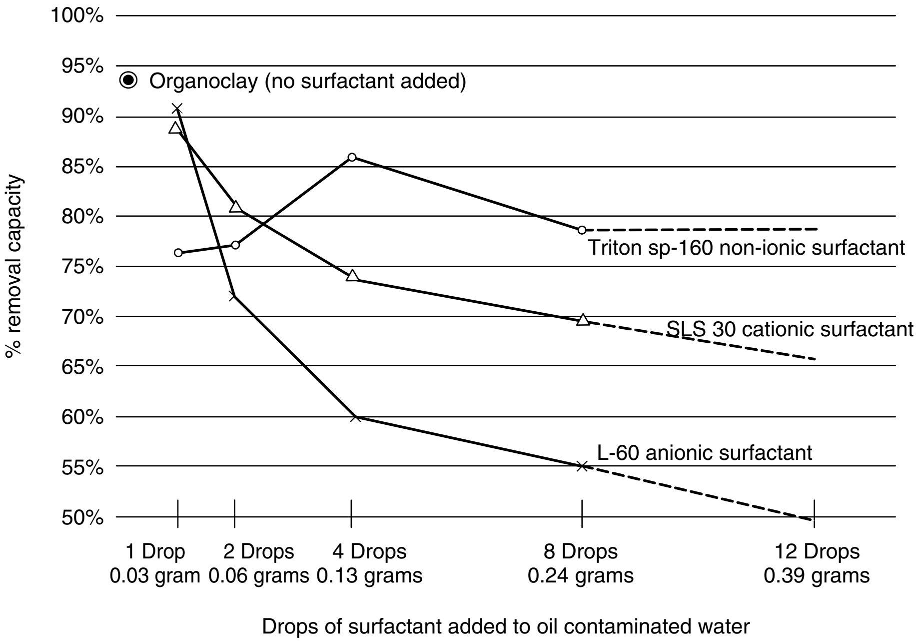


Figure 9. Percent removal capacity of organoclay for oil after adding a surfactant.

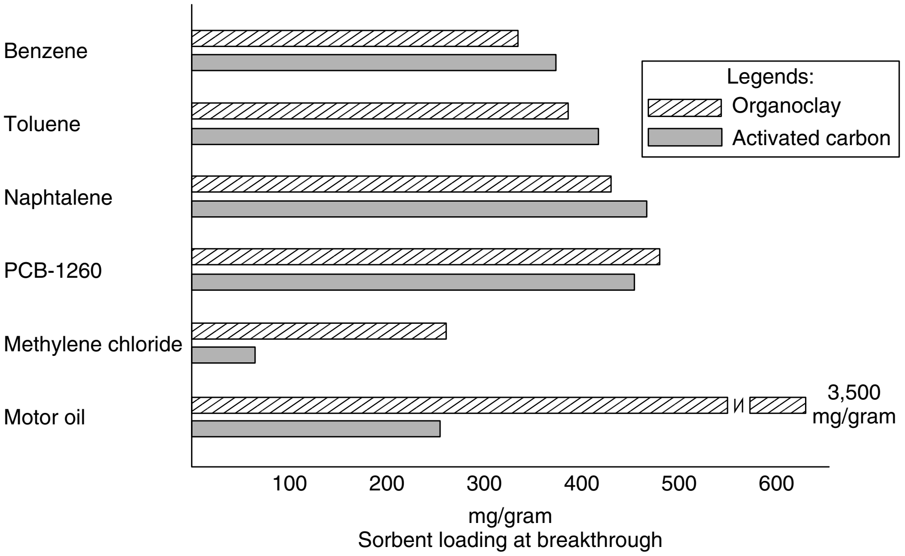


Figure 10. Minicolumn tests.

The results in Fig. 11 illustrate that benzene breaks through first, followed by toluene, and lastly naphthalene. This was expected based on their solubilities in water. The competition, however, is not 100% proof. The total adsorbed amounts are higher than the individually adsorbed amounts of the three solvents at breakthrough, probably because the geometrically arranged packing of the solvents of different sizes, either within the carbon pores or around the amine chains, favors a higher packing density.

The most important result is shown in the "total combined" graph. By placing the organoclay in front of the carbon, the removal capacity is doubled compared with the removal capacity of carbon and organoclay individually. This is also shown in a standard permeation column experiment with gasoline (Fig. 12). Again, the combination of organoclay/anthracite, followed by activated carbon, is much more effective in removing gasoline from water than either sorbent by itself, even though the amount of sorbent in each column is twice that in the combined column. Table 2 shows results from an actual groundwater cleanup project. The organoclay removes the oil completely and also a significant amount of other solvents and increases the effectiveness of activated carbon in removing volatile organic compounds. Because of the roll-off phenomenon, where less soluble compounds such as toluene and xylene, knock benzene off sorption sites within activated carbon, thus recontaminating the effluent, it is important to prepolish the water with organoclay, followed by activated carbon, which these results clearly illustrate.

The improved performance of an organoclay as the chlorination of the organic compound increases, along with a corresponding decrease in solubility in water, is shown in Figs. 13 and 14 (8). Organoclay is effective in removing phenol from water, but much more so, and far superior to activated carbon, for pentachlorophenol (PCP).

Freundlich isotherms confirm the results previously discussed, illustrated in Figs. 15–18. Figure 19, which shows the effectiveness of organoclay in removing methylene chloride, is impressive.

Figure 20 shows a time study, comparing how effectively nonionic organoclay and activated carbon remove turpentine from water. This test was conducted by pumping water spiked with turpentine through minicolumns and removing and analyzing a water sample every 50 minutes. Once the curve flattens out, saturation of the sample has occurred. These test results confirmed that the retention time of 6–10 minutes for water in an adsorber

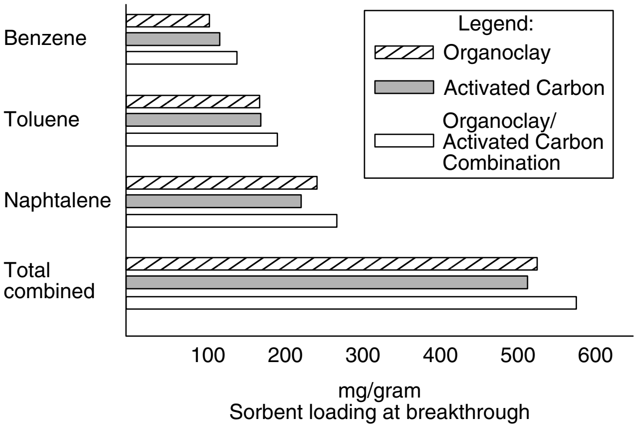


Figure 11. Minicolumn tests.

Table 2. Organoclay/Carbon Sequence for Treating Contaminated Groundwater at an Abandoned Manufacturing Site

Organic Compound	Solubility, mg/L at 20–25 °C	Influent, μg/L	Effluent After O. Clay, μg/L	Effluent After Carbon, μg/L
Oil, mg/L	0.02	5.0	ND	ND
1,1,1-Trichloroethane	480–4000	42,622	26,044	ND
Trichloroethane	110	688	271	ND
1,1-Dichloroethene	335	285	ND	ND
Toluene	535	967	242	ND
pH		8.64	8.01	9.2

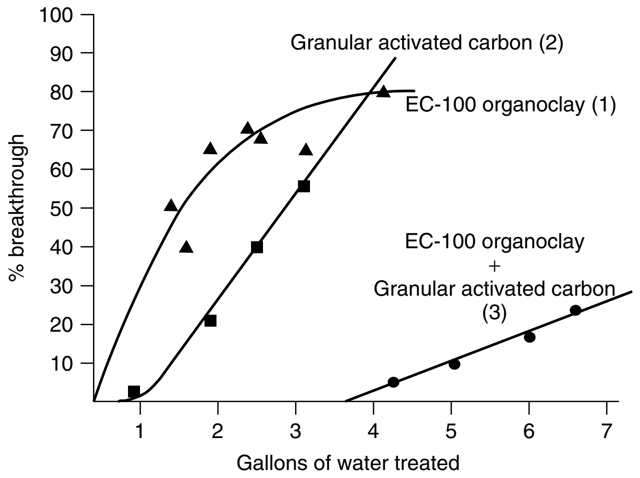


Figure 12. Breakthrough curves for gasoline saturated water.

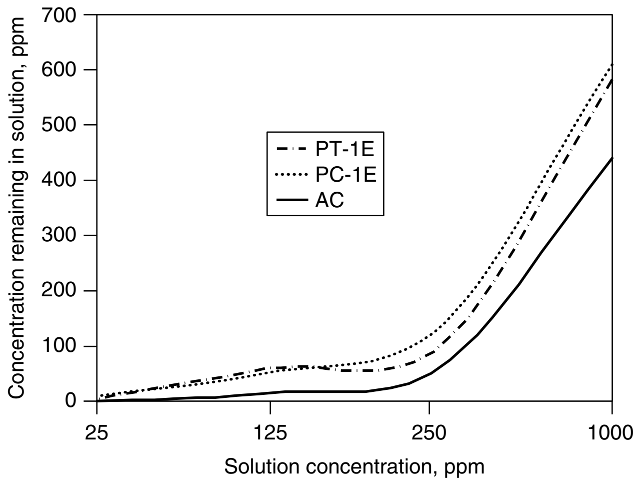


Figure 13. Adsorption of phenol by organoclay and activated carbon.

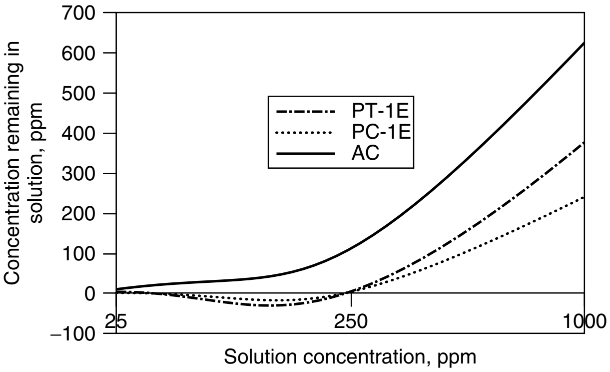


Figure 14. Adsorption of pentachlorophenol (PCP) by organoclay and activated carbon.

filled with either medium as is standard operating procedure, is applicable to both media. Another test showed that the organoclay may need a slightly longer retention time (8–12 minutes?) for more soluble benzene.

Bentonite is a natural ion exchange resin. Thus is an organoclay, even though a portion of its surface is covered with the chains of the quaternary amines. Some capacity for removing metals is still available in both media.

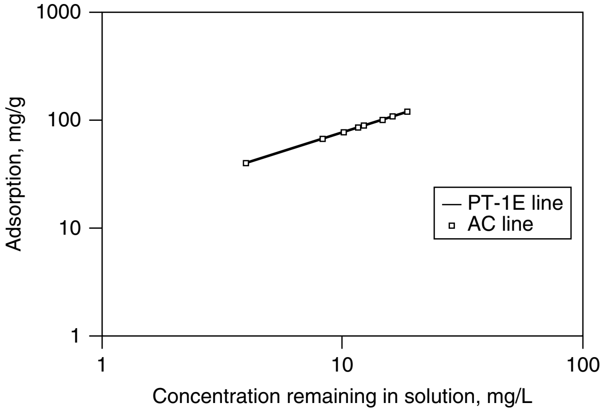


Figure 15. Isotherm showing a comparison of organoclay and activated carbon for *o*-xylene adsorption.

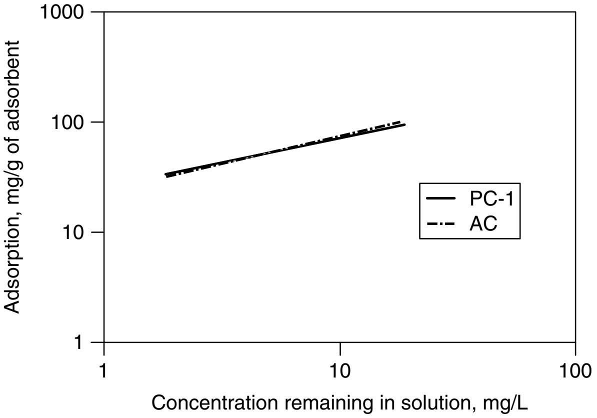


Figure 16. Isotherm showing a comparison of the removal capacity of organoclay and activated carbon for toluene.

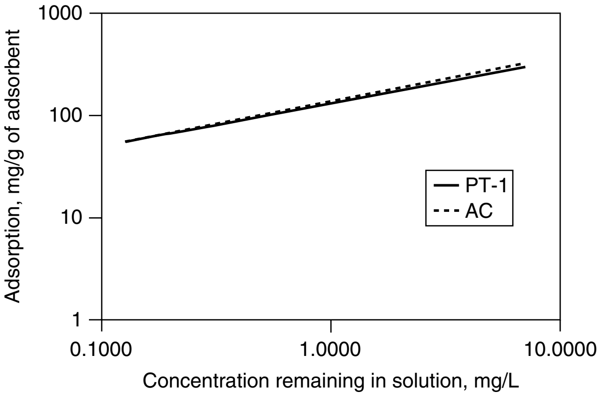


Figure 17. Isotherm showing a comparison of organoclay and activated carbon for the adsorption of naphthalene.

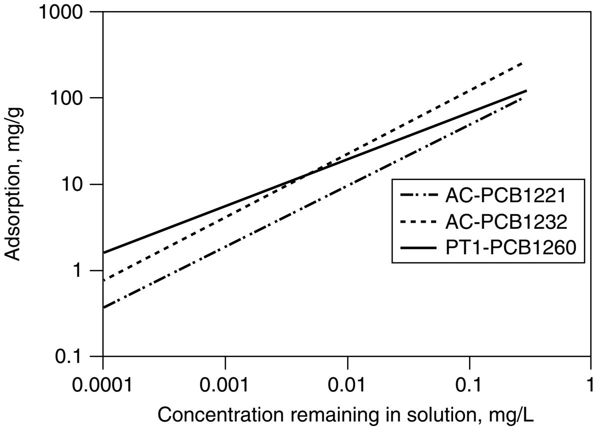


Figure 18. Isotherms showing a comparison of organoclay and activated carbon for the adsorption of PCB.

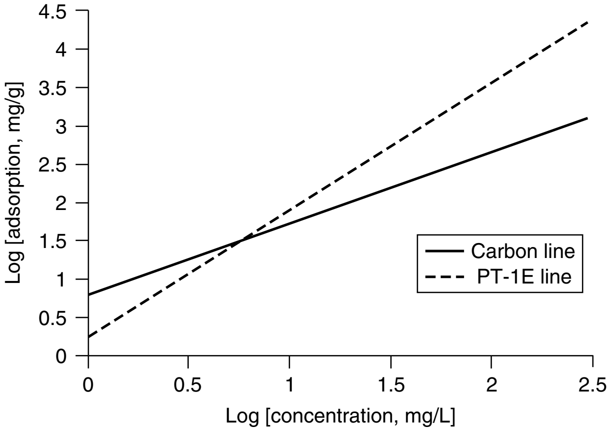


Figure 19. Isotherms showing a comparison of organoclay and activated carbon for the adsorption of turpentine.

Cation Exchange Capacity (CEC)

Organoclay/anthracite; 0.04 meq/gram; Organoclay: 0.04 meq/gram.

Surface Area (m^2/gram)

Organoclay/anthracite: 0.97 ± 0.05; Organoclay: 1.23 ± 0.69. A series of column tests were conducted in the

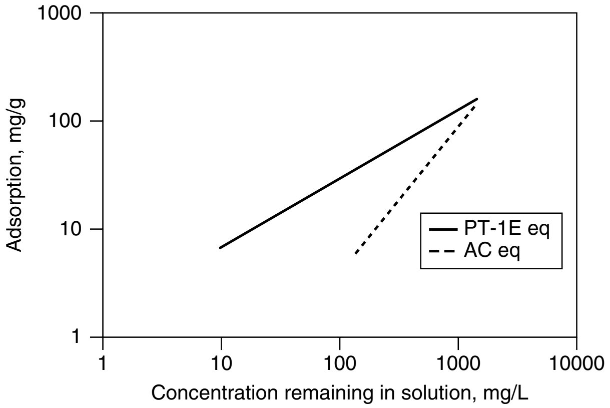


Figure 20. Isotherm showing a comparison of organoclay and activated carbon for the adsorption of methylene chloride.

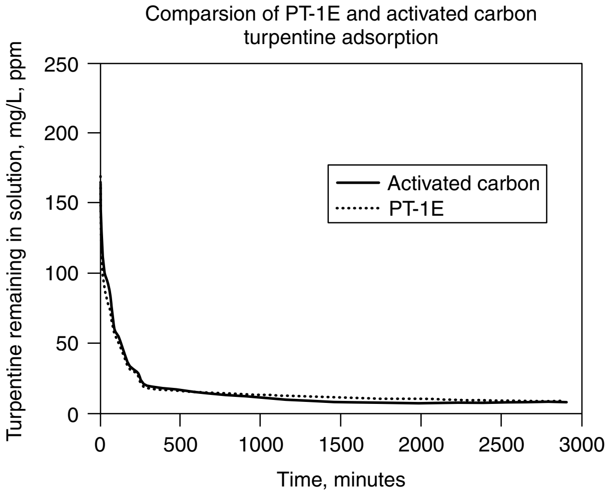


Figure 21. Time study showing a comparison of organoclay and activated carbon for the adsorption of turpentine from water.

same manner as that described for oil removal (Fig. 3), and the capacities of organoclay/anthracite and straight organoclay for removing various metals were determined. Bar charts were then constructed to illustrate the results, shown in Figs. 21 and 22 (24). The fact that the straight organoclay is not much better than organoclay/anthracite suggests that the diluting action of the anthracite results in improved access to sites on the organoclay. The U.S. Standard mesh size of the medium is 8 × 30 mesh. This capacity to remove small amounts of metals is not of great importance, but it can be a factor in calculating whether an ion exchange resin needs to be added to the treatment train if metal removal is required.

Figure 23 shows the ability of a cationic organoclay to remove chlorine from water. This isotherm proves that a cationic organoclay is an excellent medium for removing humic and fulvic acids (natural organic matter) and is far superior to bituminous activated carbon (Fig. 24). A minicolumnn test compares the removal capacity of cationic organoclay, bituminous activated carbon, and an “organotrap” ion exchange resin, again showing superior results for the cationic organoclay (Fig. 24). These results are thoroughly discussed in Alther (26).

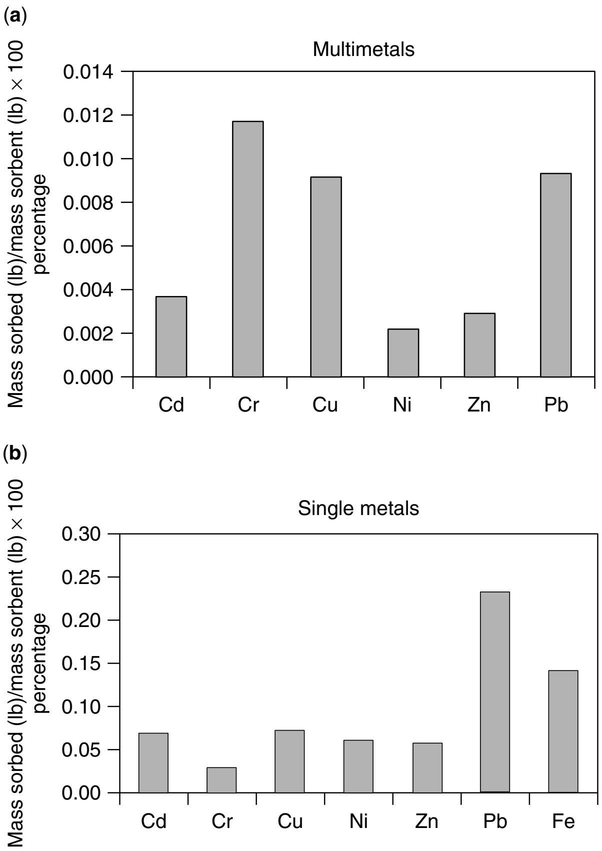


Figure 22. Adsorption of heavy metals from water by an organoclay/anthracite blend: Column study.

Table 3 shows the results of minicolumn tests to determine the removal capacity of cationic organoclay for negatively charged metals, including hexavalent chromium, selenite, arsenate, and fluoride. These results are in line with the capacity of this clay for chlorine removal.

An anionic organoclay was developed and tested in a minicolumn to show its capacity to remove cations, including ethylenediaminetriacetate (EDTA) (Fig. 25). The results are that coal based activated carbon removes 21.8% EDTA from the spiked solution, nonionic organoclay removes 47.3%, and anionic organoclay removes 70% of the EDTA.

Another set of minicolumn tests (Fig. 26) on water spiked with monoethanol amine revealed the following results: coal-based activated carbon removed 41.4%, nonionic organoclay removed 45.2%, anionic organoclay removed 29%, and cationic organoclay removed 79% of the monoethanolamine from the spiked water.

These results reveal the extreme versatility of organoclays in removing a variety of contaminants.

As a final test, the iodine numbers were determined for the organoclays, using the ASTM D-4607-94 testing method, to see if this test could be used to compare the two media. The results are as follows:

activated carbon (coal based): 700–900
nonionic organoclay: 275
cationic organoclay: 190
anionic organoclay: 410

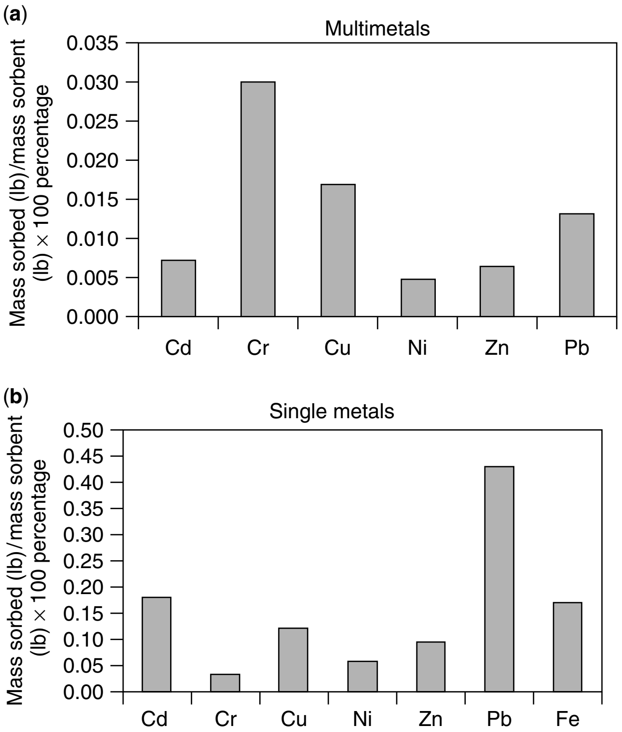


Figure 23. Adsorption of heavy metals from water by straight organoclay: Column study.

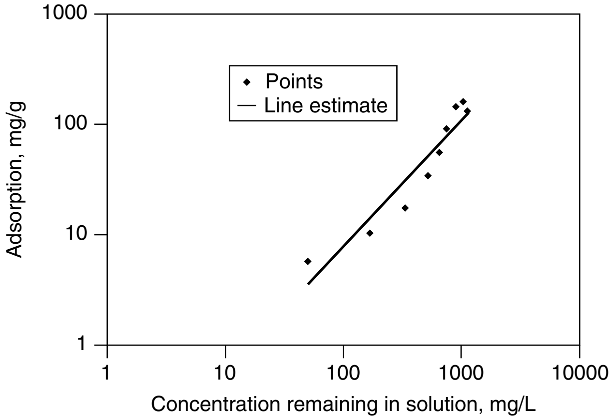


Figure 24. Isotherm showing the adsorption capacity of cationic organoclay for chlorine from water.

Performance of activated carbon in this test is superior because iodine molecules fit inside the pores and do not cause blinding and all adsorption on the organoclay takes place outside the clay platelets. Therefore, it is concluded that this test is of no use for organoclay, although the results are interesting.

Below are several case histories, which give a practical appreciation of organoclays to the engineer who designs remediation systems.

Table 3. Laboratory Column Study with Cationic Organoclay

Arsenate
Amount of cationic organoclay used: 16.5 grams (16 × 30 mesh) Amount of spiked water passed through column: 8.31 liters
Removal capacity of cationic organoclay for arsenate by weight: 0.3%, or 3 grams per 1000 grams cationic organoclay
Fluoride
Amount of cationic organoclay used for fluoride removal: 16.5 grams (16 × 30 mesh) Amount of spiked water passed through column: 0.54 liters.
Removal capacity of cationic organoclay by weight: 0.1% or 1 gram fluoride per 1000 gram of cationic organoclay
Chromate
Batch test: 100 mL water spiked with 5 mg/L hexavalent chromium, added 2 grams powdered cationic organoclay: Removed 96% of 5 mg/L.
Conclusion
Aside from the extreme efficiency with which cationic organoclay removes humic acids from water, it also removes negatively charged metals, such as those shown above, and selenite.

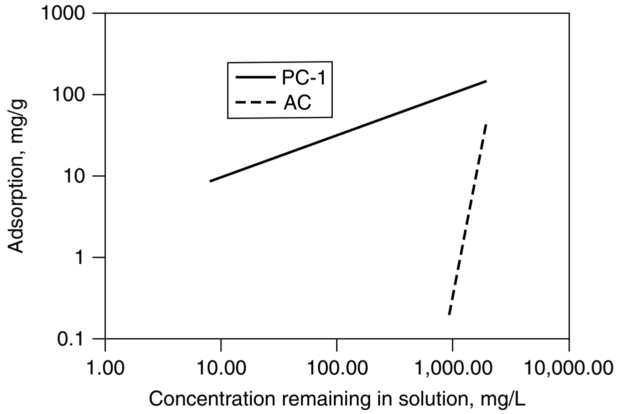


Figure 25. Isotherm showing the adsorption capacity of cationic organoclay with that of activated carbon.

Case Histories

1. A creosote superfund site on the East Coast installed a pump and treat system consisting of two filter vessels, each containing 20,000 lb activated carbon. The flow rate was 170 gpm. The COD consisted of 40–60 ppm, including benzene, VOCs, and phenols. The activated carbon lasted about 2 weeks with a breakthrough of 7–12 ppm COD; then it had to be replaced. After another vessel containing 19,000 lb of organoclay was installed, the effluent after the activated carbon was not detectable. Furthermore, there was a TSS content of 32–35 ppm (discharge limit is 40 ppm), primarily due to the presence of ferric iron. Once the organoclay was installed, the TSS content in the effluent was 3 ppm because the organoclay, a bentonite, also removes heavy metals by ion exchange.

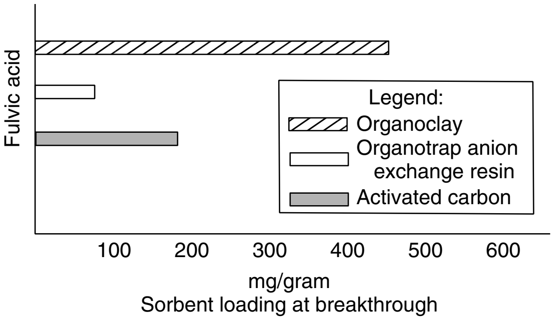


Figure 26. Microcolumn study data comparing the adsorption capacity of cationic organoclay and activated carbon for fulvic acids.

2. An old wood-treating site in Colorado is situated above an aquifer, which had a concentration of 30 ppm of an oil and 25 ppm of PCP. The discharge limit for PCP is 50 ppb. When an activated carbon system was installed, replacement was required within 1 month. After 20,000 lb of organoclay was installed prior to the activated carbon, discharge limits were met, and replacement was required only after 12 to 15 months.
3. An old railroad site in southeastern United States, where railroad ties were once treated with creosote, required excavating the soil and thermally treating it to destroy the creosote. A condensate built up that contained PCP. Rather than accepting the high cost of incinerating the condensate water, it was passed through an organoclay/carbon system and discharged locally.

This brief description of the use of organoclays for water treatment should convince the reader of their usefulness. Anyone who is interested in more detail should consult the references.

BIBLIOGRAPHY

1. Alther, G.R. (2002). Removing oils from water with organoclays. *J. Am. Water Works Assoc.* **94**(7): 115–121.
2. Alther, G.R. (1997). Working hand in hand with carbon for better results. *Soil & Groundwater Cleanup* **May**: 17–19.
3. Sheng, G., Xu, S., and Boyd, S.A. (1996). Co-sorption of organic contaminants from water by hexadecyltrimethylammonium exchanged clays. *Water Res.* **30**(6): 1483–1489.
4. Smith, J.A. and Jaffe, P.R. (1994). Benzene transport through landfill liners containing organophilic bentonite. *J. Environ. Eng.* **120**(6): 1559–1577.
5. Wolfe, T.A., Demiral, T., and Bowman, E.R. (1985). Interaction of aliphatic amines with montmorillonite to enhance adsorption of organic pollutants. *Clays Clay Miner.* **33**(4): 301–311.
6. Jaynes, W.F. and Boyd, S. (1991). Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Sci. Soc. Am. J.* **55**(1): 43–48.
7. Jordan, J.W. (1949). Organophilic bentonites. I. Swelling in organic liquids. *J. Phys. Colloid Chem.* **53**(2): 294–306.
8. Alther, G.R. (2004). A winning combination. *Water Wastewater Prod.* **July/August**: 22–27. Available at www.wwp-online.com.
9. Alther, G.R., Evans, J.C., and Tarites, R. (1991). The use of organoclays for stabilization of hazardous wastes. *Proc. 4th Annu. Hazardous Waste Manage. Conf./Central*, pp. 547–552.
10. Alther, G.R., Evans, J.C., and Pancoski, S. (1989). *A Composite Liner System to Retain Inorganic and Organic Contaminants*. Hazardous Materials Research Institute, Superfund 89, Silver Spring, MD.
11. Alther, G.R., Evans, J.C., and Pancoski, E.S. (1988). Organically modified clays for stabilization of organic hazardous waste. Hazardous Materials Control Research Institute *9th Natl. Conf., Superfund 88*, Silver Spring, MD, pp. 440–445.
12. Cowan, C.T. and White, D. (1962). Adsorption by organoclay complexes, I. *Proc. 9th Natl. Clay Conf.*, pp. 4509–4517.
13. Slabough, W.H. and Hanson, D.B. (1969). Solvent selectivity by an organoclay complex. *J. Colloid Interface Sci.* **29**(3): 460–463.
14. Street, G.B. and White, D. (1963). Adsorption by organoclay derivatives. *J. Appl. Chem.* 288–291.
15. Lagaly, G. (1981). Characterization of clays by organic compounds. *Clay Miner.* **16**: 1–21.
16. Lagaly, G. (1979). The "layer charge" of regular interstratified 2:1 clay minerals. *Clays Clay Miner.* **27**: 1–10.
17. Fashan, A., Tittlebaum, M., and Cartledge, F. (1993). Nonionic organic partitioning onto organoclays. *Hazardous Waste Hazardous Mater.* **10**(3): 313–322.
18. Mortland, M.M. (1970). Clay–organic complexes and interactions. *Adv. Agron.* **22**: 75–117.
19. Theng, B.K.G. (1974). *The Chemistry of Clay-Organic Reactions*. Halstead Press, John Wiley & Sons, New York.
20. Alther, G.R. (1999). Organoclays remove oil, grease, solvents and surfactants from water. *CleanTech 99 Proc.*, Witter, Flemington, NJ, pp. 72–79.
21. Alther, G.R. (1998). Put the breaks on oil and grease. *Chem. Eng.* **March**: 82–88.
22. Alther, G.R. (1996). Organically modified clay removes oil from water. *Waste Manage.* **15**(8): 623–628.
23. Alther, G.R. (1995). Organically modified clay removes oil from water. *Waste Manage.* **15**(8): 641–650.
24. Jaynes, W.F. and Vance, G.F. (1996). BTEX sorption by organo-clays: Cosorptive enhancement and equivalence of interlayer complexes. *Soil Sci. Soc. Am. J.* **60**: 1742–1749.
25. Mortland, M.M., Shaobai, S., and Boyd, S.A. (1986). Clay–organic complexes as adsorbents for phenols and chlorophenols. *Clays Clay Miner.* **34**(5): 581–585.
26. Alther, G.R. (2001). Organoclays remove humic substances from water. In: *Humic Substances*. E.A. Ghabbour and G. Davis (Eds.). Royal Society of Chemistry, Cambridge, UK, pp. 277–288.
27. Tillman, F.D., Bartelt-Hunt, S.L., Craver, V.A., Smith, J.A., and Alther, G.R. (2004). Relative metal ion sorption on natural and engineered sorbents: Batch and column studies. *Environ. Eng. Sci.* (submitted).
28. Alther, G.R. (2002). *Using Organoclays to Enhance Carbon Filtration. Waste Management* 22. Pergamon Press, New York, pp. 507–513.
29. Alther, G.R. (2000). Maximize water cleanup performance. *Environ. Prot. Mag.* **Feb.**: 37–39. Available at www.wp-online.com.
30. Alther, G.R. (1999). Organoclay filtration technology for oil removal. *Fluid/Part. Sep. J.* **12**(2): 96–102.

COMBINED SEWER OVERFLOW TREATMENT

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INTRODUCTION

Combined sewer overflows (denoted hereafter as CSOs) occur when flows exceed the hydraulic capacity of either the wastewater treatment plant (denoted as WWTP) or the collection system that transports the combined flow of storm water and sanitary sewage to the WWTP. The principal components of a combined sewer system include (1) the contributing drainage area (catchment) and wastewater sources, (2) the combined sewer pipe network and interceptor(s), (3) the regulator and diversion structures, and (4) the CSO outlets (Fig. 1).

When an overflow occurs, the excess flows tend to be discharged into the neighboring receiving body of surface water. CSOs typically discharge a variable mixture of raw sewage, industrial/commercial wastewater, polluted runoff, and scoured materials that build up in the collection system during dry weather. These discharges contain a variety of pollutants that may adversely impact the receiving waterbody, including pathogenic microorganisms, viruses, cysts, and chemical and floatable materials. Health risks associated with bacteria-laden water may result from dermal contact with the discharge, from ingestion of contaminated water, as well as from consumption of fish or shellfish.

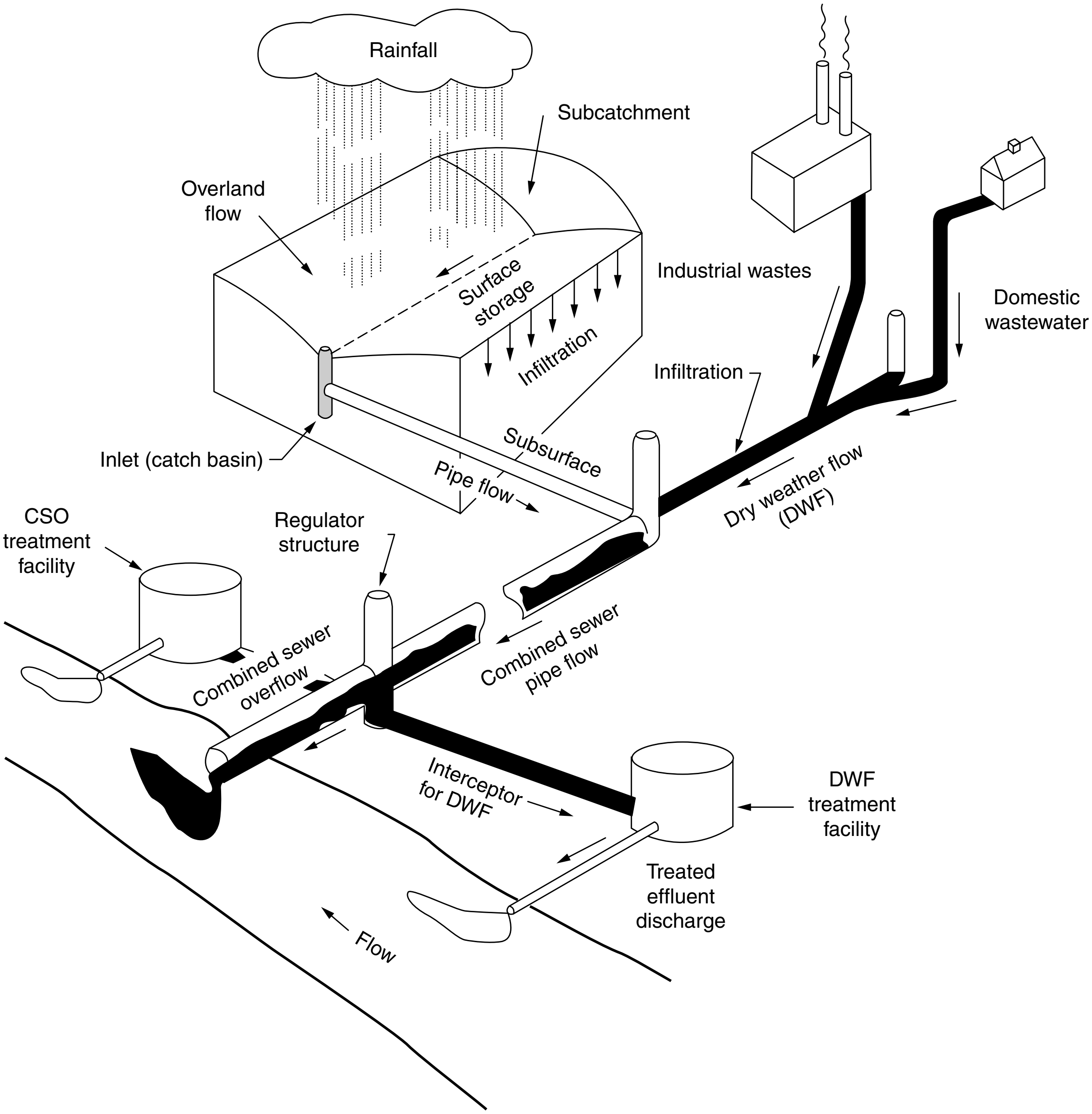

Figure 1. Schematic diagram of a combined sewer system (2).

The methods used to treat CSOs can be classified as physical, chemical, and biological and methods that include a combination of some or all the above, such as treatment by constructed reed beds (1).

PHYSICAL TREATMENT

Physical treatment alternatives include sewer separation, retention basins, swirl/vortex technologies, screening, netting systems for floatable control, dissolved air flotation, and filtration. Most of these physical unit operations have been in use for many years and are considered reliable. Physical treatment operations are usually flexible enough to be readily automated and can operate over a wide range of flows. They can also stand idle for long periods of time without affecting treatment efficiency (1).

Sewer Separation

Separation is conversion of a combined sewer system into separate storm water and sanitary sewage collection systems. This alternative, historically considered the ultimate answer to CSO pollution control, has been reconsidered in recent years because of increased cost and major disruptions to traffic and other daily community activities from separated collection systems. Several potential benefits of sewer separation might warrant its consideration in specific cases:

1. Eliminating CSOs and preventing untreated sanitary sewage from entering the receiving waters during wet weather. Sanitary sewage is a more objectionable source of certain pollutants, such as TSS, sanitary floatables, and bacteria.
2. Reduced volume of flow to be treated at the publicly owned treatment works (POTWs), thus reducing operating and maintenance (O & M) costs by eliminating surface runoff inflows during wet weather.
3. Reduced infiltration and excess flow to a POTW for new sanitary sewer construction, replacing old combined sewers.
4. Reducing upstream flooding, as well as overflows, when the existing combined sewers are undersized and back up frequently during storms.
5. Being more effective and economical than treatment facilities for remote segments of a combined sewer system, serving relatively small areas.

Retention Basins

CSO retention basins (RBs) capture and store some of the excess combined sewer flow that would otherwise be bypassed to receiving waters. Stored flows are subsequently returned to the sewer system during dry weather, when the in-line flows are reduced and more capacity is available at the treatment facility. RBs can be designed to control both flow rate and water quality.

Figure 2 shows an example of a multistage CSO RB that has some treatment capabilities. This facility handles peak flows by routing them through a mechanical bar screen and then pumping them into the first compartment. The main function of the first compartment is to allow primary settling and grit removal. If the flows continue to rise, the

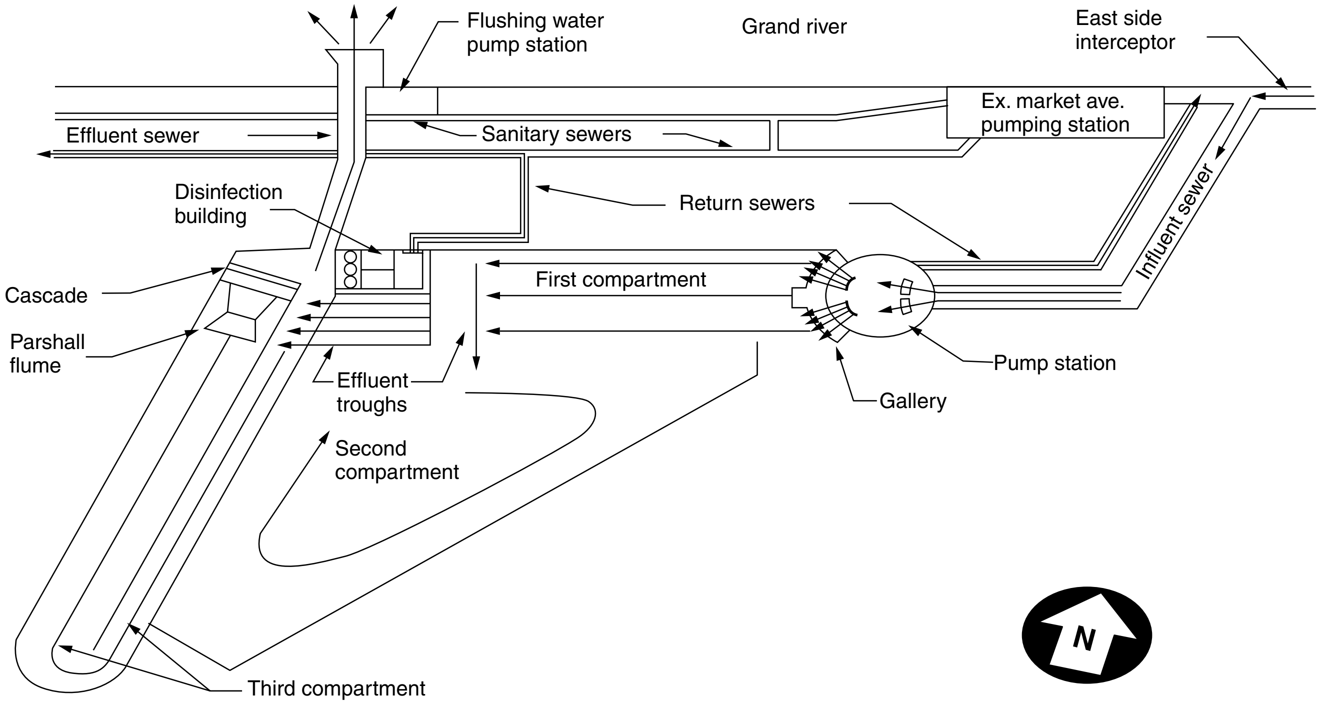

Figure 2. Multistage CSOs RBs (3).

first compartment fills and then spills over into the second compartment. This compartment is designed specifically to store most of the overflow from the first compartment. The second compartment is also equipped with a floor wash system that flushes all settled sediments into a collection trough. If the flows continue to rise, the water spills over into a series of troughs, where sodium hypochlorite is applied for disinfection. The flow is then routed to a contact tank (third compartment), which eventually returns the water to the nearby surface waters (2).

These are the primary concerns in the operation of RBs:

1. Managing flows to and from the retention basin.
2. Preventing the combined sewage from becoming septic or handling the wastewater appropriately after it has become septic.
3. Removing accumulated solids and floatables.
4. Disinfecting basin overflows to receiving waters.

Swirl/Vortex Technologies

Solids separation devices, such as swirl concentrators and vortex separators, have been used in Europe and (to a lesser extent) in the United States. These devices are relatively small, compact solids separation units with no moving parts. A typical vortex-type CSO solids separation unit is illustrated in Fig. 3. During wet weather, the outflow from the unit is throttled, causing the unit to fill and to self-include a swirling vortex-like flow regime. Secondary flow currents rapidly separate settleable grit, as well as floatable matter. The concentrated foul matter is intercepted for treatment, whereas the cleaner, treated flow can be discharged to receiving surface waters. These devices are usually intended to operate under very high hydraulic flow regimes.

Screening

Generally, there are two types of bar screens, coarse and fine. Both are used at CSOs control facilities; with each type provides a different level of solids removal efficiency. Although there is no industrial standard for classifying screens based on aperture size, coarse bar screens generally have a 0.04 to 0.08 m clear spacing between bars, whereas fine screens generally have rounded or slotted openings of 0.3 to 1.3 cm clear space.

Coarse Screens. Coarse screens are constructed of parallel vertical bars and are often referred to as *bar racks* or *bar screens*. In CSO control and treatment facilities, coarse screens are usually the first unit of equipment in the system. These screens are usually set at 0 to 30° from the vertical and are cleaned by an electrically or hydraulically driven rake mechanism that removes the collected material from the screen continuously or

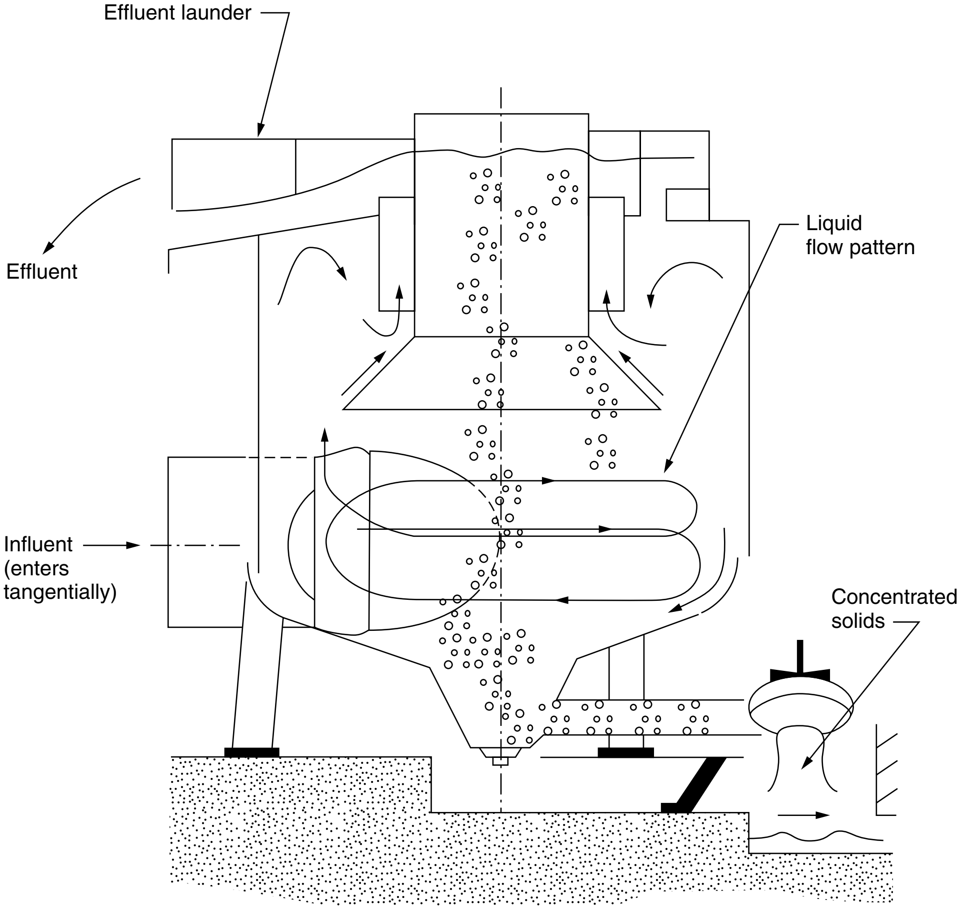

Figure 3. Cross section through a typical vortex-type solids separation device (1).

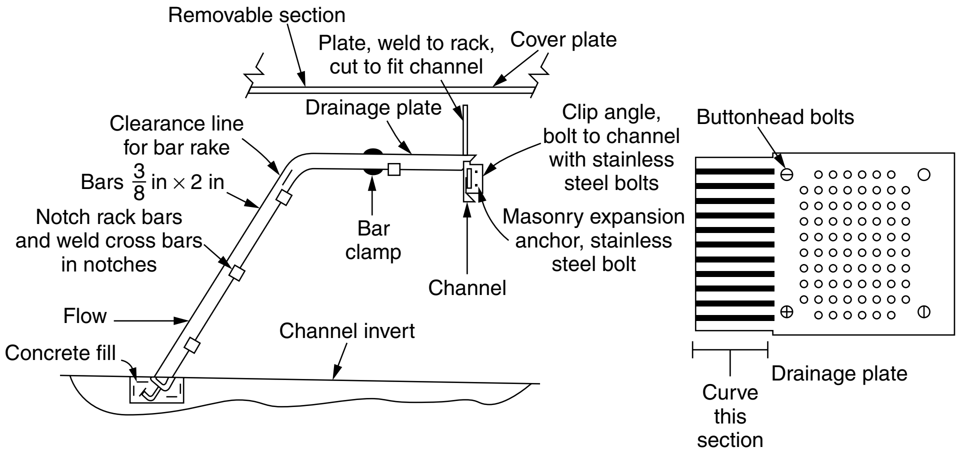

Figure 4. Diagram of trash rack used for treating CSOs (2).

periodically. The most common type of bar screen used at CSO control facilities is a trash rack. Trash racks typically have 0.04 to 0.08 m clear spacing between bars. Figure 4 is a diagram of a typical trash rack.

Fine Screens. Fine screens at CSO facilities typically follow coarse bar screening equipment and provide the next level of physical treatment in removing the smaller solid particles from the waste stream. Both fixed (static) and rotary screens have been used in CSO treatment facilities.

Fixed fine screens are typically provided with horizontal or rounded slotted openings of 0.02 to 1.27 cm. The screens are usually constructed of stainless steel in a concave configuration, at a slope of approximately 30° from the vertical. Flow is discharged across the top of the screen. The flow then passes through the slotted openings, and solids are retained on the screen surface. Solids are discharged from the screen surface by gravity and by washing onto a conveyor belt or other collecting system.

Rotary fine screens include externally and internally fed screens. Externally fed screens allow the wastewater to flow over the top of the drum mechanism and through the screens surfaces, while collecting solids onto the screen surface. As the screen rotates, a system of cleaning brushes or sprayed water removes debris from the drum. Internally fed systems discharge wastewater in the center of the drum, allowing the water to pass through the screen into a discharge channel, while solids are removed from the screen surface by cleaning brushes or a water spray.

In response to the need for solids and floatables control during storms, proprietary screen products, such as the ROMAG^{TM} screen, have been designed for wet weather applications (Fig. 5). The ROMAG^{TM} screen partitions the flow, sending screened flow to the CSO discharge point, while keeping solids and floatables in the flow directed toward the sanitary sewer. This screen works as follows: excess flow enters the screening chamber, flows over a spill weir, and proceeds through the screen into a channel, which discharges flow to a neighboring receiving waterbody. Floatables trapped by the screen move laterally along the face of the screen via combs/separators to the transverse end section of the pipe, where they can be directed to the sanitary sewer line for ultimate removal at the wastewater treatment plant. Screen blinding is prevented by a hydraulically driven rake assembly.

Netting Systems for Floatables Control

Floatables control technologies are designed to reduce or eliminate the visible solid waste that is often present in CSO discharges. The Netting Trash-Trap^{TM} system is a modular floatables collection system, located at the CSO outfall. It uses the passive energy of the effluent stream to drive the floatable materials into disposable mesh bags. These bags are suspended horizontally in the CSO flow stream within a support structure. The construction methodology and method of installation at the outfall are determined site-by-site. Ever since, several other end-of-pipe, but also in-line configurations have been developed and implemented.

The standard nets used in the system are designed to hold up to 0.7 m^3 of floatables and a weight of 227 kg each. For the floating units, the effluent stream and the collected floatables are directed into the bags by two floating booms and curtains, which run from the front corners of the pontoon to either side of the outfall, where they attach to a vertical piling that has a roller

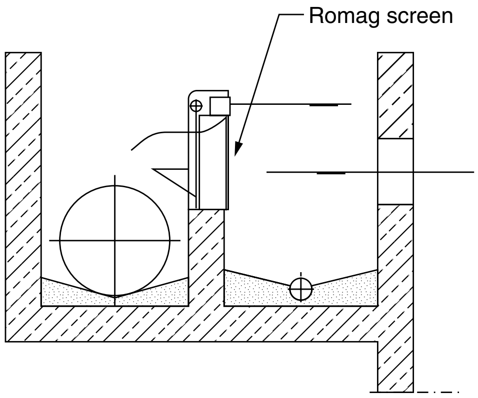

Figure 5. ROMAG^{TM} “combing” mechanical screen (vertical) for CSO floatables control (4).

mechanism or a shoreline support. This design allows the boom to float and accommodate changes in the water level. The extended curtains are weighted to conform to the water bottom. The maximum high water level, expected at the site, determines the depth of the curtain. Certain modifications of the outfall design may include adding structural support, attaching structural struts and strut anchor support, and adding foundations.

Dissolved Air Flotation

Dissolved air flotation (DAF) removes solids by introducing fine air bubbles into the CSO stream. The air bubbles can attach to solid particles suspended in the liquid, causing the solids to float toward the surface, from where they can be skimmed off. This technology has been tested in several CSO applications. A major advantage of DAF is its relatively high overflow rate and short detention time, which results in reduced facility size, compared to conventional sedimentation. Oil and grease are also more readily removed by DAF. Operating costs for DAF are high, due to larger energy demand, and skilled operators are usually required for efficient operation.

Filtration

Dual media high rate filtration has been piloted for treating of CSO flows. A two-layer bed, consisting of coarse anthracite particles on top of less coarse sand, was used. After backwash, the less dense anthracite remains on top of the sand. Filtration rates of 16 gal/ft^2/min or more were used, resulting in substantially smaller space requirements, compared with sedimentation. Demonstration test systems included pretreatment by fine-mesh screens. The addition of chemical coagulant agents improved the performance considerably. Filtration is more appropriately applied after pretreatment by fine screening. Operation may be automated but tends to be rather O & M intensive. Intermittently operated sand filters can also be used for CSO treatment and show considerable promise for larger scale operations (3).

CHEMICAL TREATMENT (MAINLY DISINFECTION)

Chlorine

Chlorine has long been the disinfectant of choice for most disinfection systems. It offers reliable reduction of pathogenic microorganisms at reasonable operating costs. Disinfection by chlorine is the most common method used to kill pathogenic microorganisms at WWTPs, but this methodology may not be feasible at all CSOs for several reasons:

1. CSOs occur intermittently, and their flow rate is highly variable, thus making it difficult to regulate the addition of disinfectant.
2. CSOs have high concentrations of suspended solids.
3. CSOs can vary widely in temperature and bacterial composition.
4. Disinfectant residuals, following the use of chlorine, may be prohibited from entering receiving waters.
5. CSO outfalls are often located in remote areas and thus, may require automated controls for the disinfection systems.

In addition to these problems, increased health and safety concerns for using chlorine to disinfect CSOs have prompted the development of alternative disinfectant agents/methods, which often present fewer problems and health hazards. Alternative methods to chlorine addition have been developed and evaluated for the continuously disinfecting wastewater discharges to small streams or sensitive waterbodies and are now also being considered for treating CSOs and other episodic discharges. These include the use of chlorine dioxide, the application of ozonation or of ultraviolet radiation, the addition of peracetic acid, and electron beam irradiation (e-beam) (5).

Ozone

Ozone is a strong oxidizer and is applied to wastewater as a gas mixture with air. Its use in CSO treatment facilities for wastewater disinfection is relatively new; few facilities are currently using ozone for disinfection. This can be attributed to the higher initial capital costs of ozone generating equipment. Ozone is equal or superior to chlorine in “killing” power for pathogenic microorganisms, but it does not cause the formation of harmful by-products (halogentated organics), as does chlorination (5).

Ultraviolet Radiation

UV radiation is electromagnetic radiation used for disinfection. UV disinfection incorporates the spectrum of light between 40 and 400 nm. Germicidal properties range between 200 and 300 nm; 260 nm is the most lethal. The primary method for using UV disinfection is to expose wastewater to a UV lamp. UV radiation is not a chemical disinfection method; it avoids the addition of chemical reagents, and it disinfects without altering the physical or chemical properties of water. However, UV efficiency is affected by the presence of suspended solids in the CSOs, which scatter and absorb light and lower the method’s efficiency. Thus, UV disinfection is not very effective for CSOs that containing high TSS (5).

Peracetic Acid

Peracetic acid (CH_3COOOH, denoted PAA), also known as ethaneperoxoic acid, peroxyacetic acid, or acetyl hydroxide, is a very strong oxidant. Based on limited demonstration data for disinfecting secondary treatment plant effluents, peracetic acid appears to be an effective disinfectant and should be further evaluated for treating CSOs. The equilibrium mixture of hydrogen peroxide and acetic acid that produces PAA is too unstable and explosive to transport; therefore, PAA must be produced on site. The decomposition of PAA results in the formation of acetic acid, hydrogen peroxide, and oxygen (5).

Electron Beam Irradiation

Electron beam irradiation (e-beam) uses a stream of high energy electrons that is directed into a thin film of water or sludge. The electrons break water molecules apart and produce a large number of highly reactive chemical species (mainly radicals), including oxidizing hydroxyl radicals, reducing aqueous electrons, and hydrogen atoms. These are the main disadvantages of this method:

1. Increased safety considerations due to the use of high-voltage technology and the generation of X-ray radiation.
2. There is no full-scale application experience for CSOs.
3. High capital costs.
4. High O & M costs.
5. Thin process flow stream.
6. Sufficient pretreatment straining of influent is also required to remove most of suspended solids for efficient application of this system (5).

BIOLOGICAL TREATMENT AND COMBINED SYSTEMS

The use of biological treatment, combined with certain of the aforementioned physical–chemical treatment processes, for treating CSO presents certain serious limitations:

1. The biomass used to assimilate the nutrients in the CSOs must also be kept alive during dry weather, which can be rather difficult, except at an existing treatment plant.
2. Biological processes are subject to upset under to erratic loading conditions.
3. The land requirements for this type of treatment plant can be excessive near an urban area.
4. Operation and maintenance can be costly, and the facilities require highly skilled operators.

Some biological treatment technologies are used in CSO control as elementary parts of a WWTP. Pump-back or bleed-back flows from CSO storage facilities commonly receive secondary (biological) treatment in the treatment plant, once wet weather flows have subsided. In a WWTP, which has maximized the wet weather flows that are accepted, the hydraulic flows are sometimes split; only a portion of the primary treated flows is subjected to secondary treatment to avoid process upset. The split flows are blended again before the exit and disinfected appropriately for final discharge (1).

Constructed Wetlands

Constructed wetlands are artificial wastewater treatment systems, consisting of shallow (usually 1 m deep) beds, that have been planted with aquatic plants, and which rely upon natural microbial, biological, physical, and chemical processes to treat CSOs. They typically have impervious clay or synthetic liners and engineered structures to control the flow direction, liquid detention time, and water level. Depending on the specific type of system, they may contain inert porous media, such as rock, gravel, or sand. Constructed wetlands have been classified in the literature into two types.

Free water surface (FWS) wetlands (also known as surface flow wetlands) closely resemble natural wetlands in appearance; they contain aquatic plants, and water flows through the leaves and stems of the plants. Vegetated submerged bed (VSB) systems (also known as subsurface flow wetlands) do not resemble natural wetlands because they have no standing water. Wastewater (i.e., CSOs) stays beneath the surface of the medium, flows in contact with the roots and rhizomes of the plants, and is not visible or available to wildlife. Finally, the term vertical flow wetland is used to describe a typical vertical-flow sand or gravel filter, which has been planted with aquatic plants. Successful operation of this type of system depends mainly on its operation as a filter (i.e., frequently applying dosing and draining cycles) (7).

Figure 6 shows a typical cross section of a horizontal subsurface flow wetland (also known as a reed bed). These systems are used to treat the excess combined sewer flow that would otherwise be bypassed to receiving waters, with good treatment efficiency that meets the tight permitting conditions. During exceptionally dry weather, secondary or tertiary treated effluent can be diverted to this system to conserve the plantings and the microorganism's population in the system (6).

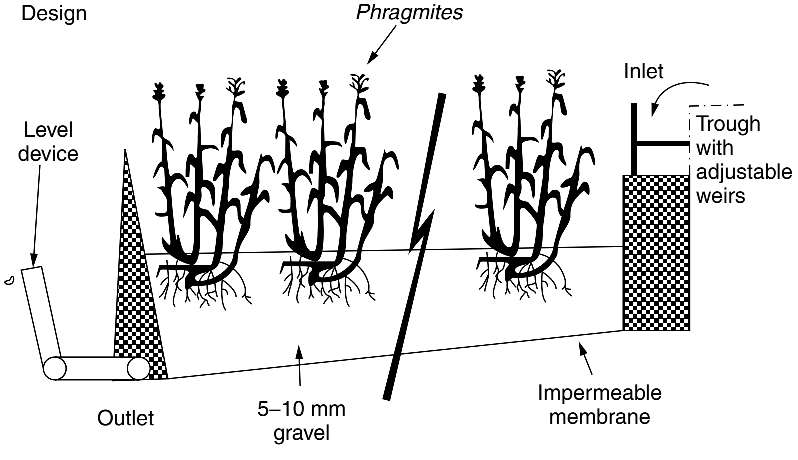

Figure 6. Diagrammatic longitudinal section of a horizontal subsurface flow wetland (6).

BIBLIOGRAPHY

1. U.S. Environmental Protection Agency. (1993). *Manual: Combined Sewer Overflow*. Report EPA/625/R-93/007. Cincinnati, OH.
2. Metcalf & Eddy, Inc. (1991). *Wastewater Engineering: Treatment, Disposal and Reuse*. McGraw-Hill, Singapore.
3. U.S. Environmental Protection Agency. (1999). *Combined Sewer Overflow Technology Fact Sheet Retention Basins*. Report EPA/832/F-99/042. Washington, DC.
4. Pisano, W.C. (1995). Comparative assessment: vortex separators, rotary sieves, and "Combing" screens for CSO floatable control. Presented at the *Water, Environ. Fed. Annu. Conf.*, Miami, FL.
5. U.S. Environmental Protection Agency. (1999). *Combined Sewer Overflow Technology Fact Sheet Alternative Disinfection Methods*. Report EPA/832/F-99/033, Washington, DC.
6. Green, M.B. and Upton, J. (1995). Constructed reed beds: Appropriate technology for small communities. *Water Sci. Technol.* **332**: 339–348.
7. U.S. Environmental Protection Agency. (2000). *Manual: Constructed Wetlands Treatment of Municipal Wastewaters*. Report EPA/625/R-99/010, Cincinnati, OH.
8. Prochaska, C.A. and Zouboulis, A.I. (2003). Performance of intermittently operated sand filters: A comparable study, treating wastewaters of different origins. *Water, Air, Soil Pollut.* **147**: 367–388.

BIOLOGICAL PHOSPHORUS REMOVAL IN THE ACTIVATED SLUDGE PROCESS

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Phosphorus often is the limiting nutrient that promotes the excessive growth of aquatic plants, especially algae, and excess quantities of phosphorus often are present in the effluent of activated sludge processes in quantities greater than those required for the growth of aquatic plants. Excess phosphorus promotes not only the undesired growth of aquatic plants but also the undesired impacts of the death of the aquatic plants upon the receiving water. Therefore, state and federal regulatory agencies limit the quantity of phosphorus in the effluent. The requirement limiting the quantity of phosphorus in the effluent of activated sludge processes is becoming more and more stringent for municipal wastewater treatment plants. For example, discharge limits for total phosphorus of 2 mg/L or lower have been applied broadly to many plants in the lower Susquehanna River Basin.

Several environmental concerns related to the excessive growth of aquatic plants include clogging of receiving waters and the production of color, odor, taste, and turbidity problems when the receiving waters are used for potable water supplies. The die-off of large numbers of aquatic plants results in oxygen depletion when the plants decompose. Those portions of the aquatic plants that do not decompose accumulate in the receiving waters and contribute to eutrophication or rapid aging of the receiving waters. Additionally, some algae release toxic compounds.

Municipal wastewater contains 10–20 mg/L of total phosphorus. The total phosphorus consists of inorganic and organic phosphorus. Inorganic phosphorus consists of phosphorus-containing compounds that do not contain carbon and hydrogen. Organic phosphorus-containing compounds do contain carbon and hydrogen. Significant and common inorganic phosphorus-containing compounds are orthophosphate (PO_4-P) and polyphosphates. Orthophosphate makes up approximately 50–70% of the total phosphorus in influent and approximately 90% of the phosphorus in the effluent of municipal wastewater treatment plants.

Orthophosphate is the preferred phosphorus nutrient for aquatic plants. The forms of orthophosphate found in the influent and effluent of wastewater treatment plants are pH dependent. At pH values <7 the $H_2PO_4^-$ form is dominant, whereas the HPO_4^{2-} form is dominant at pH values >7. The forms of orthophosphate in the influent and effluent are produced through dissociation (Eq. 1).

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \tag{1}$$

Significant and common organic phosphorus-containing compounds include phytin, nucleic acids, and phospholipids. Phytin is an organic acid found in vegetables such as corn and soybean. Phytin is difficult to digest and is found in domestic wastewater. Nucleic acids are large complex molecules that contain genetic material. Phospholipids also are large and complex molecules that are used in the production of structural materials. Phytin, nucleic acids, and phospholipids degrade slowly in the activated sludge process. Their degradation results in the release of orthophosphate. It is the orthophosphate that is used as the phosphorus nutrient by bacteria and incorporated into cellular material or MLSS (mixed liquor suspended solids) in the activated sludge process.

The degradation of organic compounds in activated sludge processes and the incorporation of phosphorus into new cellular material are achieved by a large and diverse population of bacteria. However, there are some bacteria that are capable of removing and storing phosphorus in quantities larger then their cellular needs. Bacteria that are capable of removing phosphorus in excess quantities are known as "phosphorus-accumulating organisms" (PAO) or "poly-P bacteria" (Table 1). Of all poly-P bacteria, *Acinobacter* is the most commonly known and studied. Phosphorus is removed from the wastewater in the orthophosphate form and stored by the poly-P bacteria as polyphosphate granules. Removal of phosphorus by poly-P bacteria often is termed "luxury uptake of phosphorus."

There are several operational measures that can be used in activated sludge processes to remove phosphorus

Table 1. Genera of Wastewater Bacteria that Contain Poly-P Species

Acinobacter	*Escherichia*
Aerobacter	*Klebsiella*
Aeromonas	*Moraxella*
Arthrobacter	*Mycobacterium*
Beggiatoa	*Pasteurella*
Enterobacter	*Pseudomonas*

Table 2. Biological and Chemical Measures Available for Phosphorus Removal

Operational Measure	Description
Chemical precipitation	Use of alum, ferric chloride, ferrous sulfate, or lime at a high pH; results in increased operational costs for chemical addition and disposal of chemical sludge
Assimilation	Phosphorus incorporated into cellular material (MLSS) as 1–3% dry weight and wasted from the activated sludge process
Biological phosphorus removal	Phosphorus incorporated into cellular material (MLSS), especially poly-P bacteria, as 6–7% dry weight and wasted from the activated sludge process
Biological/chemical techniques	Precipitation of phosphorus released by poly-P bacteria under anaerobic condition and chemically precipitated with alum, ferric chloride, ferrous sulfate, or lime

from the effluent. These measures include biological and chemical techniques (Table 2). Phosphorus as orthophosphate can be removed from wastewater through its chemical precipitation as a metal salt at a high pH. Chemical compounds commonly used to precipitate orthophosphate include alum, ferric chloride, ferrous sulfate, and lime. Orthophosphate also can be removed through its incorporation as cellular material. By increasing the MLSS, more orthophosphate is incorporated into bacterial cells. However, the amount of phosphorus in the bacterial cells is only 1–3% by dry weight. Orthophosphate also can be removed by combined biological and chemical techniques and through biological phosphorus removal.

Of the biological and chemical measures available for phosphorus removal, biological phosphorus removal offers several advantages when compared to other measures. For example, biological phosphorus removal is relatively inexpensive due to the reduction in chemical costs and sludge disposal costs associated with chemical addition to precipitate orthophosphate. Biological phosphorus removal is also capable of removing phosphorus to low effluent concentrations.

Biological phosphorus removal or luxury uptake of phosphorus occurs when orthophosphate uptake by poly-P bacteria exceeds cellular requirements. If luxury uptake of phosphorus does not occur in an activated sludge process, the phosphorus content of the activated sludge is approximately 1–3% on a dry weight basis. If luxury uptake of phosphorus does occur, the phosphorus content of activated sludge is approximately 6–7%.

Bacteria that are capable of luxury uptake of phosphorus enter activated sludge processes in fecal waste and through inflow and infiltration as soil and water bacteria. These bacteria are unique and remove phosphorus in excess of cellular needs in the presence of rapidly degradable organic compounds when transferred from an anaerobic (fermentative) tank to an aerobic tank.

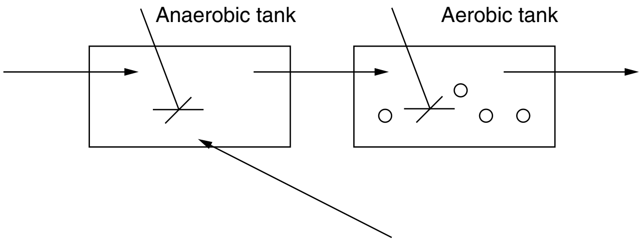

Figure 1. Microbial activity in the anaerobic tank. In the anaerobic tank, soluble cBOD is fermented in the absence of free molecular oxygen and nitrate ions. The fermentation process produces a variety of fatty acids. The acids are rapidly absorbed by the poly-P bacteria and stored as an insoluble starch (PHB). In order to absorb the fatty acids and store them as starch, energy in the form of orthophosphate is released by the poly-P bacteria to the bulk solution.

Table 3. Soluble Fatty Acids Produced in the Anaerobic Tank

Fatty Acid	Formula
Formic acid	$HCOOH$
Acetic acid	CH_3COOH
Propionic acid	CH_3CH_2COOH
Butyric acid	$CH_3CH_2CH_2COOH$
Valeric acid	$CH_3CH_2CH_2CH_2COOH$
Caproic acid	$CH_3CH_2CH_2CH_2CH_2COOH$

In the anaerobic tank (Fig. 1) that has a retention time of 1–2 h, fatty acids are produced in large quantities through fermentation (Table 3). Fermentation is the microbial degradation of organic compounds without the use of free molecular oxygen (O_2) or nitrate ions (NO_3^-). Poly-P bacteria quickly absorb the fatty acids produced through fermentation. Although the fatty acids are absorbed, the acids are not degraded. Instead, the soluble fatty acids are stored in the form of insoluble starch granules (poly-β-hydroxybutyrate or PHB).

The conversion of fatty acids to insoluble starch granules and the storage of the granules requires the expenditure of energy by the poly-P bacteria. The expenditure of energy results in a release of orthophosphate from the poly-P bacteria into the fermentative tank. With the production of PHB in the poly-P bacteria, the fermentative tank contains two "pools" of phosphorus—influent phosphorus and poly-P bacteria released orthophosphate.

In the aerobic tank (Fig. 2) that has a retention time of 1–2 h, PHB granules are solubilized and degraded with the use of free molecular oxygen. The degradation of PHB granules results in the release of a large quantity of energy that is captured and stored by the poly-P bacteria. The energy is stored in the bacteria in the form of insoluble phosphate granules or voluntin. Phosphorus is removed from the activated sludge process when MLSS (bacteria) is wasted.

There are several processes available for the biological removal of phosphorus. Often biological phosphorus removal is combined with nitrification and denitrification. Nitrification is the oxidation of ammonium ions (NH_4^+) to nitrate ions (NO_3^-), while denitrification is the reduction

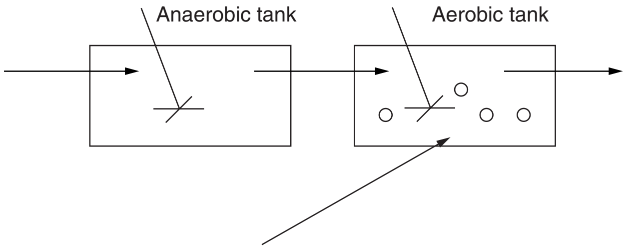

Figure 2. Microbial activity in the aerobic tank. In the aerobic tank, PHB is solubilized and degraded in the presence of free molecular oxygen. The degradation of PHB results in the production of carbon dioxide, water, and new bacterial cells. Phosphorus released in the anaerobic tank as well as phosphorus present in the waste stream are absorbed by poly-P bacteria and stored in phosphorus granules.

of nitrate ions to molecular nitrogen (N_2) and nitrous oxide (N_2O). Nitrification and denitrification are responsible for the biological removal of nitrogen from wastewater. When nitrification and denitrification are combined with biological phosphorus removal, these three biological processes are known as biological nutrient removal (BNR). There are five significant processes used for biological phosphorus removal or BNR. Several of these processes are proprietary. These processes are the A/O, Phostrip, A2O, Bardenpho, and UCT.

Biological nutrient removal processes are either mainstream or sidestream (Table 4). A mainstream process contains an anaerobic tank within the major wastewater flow from influent to effluent. A sidestream process contains an anaerobic tank outside the major wastewater flow.

Of the nutrient removal processes, two are designed to remove phosphorus only. These processes are the A/O and the Phostrip. The A/O (anaerobic/oxic) process is a mainstream process (Fig. 3). The A/O process is patented by Air Products and Chemicals, Incorporated and is similar to a conventional activated sludge process.

The Phostrip process is a sidestream process and includes biological and chemical phosphorus removal (Fig. 4). A stripper tank is included in the Phostrip process. This tank has an anaerobic condition where phosphorus is released by poly-P bacteria from the return activated sludge (RAS). The released phosphorus is removed from the stripped tank by elutriation water. Lime is added to the elutriation water as it leaves the stripper tank. The addition of lime results in the precipitation of phosphorus as calcium phosphate.

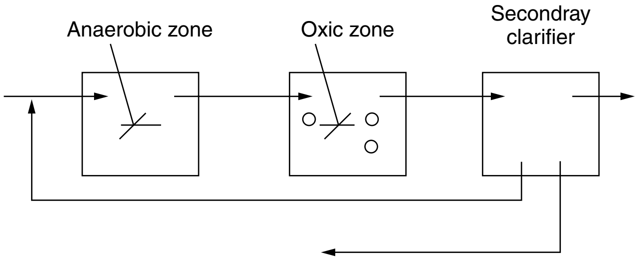

Figure 3. The A/O process.

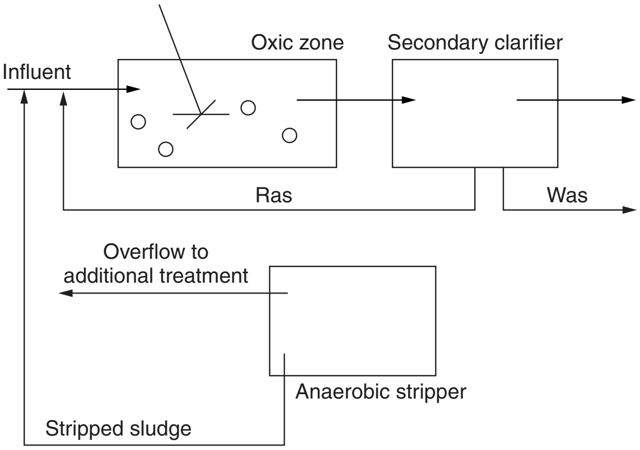

Figure 4. The Phostrip process.

The A2/O process consists of an anaerobic zone, an anoxic zone, and an oxic zone. As wastewater and bacteria move through these three zones, phosphorus is removed biologically and nitrogen is removed through nitrification and denitrification. Fermentation occurs in the anaerobic zone and phosphorus is released to the bulk solution by poly-P bacteria. In the anoxic zone nitrate ions are used (denitrified) by facultative anaerobic bacteria (denitrifying bacteria) to degrade soluble carbonaceous BOD. In the oxic zone ammonium ions (NH_4^+) in the wastewater and ammonium ions released from nitrogen-containing compounds are oxidized (nitrified) to nitrate ions (NO_3^-).

The Bardenpho process is licensed and marketed in the United States by Eimco Process Equipment Company. The Bardenpho process includes five zones (anaerobic zone, anoxic zone, oxic zone, anoxic zone, and oxic zone). The University of Capetown or UCT process also contains anaerobic, anoxic, and oxic zones. However, the UCT

Table 4. Nutrient Removal Processes

Process Name	Nutrient Removed		Process		Chemical Precipitation
	Nitrogen	Phosphorus	Mainstream	Sidestream	
A/O		X	X		
Phostrip		X		X	X
A2/O	X	X	X		
Bardenpho	X	X	X		
UCT	X	X	X		

process is designed to reduce the quantity of nitrate ions returned to the anaerobic zone in order to optimize the phosphorus removal.

As phosphorus and nitrogen discharge limits become more stringent for activated sludge processes in the United States, these nutrient removal systems will become more popular. The choice of the biological nutrient removal system is based on cost, wastewater composition, and nutrient removal requirements.

PHOTOCATALYTIC MEMBRANE REACTORS IN WATER PURIFICATION

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INTRODUCTION

General

Potable water, industrial water, and wastewater are often polluted by toxic organic species. Some classical methods (1,2) to cleanup waters, before sending them to rivers or to municipal drinking water supplies, transfer pollutants from one phase to another, hence creating further waste streams. New methods, such as those involving heterogeneous photocatalytic reactions, allow in many cases a complete degradation of organic pollutants to small and non-noxious species, without using chemicals, thus avoiding sludge production and its disposal.

Membrane separation processes, thanks to the selective property of membranes, have already proved to be competitive with other separation processes (3–7). Photocatalytic membrane reactors (PMRs) have some advantages compared to conventional photoreactors. Indeed, confining the photocatalyst to the reaction environment as a result of the presence of the membrane enables operation with high amounts of catalyst, control of the residence time of the molecules in the reactor, and realization of a continuous process with simultaneous product(s) separation from the reaction environment. Some PMR configurations using membranes ranging from microfiltration (MF) to reverse osmosis (RO) have been investigated (8–13).

The influence of various operating parameters on the photodegradation rate of pollutants present in aqueous effluents by means of discontinuous and continuous photocatalytic processes in the presence of NF membranes has been reported (14). Moreover, the possible use of solar radiation (15–18) in PMRs is of particular interest as the energy cost is one of the main drawbacks for industrial applications. Although many papers on photocatalysis have been published, the cases where membrane and photocatalyst are coupled are very few.

Historical Background

The use of photocatalysis in waste treatment is usually based on the electronic excitation of a polycrystalline semiconductor caused by light absorption that drastically alters its ability to lose or gain electrons, promoting decomposition of pollutants to harmless by-products. Photocatalytic processes in liquid phase have been applied to the degradation of several organic compounds (19–24). Only a few compounds such as chlorofluorocarbons, trifluoroacetic acid, and 2,4,6-trihydroxy-1,3,5-triazabenzene (cyanuric acid) cannot be completely degraded by photocatalytic methods (24). The formation of transient by-products, more toxic than the starting substrates, could be observed in some cases. The research on types of reactors that can be used in photocatalysis is very active, and slurry photocatalytic reactors suitable for the requirement of continuous operation are described in the literature (25,26). Nevertheless, as the chemical industry is characterized by an almost exclusive use of continuous processes, a photocatalytic powder for potential application purposes should possess a suitable size and mechanical characteristics in addition to good catalytic properties. To date, only rare examples of pilot plant photoreactors have been reported, as the difficulty of making a clear assessment of the costs of the photocatalytic processes (which are typically efficient only in dilute systems) have prevented a wider development of them from an application perspective. Some authors have immobilized the semiconductor on Pyrex glass sheets (27,28), on aerogels (29), or on particles having high surface area (e.g., alumina or silica gel) (30,31). In all these methods, a drawback is the mass transfer resistance of the reacting species, which could control the reaction rate. Despite the potential advantages of using hybrid membrane photoreactors, the research on coupling photocatalysis and membranes is not yet sufficiently developed. Some papers reported in the literature concern the use of cellulose microporous membranes (32); porphyrin containing membranes (33); porphyrins immobilized as photosensitizers on sulfocationic membranes (34); filtration coupled to catalysis (35,36); and TiO_2 immobilized inside the membrane (37), physically deposited on the membrane surface (38), or confined in suspension by means of the membrane (8,9,10,39).

FUNDAMENTALS OF HETEROGENEOUS PHOTOCATALYSIS

A simple definition of heterogeneous photocatalysis implies only the acceleration of a photoreaction by the action of a solid catalyst, which may interact with the species to be degraded and/or with the intermediates, depending on the reaction mechanism. The catalytic nature of the process should be demonstrated by checking that the turnover number (TON) is greater than 1. TON can be defined as the ratio of the number of photoinduced transformations for a given period of time to the number of photocatalytic sites. The total surface area of the solid photocatalyst can be considered when the number of sites is unknown, but figures of TON obtained in this way are lower limits. The most widely used semiconductor

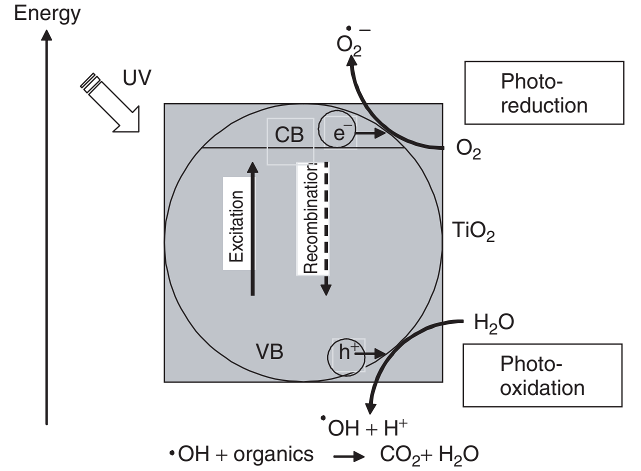

Figure 1. Basic photocatalytic mechanism occurring when a semiconductor particle (e.g., TiO_2) is irradiated.

photocatalyst is polycrystalline TiO_2, in the allotropic phases of both anatase and rutile (the anatase phase appears generally more photoactive), although the use of many other solids (ZnO, WO_3, CdS, MoS_2, CdSe, Fe_2O_3, etc.) has also been reported (40–42). When a semiconductor is illuminated with light of suitable energy (i.e., greater than its bandgap), electrons are promoted from the valence band (vb) to the conduction band (cb), acquiring the reducing power of the cb energy; positive holes are created in the vb, acquiring the oxidation power of the vb energy. This photoproduced pair can give rise to recombination with emission of thermal energy and/or luminescence or to redox (reduction–oxidation) reactions involving electron acceptor or donor species adsorbed on the surface of the catalyst particles (Fig. 1). Consequently, the recombination rate of the photoproduced electron–hole pairs should be as low as possible in order to favor their availability on the surface of the catalyst particle.

A photocatalyst should possess some essential characteristics: (1) light absorption should occur in the near UV and possibly in the visible wavelength ranges; (2) the stability should be such that its re-utilization is possible; and (3) some thermodynamic and kinetic constraints should be fulfilled (43). The photoreactivity depends not only on the intrinsic electronic characteristics of the photocatalysts, but also on their structural, textural, and surface physicochemical features. Among them we can cite the vb and cb energies, the bandgap value, the lifetime of photogenerated electron–hole pairs, the crystallinity, the allotropic phase, the particle sizes, the presence of defects and dopants, the specific surface area, the porosity, the surface hydroxylation, and the surface acidity and basicity. The relative weight of their importance for the studied reaction determines the final level of the photoreactivity. For this reason, it is often difficult to explain and to discuss exhaustively the observed photoreactivity trends by considering only a few properties of the photocatalysts. The steps shown in Table 1 occur when polycrystalline TiO_2 is used in aqueous medium in the presence of O_2 and a generic substrate.

The oxidant radicals along with the holes can give rise to oxidant attacks on a wide variety of substrates. The presence of O_2 is essential in order to trap photoproduced electrons, improving the charge separation and consequently the availability of the holes.

The application of heterogeneous photocatalysis to the purification of aqueous effluents containing dissolved organic and/or inorganic species (e.g., CN^-) has been widely studied. Nevertheless, it is worth noting that analytical studies to check if noxious intermediates are produced under irradiation are essential when the scale-up of photoreactors is proposed for application purposes.

FUNDAMENTALS OF MEMBRANE PROCESSES

Membrane processes are separation methods at the molecular level that have received more interest in recent years for their possibility of being used in many industrial applications. The main goals of such processes are concentration of a solute by removing the solvent, purification of a solution by removing nondesirable components, and fractionation of liquid or gaseous mixtures. Membrane separation processes offer interesting opportunities in pollution control, in the production of drinking water (44), and in the treatment of industrial wastewater (45). A membrane can be defined as a selective barrier between two phases (46,47); it can be thin or thick, natural or synthetic, neutral or charged, the structure can be homogeneous or heterogeneous; and the mass transport can be active or passive. In the last case the driving force can be due to a difference of pressure, concentration, or temperature. The driving force has the capacity to transport a component more rapidly

Table 1. Some Essential Steps When Polycrystalline TiO_2 Is Used in Photodegradation Processes of Noxious Organic and Inorganic Substrates

Role of TiO_2	*Role of* O_2
$TiO_2 + h\nu \rightarrow TiO_2\,(e^-_{(cb)} + h^+_{(vb)})$	$O_2 + e^-_{(cb)} \rightarrow {}^\bullet O_2{}^-$
$OH^- + h^+_{(vb)} \rightarrow {}^\bullet OH$	${}^\bullet O_2{}^- + H^+ \rightarrow {}^\bullet HO_2$
	$2{}^\bullet HO_2 \rightarrow O_2 + H_2O_2$
	$H_2O_2 + {}^\bullet O_2{}^- \rightarrow OH^- + {}^\bullet OH + O_2$

Substrate Degradation
Substrate $+ {}^\bullet HO_2 \rightarrow$ products
Substrate $+ {}^\bullet OH \rightarrow$ products
Substrate $+ h^+_{(vb)} \rightarrow$ products

than others owing to different physical and/or chemical properties between the membrane and the components. The membrane is assembled in a module whose geometry is generally plane or cylindrical and in which the feed is separated into two streams called retentate (the treated feed) and permeate.

Each membrane process is characterized by the employement of a particular type of membrane. Some processes are microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (48) in decreasing order of particles size and increasing pressures (0.1–0.2 to 50–100 bar) used as driving forces. Other membrane processes concern the separation of ionic species by applying an electrical potential (electrodialysis), the separation of mixtures of volatile liquids (pervaporation), and the separation of water from nonvolatile solutes (membrane distillation) by means of a temperature difference (49).

SOME CASE STUDIES OF PHOTOCATALYTIC MEMBRANE REACTORS USED TO PHOTODEGRADE POLLUTANTS

Preliminary Remarks

The pioneering studies for coupling photocatalysis and membrane separations focused on the optimization of the system configuration (14). A continuous operation system (feed feeding and permeate withdrawing) was reported by Molinari et al. (39) involving the use of TiO_2 particles in suspension (Fig. 2). This configuration seems appropriate for industrial applications, so experimental results deriving from this system will be mostly reported in the following. Membrane rejection of the target species with and without photodegradation was measured to obtain information on the performance of the system. Degussa P25 TiO_2 (specific surface area $\cong 50\ m^2/g$; crystallographic phase, ~80% anatase and 20% rutile) was used as the photocatalyst. Some of the molecules chosen as model pollutants were 4-nitrophenol (4-NP) and two dyes—patent blue ($C_{27}H_{31}N_2NaO_6S_2$) and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$). The extent of the degradation of the contaminant was determined by UV-visible measurements and total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC) determinations.

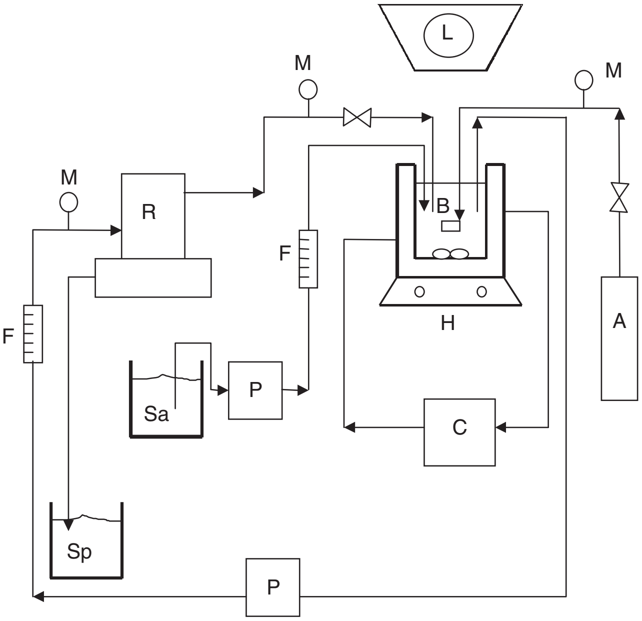

Figure 2. Scheme of a continuous membrane photoreactor system with suspended catalyst. A, oxygen cylinder; B, recirculation reservoir (reactor); C, thermostatting water; L, UV lamp; M, pressure gauge; F, flowmeter; R, membrane cell; H, magnetic stirrer; P, peristaltic pump; Sa, feed reservoir; Sp, permeate reservoir (39).

4-Nitrophenol Degradation in Batch and Continuous Membrane Photoreactors

When NF-PES-010 or N30F nanofiltration membranes were tested (the first one was the most permeable), the permeate fluxes through the membranes in the presence of suspended catalyst were a little lower than those found in the absence of catalyst. Deposition of the catalyst on the membrane was mimimized by using a cell geometry that guaranteed turbulence and presence of vortexes in the bulk of the solution above the membrane.

Photodegradation of 4-NP in batch (recycle) and continuous system configurations showed, for both types of membranes, bell-shaped curves of permeate concentration as a function of time. The concentration of 4-NP in the permeate was attributed to three factors: rejection, photocatalytic degradation, and adsorption. The increase of the initial concentration of permeate in the bell-shaped curves was lowered by the photocatalytic degradation that was responsible for the decrease of the concentration both in the retentate and in the permeate. Although 4-NP concentration in the retentate for the continuous configuration decreased less quickly than for the discontinuous one, the continuous system seems more promising for industrial application (39). In this system the optimum choice of the ratio between the irradiated volume and the total volume, V_i/V_t, was important. When the total suspension volume was increased from 400 to 700 mL, for instance, V_i/V_t increased owing to a constant recycle volume and, consequently, 4-NP abatement was higher due to an increased percentage of irradiated with respect to recycled suspension. The UV radiation mode was also important. The immersed lamp was found to be three times more efficient than the external lamp. Indeed, 99% w/w 4-nitrophenol degradation was achieved after about 1 h in the first case, whereas about 3 h were needed in the second case (39).

Photodegradation of Other Pollutants

NF-PES-010 and NTR-7410 nanofiltration membranes were tested in degradation runs after determination of their permeability and rejection for a variety of pollutants (50). It was found that membranes hold both catalyst and pollutants, but the NTR-7410 membrane tested at 8 bar gave a higher water permeate flux ($105\ L/h \cdot m^2$) than the NF-PES-010 one ($30\ L/h \cdot m^2$). The NTR-7410 membrane was also able to retain small molecules carrying negative charges (like the membrane) as a result of Donnan exclusion and, at 6 bar, yielded fluxes ranging between 20 and 40 $L/h \cdot m^2$. The results of rejection tests and photodegradation studies of humic acids, patent blue dye, and 4-NP in a system utilizing this membrane are described in the following.

The NTR-7410 membrane, not surprisingly, provided 100% retention of humic acids as they are made up of oligomers with molecular sizes greater than the membrane cutoff (600–800 g/mol). For patent blue (molar weight = 567 g/mol and initial concentration 10 mg/L), membrane rejection was about 78.6%. With respect to 4-NP, 0% rejection occurred at pH 6.75, while at pH 11 a rejection of about 77% and a negligible adsorption were observed. The pH dependence of rejection of 4-NP is to be expected by taking into account its acid–base properties and the resultant electrostatic interaction between 4-NP and the membrane (51,52):

$$C_6H_4NO_2OH + H_2O \rightleftharpoons C_6H_4NO_2O^- + H_3O^+$$

$$R\text{—}SO_3{}^-H^+ + H_2O \rightleftharpoons RSO_3^- + H_3O^+$$

Humic acids are found in many natural waters (53) and often induce fouling problems when membranes are used. The interaction between humic acid and the particulate TiO_2 photocatalyst has been explored by Lee et al. (54) who found that (1) humic solution or TiO_2 suspension alone produced essentially a constant membrane flux of 160–170 $L/h \cdot m^2$ and (2) the mixture gave initial flux of 145 $L/h \cdot m^2$ that decreased to 101 $L/h \cdot m^2$ (a decrease of approximately 30%) in the first 30 min of operation. When the photoreactor was illuminated, a constant flux was measured during 6 h, consistent with destruction of humic acid. These authors proposed that the photocatalyzed conversion of humic acid into smaller and/or less absorptive species was occurring and concluded that "photocatalytic reactions appear to be attractive for the control of fouling materials such as natural organic matter."

Continuous Membrane Photoreactor at High Pollutant Concentrations

The detrimental effect caused by a high pollutant concentration could be minimized by taking advantage of the ability of the membrane to retain both the catalyst and the pollutant. In order to investigate this, the photocatalytic system was tested in a continuous process with an initial concentration of pollutant in the photoreactor equal to zero, that is, in the presence of distilled water. A concentrated solution was continuously fed with a flow rate equal to that of the removed permeate. This solution was immediately diluted in the reactor, so photodegradation was effective at low pollutant concentration, although it was continuously fed at high concentration. Control of the residence time of the pollutant in the reactor was possible with the result that very low concentrations in the permeate could be obtained.

This approach was tested by performing humic acid photodegradation studies (50) with an initial concentration in the photoreactor equal to zero and feeding a 200-mg/L solution. It was possible to maintain steady-state pollutant concentrations lower than 5 mg/L and 2 mg/L in the retentate and in the permeate, respectively. It was observed that the humic acid rejection was not 100% and this was mainly due to the lower size of the humic acid oligomers produced during the photodegradation process.

The continuous process was also tested for high concentration (500 mg/L) feeds of patent blue dye and 4-NP. The photodegradation rate of patent blue was found to be lower than that obtained for other pollutants, possibly because of adsorption of the acid dye on the amphoteric catalytic surface, preventing UV light absorption. Indeed, at the end of the run, the catalyst was a dark blue color.

Degradation of Dyes in the Continuous Membrane Photoreactor

In order to achieve a better control of the residence time of pollutants, such as the dyes during the photodegradation process, a hybrid photoreactor was used in which the nanofiltration membrane was able to confine selectively dyes (congo red and patent blue) and catalyst in the reaction ambient while the permeate was withdrawn (55). The experimental results of runs carried out with patent blue in the membrane photoreactor with suspended catalyst showed that the photodegradation reaction followed pseudo-first-order kinetics (observed rate constant equal to 3.76×10^{-3} min^{-1}). A similar run carried out in the absence of membrane showed an observed rate constant of 1.02×10^{-2} min^{-1}. The lower reaction rates for both dyes obtained by using the membrane with respect to that obtained in its absence were due to the smaller volume of irradiated suspension (320 against 500 mL) because a part (180 mL) circulated in the pipes of the plant and in the membrane cell.

The possibility of successfully treating highly concentrated solutions of both dyes was examined, allowing the setup shown in Fig. 2 to work as a continuous system. In particular, the transient condition in the membrane photoreactor was studied by separating the effects of accumulation, adsorption, and photodegradation. Results of three runs with congo red for which the initial concentration of pollutant inside the photoreactor was zero are reported in Fig. 3.

The first run, carried out in the absence of UV light and photocatalyst, indicated that the initial rate of dye accumulation in the photoreactor was 0.151 mg/min. The second run, carried out in the absence of UV light but in the presence of TiO_2, indicated that no increase of dye concentration occurred in the photoreactor during the first 45 min of continuous working of the plant because the congo red feed was adsorbed onto the catalyst surface. After the active sites of the catalyst were saturated, the concentration of the dye in the retentate increased linearly with an accumulation rate of 0.136 mg/min, very close to that determined for the first run. In the third run the continuous degradation of congo red in the presence of UV light and catalyst was performed and concentrations in the retentate and in the permeate versus irradiation time are reported. It can be noticed that, due to the concurrent

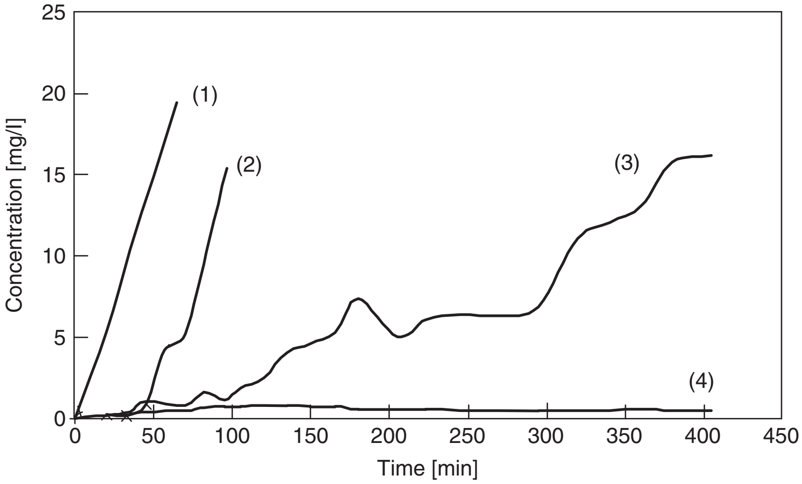

Figure 3. Concentration of congo red in the retentate and in the permeate versus time for three different continuous runs. (1) Absence of UV light and TiO_2; (2) absence of UV light and presence of TiO_2; (3) presence of UV light and TiO_2 for retentate; and (4) presence of UV light and TiO_2 for permeate. $V = 500$ mL; $T = 303$ K; $C_0 = 0$ mg/L; $C(O_2) = 22$ ppm; TiO_2 amount = 1 g/L; $C_{feed} = 500$ mg/L; initial permeate flux, $J_{p_{in}} = 74.2$ L/(m$^2 \cdot$ h); final permeate flux, $J_{p_{fin}} = 29.8$ L/(m$^2 \cdot$ h); lamp, 125-W medium pressure Hg immersed lamp; initial pH = 6.42; membrane, NTR-7410; $\Delta P = 3.5$ bar.

effect of dilution, adsorption, and photodegradation, the accumulation rate in the retentate was lower than that observed during the other two runs. The concentration of congo red in the permeate was virtually zero because the membrane maintained the substrate in the reacting ambient. The permeate flux (J_p) throughout all the runs decreased from the initial value of 74.2 L/m$^2 \cdot$ h to the value of 29.8 L/m$^2 \cdot$ h and, consequently, the dye feeding rate also decreased. It is worth noting that the average photodegradation rate (0.274 mg/min) calculated for the overall run was lower than the average feeding rate (0.416 mg/min), calculated for the first 180 min, while it was 0.049 mg/min higher for longer time (average feeding rate 0.225 mg/min).

Degradation of patent blue was also tested in the continuous system under the same experimental conditions used for congo red and the results are reported in Fig. 4. During the transient state (250–300 min in this specific case) the dye accumulated in the photoreactor because the photodegradation rate (0.570 mg/min) was lower than the feeding rate (0.863 mg/min). Subsequently, steady-state conditions were achieved, owing to the lower permeate flowrate, and no difference was observed between photodegradation and feeding rates. The rejection of NTR-7410 membrane at steady-state conditions with respect to patent blue was 44.6%.

Use of the membrane was beneficial because in addition to its role as a barrier for the catalyst, the product [i.e., cleaned up water (the permeate)] contained a very low concentration of dye with respect to the feed. It was approximately 1% in the case of congo red and approximately 11% in the case of patent blue with respect to 500 mg/L of the feed. It is worth noting that the concentration of the product corresponded to that of the retentate (approximately 3% for congo red and approximately 22% for patent blue) if the membrane was not used.

CONCLUSIONS

The continuous membrane photoreactor that combines both the advantages of classical photoreactors (catalyst in suspension) and membrane processes (separation at molecular level) appears very promising. Photocatalytic degradation can be carried out in reasonable times due to the high irradiated surface area of the suspended particles in the batch.

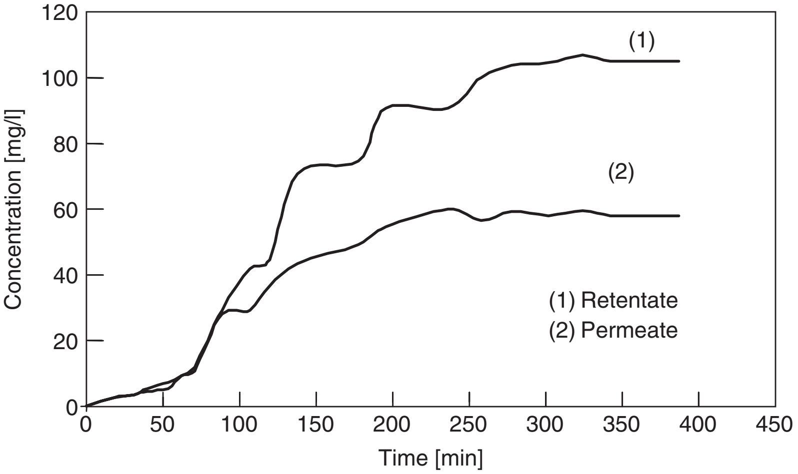

Figure 4. Concentration of patent blue in the retentate and in the permeate versus time for a continuous photodegradation run carried out in the setup showed in Fig. 2. $V = 500$ mL; $T = 303$ K; $C_0 = 0$ mg/L; $C(O_2) = 22$ ppm; TiO_2 amount = 1 g/L; $C_{feed} = 500$ mg/L; regime permeate flux, $J_{p_{regime}} = 78.4$ L/(m$^2 \cdot$ h); lamp, 125-W medium pressure Hg immersed lamp; initial pH = 5.61; membrane, NTR-7410; $\Delta P = 7.0$ bar.

Properly selected membranes should have both the capability to retain the catalyst and to partially reject organic species, enabling control of the residence time in the reacting system.

In studies of 4-nitrophenol degradation, three factors—rejection, photocatalytic degradation, and adsorption—were found to contribute to maintain the steady-state 4-NP concentration in the permeate at very low values. The adsorption phenomenon is particularly important when oscillating concentrations of pollutant are fed to the membrane photoreactor, resulting in a negligible variation of concentration in the permeate.

Photoreactors with an immersed lamp are generally more efficient than systems with external lamp. In addition, the pH of the polluted water, the molecular weight of the pollutant, and the type of pollutant and membrane are variables influencing pollutant rejection as a result of charge repulsion (Donnan exclusion) effects.

In order to select a suitable membrane, rejection should be determined during operation of the photoreactor. The pressure in the membrane cell, the pH of the polluted water, the molecular size of the pollutants, and the photogenerated by-products and intermediate species can influence the permeate flux of the membrane and consequently its choice.

High initial concentrations of the pollutants (e.g., 4-NP, patent blue, congo red) lower the photodegradation rate; however, this problem can be solved by diluting the feed in the reactor and by controlling the residence time of the pollutant by means of the membrane.

The experimental results available in the literature indicate that the choice of a suitable membrane is essential for applying the photocatalytic membrane processes to the treatment of real effluents. Furthermore, use of photocatalysis combined with RO processes for drinking water production can eliminate the membrane fouling problem and the need for plant sanitizing.

The hybrid continuous photoreactor where a nanofiltration membrane is used can give advantages over other approaches: simplification of clean-up or purification of various types of waters (for industrial, municipal/domestic, and agricultural uses), no sludge production, and saving in chemicals usage. It is expected that these hybrid processes will be considered particularly when plant upgrade is planned and, especially, if sunlight energy can be used for irradiation.

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BIBLIOGRAPHY

1. Gorenflo, A., Hesse, S., and Frimmel, H. (1998). A concept for advanced biodegradation. In: *Proceedings of the European Research Conference on Natural Waters and Water Technology: Catalytic Science and Technology for Water*. Acquafredda di Maratea, (I), October 3–8, p. 32.
2. Martin, R.J., Iwugo, G., and Pawlowski, L. (Eds.). (1989). *Physicochemical Methods for Water and Wastewater Treatment*. Elsevier, New York, p. 265.
3. Drioli, E. (Ed.). (1994). *Proceedings of the International Symposium on Membrane and Membrane Processes*. Hangzou, China, April 5–10.
4. Howell, A.J. and Noworyta, A. (Eds.). (1995). *Towards Hybrid Membrane and Biotechnology Solutions for Polish Environmental Problems*. Wroclaw Technical University Press, Wroclaw.
5. Caetano, A., De Pinho, M.N., Drioli, E., and Muntau, H. (Eds.). (1995). *Membrane Technology: Applications to Industrial Wastewater Treatment*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
6. Pramauro, E. et al. (1993). Preconcentration of aniline derivatives from aqueous solutions using micellar-enhanced ultrafiltration. *Analyst* **118**: 23.
7. Pramauro, E. and Bianco Prevot, E. (1998). Application of micellar ultrafiltration in environmental chemistry. *Chim. Ind. Milan* **80**: 733.
8. Sopajaree, K., Qasim, S.A., Basak, S., and Rajeshwar, K. (1999). An integrated flow reactor–membrane filtration system for heterogeneous photocatalysis. Part I: Experimental and modelling of a batch-recirculated photoreactor. *J. Appl. Electrochem.* **29**: 533.
9. Sopajaree, K., Qasim, S.A., Basak, S., and Rajeshwar, K. (1999). An integrated flow reactor–membrane filtration system for heterogeneous photocatalysis. Part II: Experiments on the ultrafiltration unit and combined operation. *J. Appl. Electrochem.* **29**: 1111.
10. Molinari, R., Palmisano, L., Drioli, E., and Schiavello, M. (2002). Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. *J. Membr. Sci.* **206**: 399.
11. Ollis, D.F. (2002). Integrating photocatalysis and membrane technologies for water treatment. In: *Proceedings of 2nd European Meeting on Solar-Chemistry and Photocatalysis: Environmental Applications*. Saint Avold, France, May 29–31, Plenary Lecture 1.
12. Karakulski, K., Morawski, W.A., and Grzechulska, J. (1998). Purification of bilge water by hybrid ultrafiltration and photocatalytic processes. *Sep. Purif. Technol.* **14**: 163.
13. Xi, W. and Geissen, S-U. (2001). Separation of titanium dioxide from photocatalytically treated water by crossflow microfiltration. *Water Res.* **35**: 1256.
14. Molinari, R., Giorno, L., Drioli, E., Palmisano, L., and Schiavello, M. (2004). Photocatalytic nanofiltration reactors, Chap. 18. In: *Nanofiltration: Principles and Applications*. A.I. Schaefer, D. Waite, and A. Fane (Eds.). Elsevier Science, London.
15. Wyness, P., Klausner, J.F., Goswami, D.Y., and Schanze, K.S. (1994). Performance of nonconcentrating solar photocatalytic oxidation reactors, part I: flat-plate configuration. *J. Solar Energy Eng.* **116**: 3.
16. Zhang, Y., Crittenden, J.C., Hand, D.W., and Perram, D.L. (1994). Fixed-bed photocatalysts for solar decontamination of water. *Environ. Sci. Technol.* **28**: 435.
17. Liu, G. and Zhao, J. (2000). Photocatalytic degradation of dye sulforhodamine B: a comparative study of photocatalysis with photosensitization. *New J. Chem.* **24**: 411.
18. Augugliaro, V. et al. (2004). Degradation of lincomycin in aqueous medium: coupling of solar photocatalysis and membrane separation. In: *Serie Ponencias, The Improving Human Potential Programme*. Access to research infrastructures activity. Research results at Plataforma Solar de Almeria within the year 2003 access campaign. CIEMAT, Madrid, pp. 43–52.

19. Barbeni, M. et al. (1984). Photodegradation of 4-nitrophenol catalyzed by TiO_2 particles. *Nouv. J. Chim.* **8**: 547.
20. Okamoto, K. et al. (1985). Heterogeneous photocatalytic decomposition of phenol over TiO_2 powder. *Bull. Chem. Soc. Jpn.* **58**: 2015.
21. Augugliaro, V., Palmisano, L., Sclafani, A., Minero, C., and Pelizzetti, E. (1988). Photocatalytic degradation of phenol in aqueous titanium dioxide dispersion. *Toxicol. Environ. Chem.* **16**: 89.
22. Augugliaro, V. et al. (1991). Photocatalytic degradation of nitrophenols in aqueous titanium dioxide dispersion. *Appl. Catal.* **69**: 323.
23. Pramauro, E., Vincenti, M., Augugliaro, V., and Palmisano, L. (1993). Photocatalytic degradation of monuron in TiO_2 aqueous dispersions. *Environ. Sci. Technol.* **27**: 1790.
24. Pichat, P. and Enriquez, R.E. (2001). Interactions of humic acids, quinoline, and TiO_2 in water in relation to quinoline photocatalytic removal. *Langmuir* **17**: 6132.
25. Brandi, R.J., Alfano, O.M., and Cassano, A.E. (2000). Evaluation of radiation absorption in slurry photocatalytic reactors. 1. Assessment of methods in use and new proposal. *Environ. Sci. Technol.* **34**: 2623.
26. Brandi, R.J., Alfano, O.M., and Cassano, A.E. (2000). Evaluation of radiation absorption in slurry photocatalytic reactors. 2. Experimental verification of the proposed method. *Environ. Sci. Technol.* **34**: 2631.
27. Aguado, M.A., Anderson, M.A., and Hill, C.J., Jr. (1994). Influence of light intensity and membrane properties on the photocatalytic degradation of formic acid over TiO_2 ceramic membranes. *J. Mol. Catal.* **89**: 165.
28. Cheng, S., Tsa, S., and Lee, Y. (1995). Photocatalytic decomposition of phenol over titanium oxide of various structures. *Catal. Today* **26**: 87.
29. Walker, S.A., Christensen, P.A., Shaw, K.E., and Walker, G.M. (1995). Photoelectrochemical oxidation of aqueous phenol using titanium dioxide aerogel. *J. Electroanal. Chem.* **393**: 137.
30. Loddo, V., Marcì, G., Palmisano, L., and Sclafani, A. (1998). Preparation and characterisation of Al_2O_3 supported TiO_2 catalysts employed for 4-nitrophenol photodegradation in aqueous medium. *Mater. Chem. Phys.* **53**: 217.
31. Lepore, G.P., Persaud, L., and Langford, C.H. (1996). Supporting titanium dioxide photocatalysts on silica gel and hydro-physically unmodified silica gel. *J. Photochem. Photobiol. A Chem.* **98**: 103.
32. Bellobono, I.R. (1995). Photosynthetic membranes in industrial waste minimization and recovery of valuable products. In: *Membrane Technology Applications to Industrial Wastewater Treatment*. A. Caetano et al. (Eds.). Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 17.
33. Solovieva, A.B. et al. (2000). Porphyrin containing membrane photocatalytic systems for steroid olefine oxidation. *Euromembrane*: 345.
34. Kotova, S.L., Rumjantseva, T.N., Solovieva, A.B., Zav'jalov, S.A., and Glagolev, N.N. (2000). Porphyrins immobilized on sulfocationic membranes as photosensitizers in singlet oxygen generation. *Euromembrane*, 355.
35. De Smet, K., Vankelecom, I.F.J., and Jacobs, P.A. (2000). Filtration coupled to catalysis: a way to perform homogeneous reactions in a continuous mode. *Euromembrane*: 356.
36. Puhlfürß, P., Voigt, A., Weber, R., and Morbé, M. (2000). Microporous TiO_2 membranes with a cut off <500 Da. *J. Membr. Sci.* **174**: 123.
37. Artale, M.A. et al. (2001). Preparation and characterization of membranes with entrapped TiO_2 and preliminary photocatalytic tests. *Ann. Chim. (Rome)* **91**: 127.
38. Molinari, R. et al. (2000). Study on a photocatalytic membrane reactor for water purification. *Catal. Today* **55**: 71.
39. Molinari, R., Grande, C., Drioli, E., Palmisano, L., and Schiavello, M. (2001). Photocatalytic membrane reactors for degradation of organic pollutants in water. *Catal. Today* **67**: 273.
40. Schiavello, M. (Ed.). (1985). *Photoelectrochemistry, Photocatalysis, Photoreactors. Fundamentals and Developments*. D. Reidel Publishing, Dordrecht, The Netherlands.
41. Pelizzetti, E. and Serpone, N. (Eds.). (1989). *Photocatalysis. Fundamentals and Applications*. John Wiley & sons, Hoboken, NJ.
42. Di Paola, A., Marcì, G., Palmisano, L., and Schiavello, M. (2000). Trattamenti innovativi delle acque mediante l'utilizzo di radiazione UV e catalizzatori: la fotocatalisi eterogenea. In: *Processi e Metodologie per il Trattamento delle Acque, a cura di L. Palmisano*. Edizioni Spiegel, Milano, Chap. 13, p. 237.
43. Palmisano, L. and Sclafani, A. (1997). Thermodynamics and kinetics for heterogeneous photocatalytic processes. In: *Heterogeneous Photocatalysis*, Vol. 3, *Wiley Series in Photoscience and Photoengineering*. M. Schiavello (Ed.). John Wiley, Chichester, Chap. 4, p. 110, and references therein.
44. Aptel, P. and Vial, D. (1992). In: *Membranes in Water Treatment and Potabilization*. C. Haber and E. Drioli (Eds.). Proc. Membrane Separation Processes, Rio de Janeiro, Brazil, May 3–8, p. 291.
45. Scott, K. (1995). *Handbook of Industrial Membranes*. Elsevier Advanced Technology, Oxford, UK.
46. Mulder, M. (1991). *Basic Principles of Membrane Technology*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
47. Hwang, S.T. and Kammermeyer, K. (1975). *Membranes in Separations*. Wiley Interscience, Hoboken, NJ.
48. Toyomoto, K. and Higuchi, A. (1992). Microfiltration and ultrafiltration. In: *Membrane Science and Technology*. Y. Osada and T. Nakagawa (Eds.). Marcel Dekker, New York, Chap. 8, p. 289.
49. Baker, R.W. (2004). *Membrane Technology and Applications*, 2nd Edn. Wiley, London.
50. Molinari, R., Borgese, M., Drioli, E., Palmisano, L., and Schiavello, M. (2002). Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water. *Catal. Today* **75**: 77.
51. van Der Bruggen, B., Schaep, J., Wilms, D., and Vandecasteele, C. (1999). Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.* **156**: 29.
52. Meares, P. (1986). *Synthetic Membranes: Science, Engineering and Applications*. D. Reidel Publishing, Dordrecht, The Netherlands.
53. Schäfer, A.I. (2001). *Natural Organic Matter Removal Using Membranes: Principles, Performance and Cost*. CRC Press, Boca Raton, FL.
54. Lee, S.A. et al. (2001). Use of ultrafiltration membranes for the separation of TiO_2 photocatalysts in drinking water treatment. *Ind. Eng. Chem. Res.* **40**: 1712.
55. Molinari, R., Pirillo, F., Falco, M., Loddo, V., and Palmisano, L. (2004). Photocatalytic degradation of dyes by using a membrane reactor. *Chem. Eng. Proc.* **43**: 1103.

EPA'S NATIONAL PRETREATMENT PROGRAM, 1973–2003: THIRTY YEARS OF PROTECTING THE ENVIRONMENT

Office of Water—United States
Environmental
Protection Agency

EPA's National Pretreatment Program has led the way to dramatically reduce or eliminate discharges of pollutants to sanitary sewer systems and to the nation's water bodies. The Program controls a complex array of industrial wastestreams in order to prevent interference or pass—through of municipal treatment system processes. Without these controls, a number of harmful pollutants could make their way into the nations' waters. Federal, state, and local partnerships are central to the successful implementation of the Program. Renewed commitment and support to the Pretreatment Program will conserve the environmental gains of the last 30 years, strengthen strategic partnerships, and prepare communities to meet the pollution challenges of the 21st Century.

THE PRETREATMENT PROGRAM

Pollutants in industrial wastewater may compromise municipal treatment plants' processes or contaminate the nation's waters. To protect municipal treatment plants and the environment, the Pretreatment Program requires industrial dischargers to use treatment techniques and management practices to reduce or eliminate the discharge of harmful pollutants to sanitary sewers. The Pretreatment Program is a core part of the Clean Water Act's National Pollutant Discharge Elimination System (NPDES), and it has helped communities:

- Maintain and restore watershed quality, at a much lower cost than upgrading treatment;
- Encourage pollution prevention;
- Increase beneficial uses of sewage sludge;
- Prevent formation of poisonous gases in the sanitary sewer system;
- Meet wastewater discharge standards; and
- Institute emergency—prevention measures.

Goleta, California's pretreatment program makes it possible for marine life—fish, sea stars, and coral—to thrive at the city's Sanitary District outfall

The Pretreatment Program's strategic partnerships go beyond ensuring the success of Publicly Owned Treatment Works (POTWs). The partnerships—involving approximately 1,500 communities and 27,000 industrial facilities nationwide—promote:

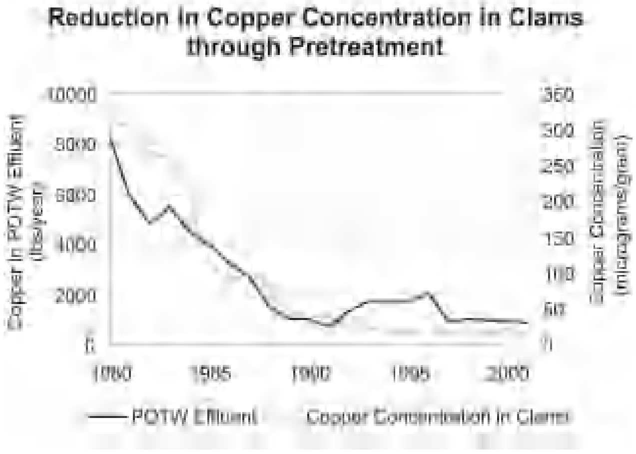
- Protection of drinking water supplies, by reducing contaminants released into source waters by POTWs;
- Prevention of overflows that include raw sewage from sewers, through controls on oil and grease;
- Extension of the life of the nation's wastewater infrastructure, which has an estimated funding gap of over $6 billion per year, through controls on corrosion;
- Worker safety, by protecting workers from harmful fumes through limits on the discharge of dangerous gases and gas—forming substances; and
- Homeland security, by ensuring proper disposal of wastes from decontamination showers.

PARTNERSHIPS THAT WORK

Through the Pretreatment Program, POTWs have worked intensively in a federal, state, and local partnership that is a model of intergovernmental cooperation.

National data affirm the Pretreatment Program's success

- Industries release fewer toxic contaminants to POTWs. Data from EPA's Toxics Release Inventory show that industries have reduced the amount of pollutants they discharge to sewage treatment plants during the past 10 years.



Through its pretreatment program, Palo Alto, California has reduced pollutants discharged to San Francisco Bay. As the quantity of copper in the POTW's effluent has improved, copper levels in clams near the city's outfall have decreased

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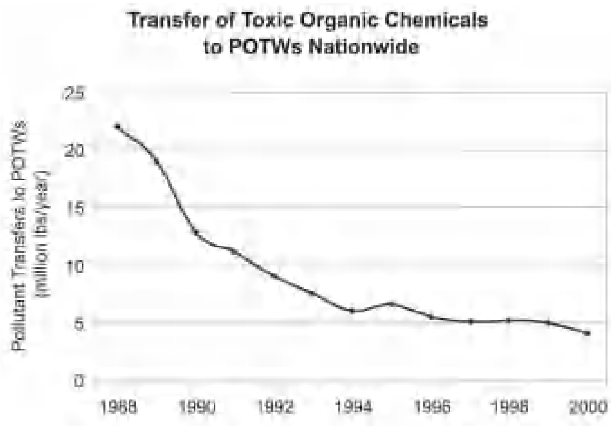
- POTWs now generate sewage sludge that poses fewer threats to public health and the environment. An Association of Metropolitan Sewerage agencies (AMSA) survey of biosolids concluded that the Pretreatment Program was directly responsible for reductions in metals found in sewage sludge. Surveyed POTWs experienced a modest 13 percent decline in metals not regulated by the Pretreatment Program. However, concentrations of metals regulated under the Pretreatment Program decreased considerably, dropping 59 percent from 1986 to 1997.
- Because of the successful implementation of industrial discharge limitations, more POTWs are able to apply sewage sludge to land. For example, six Midwestern states saw a significant increase in the percentage of POTWs whose sludges qualified for the term 'biosolids.' More than 90 percent met metals limitations that allow POTWs to land apply their biosolids. As a result of this national progress, many POTWs, like the Unified Sewerage Agency of Washington County, Hillsboro, Oregon, have been able to use 100 percent of the biosolids they produce. Hillsboro applies 11,000 dry metric tons annually to amend soils and improve crop production.

SUPPORTING KEY ENVIRONMENTAL AND PUBLIC HEALTH PROGRAMS

Drinking Water Protection. EPA's Pretreatment Program has been helping communities protect their sources of drinking water for the last 30 years by:

- Protecting POTWs' treatment processes from upsets, which could compromise the treatment facility's ability to treat harmful substances, such as pathogens. Elevated pathogen levels could have substantial impacts on public health if the pathogens exit POTWs and enter surface waters. Downstream drinking water treatment facilities may be challenged by significantly higher—than—normal pathogen levels.

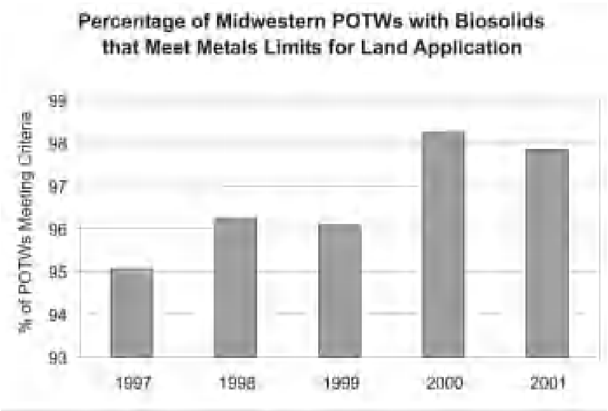


The Toxics Release Inventory is a publicly available EPA database that contains information on toxic chemical releases and other waste management activities reported annually by covered industry groups and the federal government

- Controlling industrial releases of carcinogenic contaminants that might otherwise be discharged to municipal sewage treatment plants. Without controls on industrial dischargers, carcinogens might pass through the sewage treatment plant and enter reservoirs tapped for drinking water supplies. Therefore, the Pretreatment Program eliminates the need to install additional, expensive water treatment equipment to protect the long—term health of consumers.

CSO, SSO, and storm water management—Combined and Sanitary Sewer Overflows (CSOs and SSOs) contain raw sewage, and may also carry industrial waste and debris. EPA's wet—weather programs recognize the importance of the Pretreatment Program in helping communities:

- Mitigate overflows. For example, many cities halt discharges of waste flows from industrial facilities to the combined sewer system during wet weather



Data obtained from EPA's Permit Compliance System, representing information reported to EPA by POTWs in Illinois, Michigan, Minnesota, Ohio, and Wisconsin

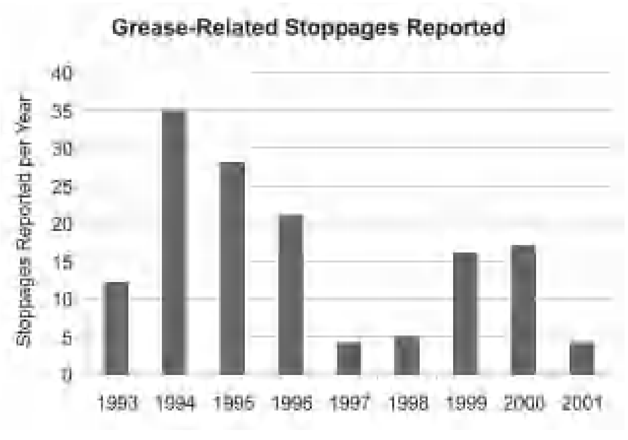
Overflowing sewer due to a sewer blockage events. In addition, industries may retain storm water from their properties and release it to the sewer system after the storm has ended and sewer system capacity is adequate.

- Control grease buildup in sewers—a major cause of SSOs. As part of their pretreatment programs, many communities require food service establishments to recycle all fats, oils, and greases or to use oil and grease removal equipment. Annapolis, Maryland's pretreatment program practically eliminated SSOs associated with the restaurant community.
- Inventory and control non—domestic sources of pollutants, the types of pollutants discharged, and the volume of industrial flow. These inventory efforts not only protect wastewater treatment plants, but also help identify industrial contributions to municipal separate storm sewer systems.

Infrastructure Protection—Pretreatment programs help to protect underground infrastructure from costly damage and the need for premature replacement. The gap between the average annual funding needed and the funding available for wastewater treatment and collection systems is estimated to be $6.1 billion per year from 2000 to 2019. EPA's Pretreatment Program helps to extend the life of infrastructure and postpones costly replacement. For example, limits on pH prevent corrosion of collection systems and treatment plants from acidic discharges. Discharge limits on sulfides and sulfate—bearing wastewaters also protect infrastructure from corrosion caused by bacteria.

Worker and Public Safety—Ensuring safety is an important goal of EPA's Pretreatment Program. The Program accomplishes this goal by:

- Protecting the physical integrity of the sewer system. Volatile organic compounds discharged to sewers may accumulate in the head space of sewer lines, increasing the potential for explosions that may cause significant damage. Discharge limitations and management practices required by the Pretreatment Program reduce the likelihood of such catastrophes.



San Antonio, Texas achieved significant reductions in grease—related stoppages through its pretreatment program

Example of a sewer pipe damaged by hydrogen sulfide corrosion

- Preventing the buildup of poisonous gases. Discharges of toxic organics can generate poisonous gases, through various kinds of mixing and chemical reactions. Appropriate pretreatment discharge limits prevent this gas build up.

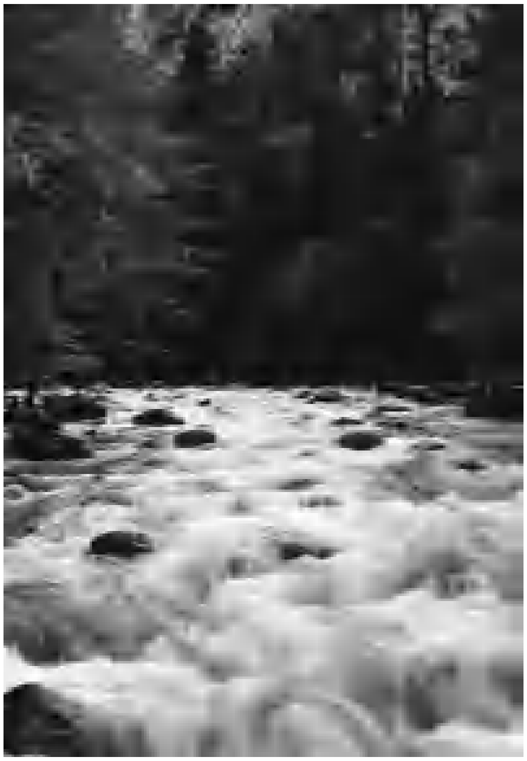
Homeland Security Initiatives—As they increase their preparedness for possible terrorist attacks, communities across the country will rely on their local pretreatment programs. The Pretreatment Program helps communities build contingency plans for the control and disposal of decontaminated wastes, such as wastes from decontamination showers. Recently, pretreatment authorities in Boca Raton, Florida managed the disposal of anthrax wastes as part of clean-up activities in that city.

FUTURE CHALLENGES

The Pretreatment Program must evolve to face tough new challenges in protecting public health and the environment. Future challenges include:

- *Addressing emerging industries and pollutants.* Every year, new industries and new pollutants of concern challenge POTWs. For example:

A safety issue: Discharges of hexane from an industry into Louisville, Kentucky's sewer system collapsed sewer lines and destroyed streets throughout the city in 1981



  - The Pretreatment Program must keep pace with the constant shifts in industrial processes and the development of new industries and chemicals. For example, in the 1980s and 1990s, the rapid growth of the semi—conductor industry required new pretreatment program strategies. Mounting evidence now suggests that persistent, bioaccumulative, and toxic (PBT) chemicals, surfactants, and hormone—disrupting substances can pass through wastewater treatment plants and endanger human health. Through their pretreatment programs, communities continue to address changes in industrial operations.
  - New effluent guidelines for transportation equipment cleaning and centralized waste treatment facilities address highly complex industries with a history of disrupting POTW treatment. Communities will rely on the Pretreatment Program as the vehicle to implement these guidelines and control these highly variable and highly toxic wastestreams.
- *Water conservation and reuse*. Industries and municipalities have a growing understanding of the economic benefits of using water more efficiently. Effluent waters from POTWs are increasingly used for irrigation and for cooling in power generation and industrial processes. The high quality waters needed for these uses emphasizes how important pretreatment is to the growing area of water reuse and conservation.
- *Improving watershed quality through Total Maximum Daily Loads (TMDLs)*. TMDLs are established to ensure that rivers and streams meet their intended uses, such as recreational areas and drinking water supplies. State and local pretreatment personnel are increasingly called upon to provide expertise in developing appropriate TMDLs and community—based strategies. These individuals are aware of the contributions from industrial pollutants within the local watershed and sewer—shed, and can share their knowledge of how to implement pollutant limits while pursuing complex watershed—based solutions.

Communities will rely on the leadership of the Pretreatment Program to meet these and other unanticipated challenges. While the Program has had many successes in the last 30 years, a firm commitment to the federal, state, and local partnerships established under the Program is critical to protecting public health and the environment in the future.

PROBLEMS ENCOUNTERED DURING PIPE REPAIR AND RENEWAL

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INSTALLATION PROBLEMS

Installation Problems—Sliplining

The major problem encountered during sliplining of an existing sewer is improper preparation of the interior of the sewer prior to the inserting the sliplining pipe.

1. Obstructions such as roots, large joint offsets, extended laterals, rocks, or other debris that would prevent the passage of or the damage to the liner pipe sections must be removed or repaired prior to the installation of the new liner pipe.
2. Prior to the insertion of the new liner pipe, a test mandrel or pipe section should be pulled through the existing line to ensure that the liner may be inserted without damage or restrictions.
   (a) The mandrel should be of a length equal to the longest pipe that will be inserted.
   (b) The mandrel test may indicate that short lengths of pipe should be used if the angular deflection negates using longer pipe.

The accurate location and installation of the laterals presents a difficult problem for the Contractor.

1. Existing lateral and sewer connection locations must be carefully determined.
2. The installation of the laterals to provide a leak-tight system is critical.

The diameter of the slipliner pipe is smaller than the host or existing sewer, so inverts and connections to existing manholes must be watched closely.

Grouting the annular space between the existing sewer and the slipliner pipe must be done with great care.

1. Flotation during grouting is a potential problem. The liner pipe should be flooded to a depth of 2 to 3 feet prior to beginning the placement of the grout.
2. The grout should be placed to ensure that the lift heights, grout density, and the sewage flow depth are coordinated to control the line pipe deformation within allowable limits. Point loads causing excessive dents or bulges should be avoided. The maximum pipe diameter deflection for sliplined pipe is 5%. Close monitoring of grout pressure is essential during grouting to prevent buckling of the liner pipe.

Installation Problems—Cured-in-Place Pipe (CIPP)

A difficult problem with CIPP is the location of laterals. The Contractor relies on the "dimples" in the new liner and accurate measurements.

A difficult problem is wrinkles or folds in the flow line in the finished product.

1. This problem could result from improper sizing of the liner bag size.
2. Wrinkles also occur due to head loss in the filling operations.

Inadequate curing of the liner, resulting from the wrong temperature or time duration, may result in soft spots. The Contractor inserts a section of material called dry liner at the soft spot in the liner, which corrects this problem when cured.

Care should be taken to determine if laterals that are to be abandoned are indeed dead. A good rule of thumb to follow is that if you cannot see a plug or cap from inside the main line, then the lateral must be reinstated.

Although not a Contractor problem, a homeowner who has a bad trap on the house sewer may experience a highly offensive odor from the chemical reaction at cure-out. It is offensive but not harmful. This problem can be reduced if the Contractor instructs the homeowners to fill the traps of floor drains with water.

Installation Problems—Gunite

Care should be taken to remove the "rebound." Some Contractors may try to trowel the rebound and leave it at the bottom of the pipe.

One of the keys for a successful gunite operation is the skill of the nozzleman. Most specifications list qualifications for the nozzleman. Apprentices should be allowed to work only with proper supervision.

Make certain that all leaks in the substrate are stopped. Running water will prevent the material from achieving the proper bond to the substrate.

RADIOACTIVE WASTE

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Radioactive waste is a concern with regard to water quality when the waste is released into the environment or has the potential to be released into the environment. Air and water containing radioactive contamination may be released directly into the environment if the activity of the contamination is within defined levels. The World Health Organization (WHO) has established release guidelines as explained below. In the United States, the Nuclear Regulatory Commission (NRC) regulates radioactive discharges from commercial nuclear facilities. The NRC regulations are found in Codified Federal Regulations (CFR) 10 CFR 20.106. Limits for radioactive air and water are given in 10 CFR 20, Appendix II, Table 2 for releases to the environment, and in 10 CFR 20, Appendix II, Table 3 for releases of radioactive water into sewers. The United States Department of Energy (DOE) has also established requirements for release of radioactive water and air from DOE facilities. These requirements are provided in DOE Order 4500. The United States Environmental Protection Agency (EPA) provides standards for releases into water sources that may potentially be used as drinking water (see Drinking Water Limits). Of the relatively few instances of radionuclides exceeding levels of concern, most are from natural sources (1,2).

RADIOACTIVITY AND RADIATION

If the energy released during radioactive decay is high enough to strip electrons from other atoms, or split the nuclei of other atoms, the radiation is called ionizing. It is this ionizing radiation that poses the health risk associated with radionuclides. Four types of ionizing radiation exist: alpha, beta, gamma, and neutron. Alpha, beta, and neutron radiation are particles that are released when the isotope decays. An alpha particle is the nucleus of a helium-4 atom, thus consisting of two neutrons and two protons, and no electrons, therefore having a $+2$ charge. Alpha radiation is easily stopped by only moderate shielding, for example, two or three pieces of paper, or human skin. Neutrons have no charge and therefore do not interact as easily with other atoms when released as radiation. Beta particles are energetic electrons and have a -1 charge. Gamma rays are not particles, but rather electromagnetic radiation, similar to x-rays. Gamma rays and beta particles have both the ability to penetrate farther than alpha particles and interact more than neutrons, and they are therefore typically the more hazardous form of ionizing radiation. However, if alpha particles are ingested, they may present a significant health hazard as an internal contamination. The time for the atoms of a radioactive compound to decay to one half of their starting concentration is called the half-life of the isotope. Two sources of radionuclides exist in drinking water, naturally occurring and anthropogenic.

NATURALLY OCCURRING SOURCES

Naturally occurring radioactive isotopes originate in Earth's crust and the upper atmosphere. Cosmic rays and other extraterrestrial ionizing radiation form the radioactive isotope tritium in Earth's upper atmosphere. This isotope is incorporated into natural rainfall and therefore eventually reaches Earth's surface. Radioactive isotopes, including uranium-238, radium-226, radium-228, and strontium-90, were formed in Earth's crust during the birth of the Solar System about 5 billion years ago. Radon is a daughter product formed when uranium decays. Groundwater may therefore contain levels of radionuclides that are somewhat elevated.

Of the two kinds of naturally occurring isotopes, stable and unstable, only unstable isotopes pose a health concern (3). Therefore, the natural isotopes of primary interest with regard to water quality are uranium-238, radium-226, radium-228, uranium-238, radon, and tritium.

Anthropogenic (Manmade) Sources

The primary sources of manmade radioactive contamination in water are tritiated cooling water effluent from nuclear reactors, tritiated water from nuclear fuel-reprocessing facilities, medical sources, and nuclear fallout from nuclear weapons testing. Effluent from nuclear facilities must meet strict regulatory requirements. In comparison with the large number of safe operating hours accumulated by nuclear facilities over the years, instances of accidental release of radioactive contamination into the environment are rare.

DRINKING WATER LIMITS

The World Health Organization (3) provided guidelines for upper limits of radioactive contamination in drinking water consumed by large populations over a lifetime as:

Gross beta contaimination	1000 pCi/L
Radium-226	10 pCi/L
Strontium-90	30 pCi/L

In the United States, if water is discharged into a water source that may be used for drinking water, such discharge is regulated by the EPA (4). The EPA has updated its standards for radionuclides in drinking water, and it has set a new standard for uranium, as required by the 1986 amendments to the Safe Drinking Water Act. The standards are as follows:

Combined radium-226/228	5 pCi/L
Beta emitters	4 mrems
Gross alpha	15 pCi/L
Uranium	30 μg/L

TREATMENT TECHNOLOGIES

Unlike other chemical contaminants, radionuclides cannot be altered by chemical reactions to form nonradioactive products through normal chemical means. The isotopes that emit radiation will continue to do so no matter what chemical compounds they form. Only through the passage of time will the radioactive compounds decay naturally into their associated daughter products, eventually becoming radioactively stable isotopes. Although the radionuclides will continue to emit radiation, the chemical compounds emitting this radiation can be removed by conventional water treatment methods. Cox (5) stated that 70–90% of the radioactive materials appearing in surface waters are removed in conventional water treatment facilities. According to DeZuane (1), more than 99% of radioactive contaminants that percolate into soils via rainwater are removed naturally. If further removal is required beyond these levels, several standard water treatment methods may effectively remove the contamination (2).

Radionuclides of primary interest that may require removal from water sources are uranium-238, radium-226, radium-228, radon, and strontium-90. Uranium may be removed by lime softening, ion exchange (anion and/or cation), reverse osmosis, electro-dialysis, activated alumina, or a combination of coagulation with sedimentation and filtering. Radium-226 and radium 228 may be removed by lime softening, cationic ion exchange, reverse osmosis, or electro-dialysis. Strontium-90 may be removed by lime softening, cationic ion exchange, reverse osmosis, ultrafiltration (UF), or electro-dialysis. A combination of air stripping and granulated activated carbon is an effective technique for removing radon from water (2).

MEMBRANE FILTRATION PROCESSES

In membrane filtration, particles in the range of 0.0001 μm to 1.0 μm are removed from water. This process involves removal of dissolved constituents, as opposed to other filtration processes that remove colloids and larger particles. In UF, the particles are separated from the water by a sieving mechanism. In reverse osmosis (RO), small particles are rejected by the water layer adsorbed on the surface of the memberane (6). An electrodialysis system passes an electric current through the solution, which causes the cations to move to the anode and the anions to move to the cathode. This movement results in alternating cells of concentrated and dilute salts, which are flushed out from the units and in this way removed from the waste water. Ref. 6, pp. 1104–1137, for additional information.

AIR STRIPPING

Air stripping is an effective method for removing radon from radon-contaminated water (Fig. 1a). In air-stripping equipment, the contaminants in the water phase are transferred into the air phase. The contact area between the clean air phase and the water phase controls the removal rate and therefore the process efficiency. Higher contact areas provide increased removal efficiencies. Water is usually introduced in the top of a cylindrical tower and air is blown in from the bottom, although other arrangements are used. Air stripping may be carried out in several types of equipment, including packed towers, sparged or agitated vessels, or tray towers. In packed towers, high-surface area packing maximizes interphase surface area. Sparged vessels, also called bubble columns, introduce the air into the water to form small bubbles that rise upward through the water. Tray towers contain multiple vertically stacked trays that are made to allow the air to move upward through the water via small openings. The water flows across the trays and down through baffled weirs to the bottom of the tower, which produces foaming and the gas–liquid contact required to produce the mass transfer (6,7).

Several gas stripping systems are being used in the United States to remove radon from drinking water. A good summary is provided in Table 1 (8).

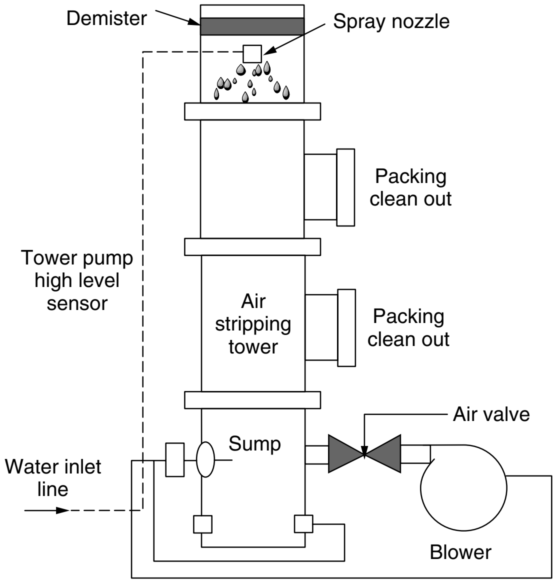

Figure 1. Air stripping town.

CHEMICAL PRECIPITATION

Heavy metals such as uranium and strontium may be removed from contaminated water by converting their soluble salts to insoluble salts that will precipitate. Typically, the pH of the waste stream is first adjusted, and an appropriate chemical is added to convert the soluble metal salts into carbonates, sulfides, or hydroxides of the metal (see Lime Softening). A flocculating agent is then added to promote discrete particle agglomeration, usually performed in a vessel with slow mixing. The flocculated particles are then removed from the stream by either filtration or settling (9). The chemical precipitants and flocculants required depend on the chemistry of the specific waste water system being considered for treatment (6).

LIME SOFTENING

Lime softening is used in a variety of ways to precipitate Group II A ionic species from water (for example, ions of magnesium, calcium, strontium, and radium) and may be used to remove uranium contamination. Lime (calcium hydroxide) is added in either lump, powder, or slurry form to carry out the following simple reactions:

1. $\mathrm{H2CO3} + \mathrm{Ca(OH)2} \rightleftharpoons \mathrm{CaCO3(s)} + \mathrm{2H2O}$
2. $\mathrm{Ca(HCO3)2} + \mathrm{Ca(OH)2} \rightleftharpoons \mathrm{2CaCO3(s)} + \mathrm{2H2O}$

Reaction 1 shows the reaction of the lime with the carbonic acid component typically in water. This reaction does not precipitate any of the desired ionic contaminants, but it must be considered because it creates a lime demand. Reaction 2 shows the removal of two calcium ions. Radioactive ionic contaminants may be removed in a similar manner. Ferrous sulfate is often used in conjunction with lime softening. Many additional chemical reactions may also occur during lime softening. For more information on these reactions, and dosing calculations, refer to Ref. 10, p. 270, and Ref. 6, p. 495 (10–12).

ION EXCHANGE

Ion exchangers operate on the principle of exchanging ions from an insoluble resin with the ions that are present in water. Ion exchange is a common method for removing heavy metals from waste water streams. Resins that typically remove metals include zeolites, anionic and cationic resins, and chelating resins. Chelating and ionic resins that are selective for uranium, strontium, and radium have been developed (6,9).

ACTIVATED CARBON TREATMENT

Activated carbon has been used in conjunction with other waste removal systems such as air stripping to remove radon (8). The radon is adsorbed onto the activated carbon, and it may be regenerated by heating the carbon to sufficient temperatures. See Air Stripping.

BIBLIOGRAPHY

1. De Zuane, J. (1997). *Handbook of Drinking Water Quality*, 2nd Edn. John Wiley & Sons, New York, pp. 341–352.
   CRC. (1995). *Handbook of Chemistry and Physics*, 75th Edn. CRC Press, Boca Raton, FL.
2. Droste, R.L. (1997). *Theory and Practice of Water and Wastewater Treatment*. John Wiley & Sons, New York, pp. 225–226.
   Davis, R.E., Gailey, K.D., and Whitten, K.W. (1984). *Principles of Chemistry*. Saunders College Publishing, New York.
3. World Health Organization. (1963).
   Alberty, R.A. (1987). *Physical Chemistry*, 7th Edn. John Wiley & Sons, New York, p. 218.

Table 1. Efficiencies, Flow, and Construction Costs for Mitigation Systems Being Used in the United States to Remove Radon from Drinking Water

Treatment Method	Removal Efficiency, %	Flow Range, $m^3\ d^{-1}$	Unit Construction Cost, $\$m^{-3}\ d^{-1}$	No. of Systems Evaluated
I. Aeration Methods				
1. Packed tower (PTA)	79 to >99%	49 to 102,740	18 to 481	11
2. Diffused bubble				
a. Single-stage	93	431	312	1
b. Multistage	71 to >99	65 to 6540	11 to 433	8
3. Spray Aeration	∼88	1,025	5.3	1
4. Slat tray	86 to 94	1989 to 2453	5.3 to 124	6
5. Cascade aeration	∼88	5,450	7.9	1
6. Surface aeration	83 to 92	54,504	42	1
II. Granular Activated Carbon	20 to >99	11 to 981	77 to 365	5

A.S.C.E—A.W.W.A. (1990). *Water Treatment Plant Design*, 2nd Edn. McGraw-Hill, New York.

4. U.S. Environmental Protection Agency. *Safe Drinking Water Act and Associated Final Rulings*. Government Printing Office, Washington, DC.
5. Cox, C.R. (1964). *Operation and Control of Water Treatment Processes*. World Health Organization, Brussels, Belgium.
6. Tchobanoglous, G., Burton, F.L., and Stensel, D.H. (2003). *Wastewater Engineering—Treatment, Disposal and Reuse*, 4th Edn. Metcalf & Eddy, Inc., McGraw-Hill, New York, pp. 1104–1137, 1162–1196.

   Dean, J.A. (1985). *Lange's Handbook of Chemistry*, 15th Edn. McGraw-Hill, New York.
7. Treybal, R.E. (1988). *Mass Transfer Operations*, 3rd Edn. McGraw-Hill Book Companies, New York, pp. 140–144, 158–211, 641–646.
8. Commission on Life Sciences. (1999). *Risk Assessment of Radon in Drinking Water*. Committee on Risk Assessment of Exposure to Radon in Drinking Water, Board on Radiation Effects Research, National Research Council, National Academy Press, Washington, DC.
9. Stocchi, E. (1990). *Industrial Chemistry*. Ellis Horwood, London, pp. 103–167.
10. Benefield, L.D., Judkins, J.F., and Weand, B.L. (1982). *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall, Englewood Cliffs, NJ, pp. 270–271, 293–294.

    Galperin, A.L. (1992). *Nuclear Energy, Nuclear Waste*. Chelsea House Publishers, New York.
11. Hafele, W. (1990). Energy from nuclear power. *Scientif. Am.* September.
12. U.S. Environmental Protection Agency. (1985). *Guidance Manual For Compliance With the Filtration and Disinfection Requirements For Public Water Systems Using Surface Water Sources*. Science and Technology Branch-Criteria and Standards Division-Office of Water, USEPA Publications, Washington, D.C., or NTIS, Springfield, VA.

READING LIST

Montgomery, C.W. (1992). *Environmental Geology*, 3rd Edn. Wm. C. Brown Publishers, Chicago, IL.

Hazardous Waste Cleanup Information, United States Environmental Protection Agency. Available: http://www.clu-in.com.

Federal Remediation Technologies Roundtable. Available: http://www.frtr.gov.

RECLAIMED WATER

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INTRODUCTION

Reclaimed water is water from a wastewater treatment plant (WWTP) that has been treated and can be used for nonpotable uses such as landscape irrigation, cooling towers, industrial processes, toilet flushing, and fire protection. The inclusion of planned water reclamation, recycling, and reuse in water resource systems reflects the increasing scarcity of water resources to meet societal demands, technological advancements, increased public acceptance, and improved understanding of public health risks.

Per capita water use in the United States has quadrupled since the beginning of the twentieth century. Americans typically consume between 60 and 200 gallons (230 to 760 liters) per capita each day. The use of reclaimed water for nonpotable purposes can greatly reduce the demand on potable water sources—this use is encouraged by diverse organizations such as FEMP, EPA, and the American Water Works Association (AWWA). Municipal wastewater reuse amounts to about 4.8 billion gallons (18 million m^3) per day (about 1% of all freshwater withdrawals). Industrial wastewater is far greater—about 865 billion gallons (3.2 billion m^3) per day.

Reclaimed water contains valuable nitrogen, phosphorus, and other nutrients, which promote plant growth. At the same time, the water meets stringent disinfection standards. Experience has shown that contact with reclaimed water does not promote waterborne disease transmission. In fact, reclaimed water quality standards are more stringent than those for surface streams, rivers, and irrigation channels. Reclaimed water is delivered through pipelines that are completely separate from the potable water system.

In some areas of the United States, reclaimed water may be referred to as irrigation quality ("IQ") water, but potential uses can extend well beyond irrigation. Using higher levels of treatment, such as reverse osmosis, reclaimed water as a potable source is technically and economically feasible. New technological breakthroughs in membrane filtration and combined biological and filtration treatment offer unprecedented opportunities for water recycling, especially in isolated locations and regions where the water supply is severely limited.

BENEFITS OF USING RECLAIMED WATER

- It saves millions of gallons of drinking water each day.
- Its use for nonpotable (nondrinking) purposes is less expensive for the vast majority of of customers.
- It delays the need for developing costly new water sources and building very expensive treatment plants.
- There is no odor or staining from its use.
- It allows a city to comply with permits relating to its water supply and wastewater treatment.
- It minimizes negative effects around underground water sources, preserving the quality of life for plants and wildlife.
- It reduces fertilizing costs because reclaimed water is rich in nitrogen and phosphorus.

POTENTIAL USES OF RECLAIMED WATER

Urban public water supplies are treated to satisfy requirements for potable use. However, potable use

Table 1. Summary of EPA Suggested Guidelines for Water Reuse[a]

Levels of Treatment	Types of Reuse	Reclaimed Water Quality	Reclaimed Water Monitoring	Setback Distances
1. Disinfected tertiary[b]	Urban reuse[c]	pH = 6–9	pH = weekly	15 m (50 ft) to potable water supply wells[d]
	Food crop irrigation	$BOD_5 \leq 10$ mg/L Turb. ≤ 2 NTU	BOD = weekly Turb. = cont.	
	Recreational impoundments	*E. coli* = none Res. $Cl_2 \geq 1$ mg/L	*E. coli* = daily Res. Cl_2 = cont.	
2. Disinfected secondary	Restricted-access-area irrigation	pH = 6–9	pH = weekly	30 m (100 ft) to areas accessible to the public (if spray irrigation)
		$BOD_5 = 30$ mg/L	BOD = weekly	
	Food crop irrigation (commercially processed)	TSS = 30 mg/L	TSS = cont.	
		E. coli = 200/100 mL	*E. coli* = daily	
			Res. Cl_2 = cont.	90 m (300 ft) to potable water supply well
	Nonfood crop irrigation	Res. $Cl_2 \geq 1$ mg/L		
	Landscape impoundments (restricted access)			
	Construction			
	Wetlands habitat			

[a] From Reference 1.

[b] Filtration of secondary effluent.

[c] Uses include landscape irrigation, vehicle washing, toilet flushing, fire protection, and commercial air conditioners.

[d] Setback increases to 150 m (500 ft) if impoundment is not sealed.

(drinking, cooking, bathing, laundry, and dishwashing) represents only a fraction of the total daily residential use of treated potable water. The remainder may not require water of potable quality. In many cases, water used for nonpotable purposes, such as irrigation, may be drawn from the same ground or surface source as municipal supplies, creating an indirect demand on potable supplies. There are opportunities for substituting reclaimed water for potable water or potable supplies for uses where potable water quality is not required. Specific water use where reuse opportunities exist include

- urban
- industrial
- agricultural
- recreational
- habitat restoration/enhancement, and
- groundwater recharge

FEDERAL GUIDELINES FOR RECLAIMED WATER REUSE

The U.S. Environmental Protection Agency (1) has suggested reclaimed water quality guidelines for the following reuse categories:

- urban reuse
- restricted-access-area irrigation
- agricultural reuse—food crops
- agricultural reuse—nonfood crops
- recreational impoundments
- construction uses
- industrial reuse
- groundwater recharge
- indirect potable reuse

Levels of treatment, minimum reclaimed water quality, reclaimed water monitoring, and setback distances are suggested for each reuse category (1). The guidelines are summarized in Table 1 for the two principal levels of treatment—disinfected tertiary (filtered secondary effluent) and disinfected secondary effluents.

CONSTITUENTS OF RECLAIMED WATER

The constituents of municipal wastewater subject to treatment may be classified as conventional, nonconventional, and emerging. Typical constituents included under each category are described in Table 2. The term conventional is used to define those constituents measured in mg/L that are the basis for designing most conventional wastewater treatment plants. Nonconventional applies to those constituents that may have to be removed or reduced using advanced wastewater treatment processes before the tank can be used beneficially. The term emerging is applied to those classes of compounds measured in the micro- or nanogram/L range that may pose long-term health concerns and environmental problems as more is known about the compounds. In some cases, these compounds cannot be removed effectively, even by advanced treatment processes.

WATER RECLAMATION TECHNOLOGIES

As noted in the previous section, the constituents of wastewater subject to treatment may be classified as conventional, nonconventional, and emerging. Conventional constituents are removed by conventional treatment technologies. Advanced treatment technologies are used most commonly for removing nonconventional constituents. The removal of emerging constituents occurs in both conventional and advanced treatment processes, but the levels to which individual constituents are removed are not well defined. Typical performance data for selected treatment combinations are presented in Table 3.

Table 2. Classification of Typical Constituents in Wastewater

Classification	Constituent
Conventional	Total suspended solids
	Colloidal solids
	Biochemical oxygen demand
	Chemical oxygen demand
	Total organic carbon
	Ammonia
	Nitrate
	Nitrite
	Total nitrogen
	Phosphorus
	Bacteria
	Protozoan cysts and oocysts[a]
	Viruses[b]
Nonconventional	Refractory organics
	Volatile organic compounds
	Surfactants
	Metals
	Total dissolved solids
Emerging	Prescription and nonprescription drugs[c]
	Home care products
	Veterinary and human antibiotics
	Industrial and household products
	Sex and steroidal hormones
	Other endocrine disrupters

[a] Value per 100 mL.
[b] Plaque-forming units/100 mL.
[c] Pharmaceutically active substances.

PLANNING FOR WASTEWATER RECLAMATION AND REUSE

In effective planning for wastewater reclamation and reuse, the objectives and basis for conducting the planning should be defined clearly. The optimum water reclamation and reuse project is best achieved by integrating both wastewater treatment and water supply needs into one plan. This integrated approach is somewhat different from planning for conventional wastewater treatment facilities where planning is done only for conveyance, treatment, and disposal of municipal wastewater. Effective water reclamation and reuse facilities should include the following elements: (1) assessment of wastewater treatment and disposal needs, (2) assessment of water supply and demand, (3) assessment of water supply benefits based on water reuse potential, (4) analysis of reclaimed water market, (5) engineering and economic analyses of alternatives, (6) implementation plan

Table 3. Treatment Levels Achievable from Various Combinations of Unit Operations and Processes Used for Water Reclamation

	Typical Effluent Quality, mg/L, Except Turbidity, NTU						
	TSS	BOD$_5$	COD	Total N	NH$_3$-N	PO$_4$-P	Turbidity
Activated sludge + granular medium filtration	4–6	<5–10	30–70	15–35	15–25	4–10	0.3–5
Activated sludge + granular medium filtration + carbon adsorption	<5	<5	5–20	15–30	15–25	4–10	0.3–3
Activated sludge/nitrification single stage	10–25	5–15	20–45	20–30	1–5	6–10	5–15
Activated sludge/nitrification denitrification separate stages	10–25	5–15	20–35	5–10	1–2	6–10	5–15
Metal salt addition to activated sludge +nitrification/ denitrification separate stages	≤5–10	≤5–10	20–30	3–5	1–2	≤1	0.3–2
Biological phosphorus removal[a]	10–20	5–15	20–35	15–25	5–10	≤2	5–10
Biological nitrogen and phosphorus removal + filtration	≤10	<5	20–30	≤5	≤2	≤2	0.3–2
Activated sludge + granular medium filtration + carbon adsorption +reverse osmosis	≤1	≤1	5–10	<2	<2	≤1	0.01–1
Activated sludge/nitrification-denitrification +granular medium filtration + carbon adsorption + reverse osmosis	≤1	≤1	2–8	≤1	≤0.1	≤0.5	0.01–1
Activated sludge/nitrification-denitrification and phosphorus removal + microfiltration +reverse osmosis	≤1	≤1	2–8	≤0.1	≤0.1	≤0.5	0.01–1

[a] Removal process occurs in the main flowstream as opposed to sidestream process.

with financial analysis, and (7) a public information program.

TECHNICAL CONSIDERATIONS

For a successful reclaimed water project, one or more of the following ingredients are required: (1) high cost water or a need to extend the drinking water supply, (2) local public policy encouraging or mandating water conservation, (3) availability of high quality effluent from a WWTP, and (4) recognition of environmental or other nontangible benefits of water reuse.

Technologies vary with end uses. In general, tertiary or advanced secondary treatment is required; either usually includes a combination of coagulation, flocculation, sedimentation, and filtration. Viruses are inactivated by granular carbon adsorption plus chlorination or by reverse osmosis, ozonation, or UV exposure. Dual water systems are beginning to appear in some parts of the country where the water supply is limited, such as Southern California. Office buildings may have two water lines coming in—one for "freshwater" and the other for reclaimed water. The former is for all potable uses, the latter for nonpotable uses.

Piping and valves used in reclaimed water systems should be color-coded with purple tags or tape. This minimizes piping identification problems and cross-connection problems when installing systems. Liberal use of warning signs at all meters, valves, and fixtures is also recommended. Note that potable water mains are usually color-coded blue, and sanitary sewers are green. Reclaimed water should be maintained at 10 psi (70 kPa) lower pressure than potable water mains to prevent backflow and siphonage in the event of accidental cross-connection. Although it is feasible to use backflow prevention devices for safety, it is imperative never to connect reclaimed and water piping directly. One additional precaution is to run reclaimed water mains at least 12 in. (30 cm) lower (in elevation) than potable water mains and to separate them from potable or sewer mains by a minimum of 10 ft (3 m) horizontally. Reclamation can be complex when the water supplier and the wastewater utility are not the same. In addition, issues of water ownership are withdrawn from one use to accommodate another.

BIBLIOGRAPHY

1. U.S. EPA. (1992). *Manual—Guidelines for Water Reuse*. U.S Environmental Protection Agency and US Agency for International Development, Washington, DC.

READING LIST

Metcalf & Eddy, Inc. (2003). *Wastewater Engineering: Treatment, Disposal, Reuse*, 4th Edn. McGraw-Hill, New York, pp. 1345–1438.

Asano, T. (Ed.). (1998). *Water Quality Management*. Vol. 10, Technomic, Lancaster, PA.

WPCF. (1989). *Water Reuse: Manual of Practice*. 2nd Edn. Water Pollution Control Federation, Alexandria, VA.

WASTEWATER TREATMENT AND RECYCLING TECHNOLOGIES

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Due to the continuous population growth, uneven distribution of water resources, periodic droughts, and water pollution, it is very important to develop water treatment and recycling technologies for economic, effective, and fast water treatment and reclamation. Different types of water treatment and recycling techniques and their basic principles, applications, costs, maintenance, and suitability are discussed. In addition, a systematic approach to water treatment and recycling, involving understanding, evaluating, and selecting parameters, is presented. A comparison of the technologies is discussed from the view points of performance, sludge production, life cycle, operation, and maintenance. Brief guidance for selecting appropriate technologies for specific applications is also evaluated.

INTRODUCTION

Water is a very important constituent of the ecosystem on the earth and an essential component of life. The quality of our water resources is deteriorating day by day due to the continuous addition of undesirable constituents to them. The main sources of water contamination are industrial, domestic, and agricultural activities and other environmental and global changes. The groundwater and surface water at many places in the world are not suitable for drinking because of the presence of toxic pollutants. If this continues, the world will be in great trouble in a few decades. Therefore, the importance of water quality preservation and improvement is essential. Continuous population growth, uneven distribution of water resources, and periodic droughts have forced scientists to search for new and effective water treatment and recycling technologies (1). There is a great need for developing suitable, inexpensive, and rapid wastewater treatment and reuse or conservation methods.

In this article, different types of wastewater treatment and recycling techniques and a systematic approach to water treatment and recycling methods are discussed. Technologies are compared in terms of their performance, sludge production, life cycle, operation, and maintenance costs. The main purpose of this article is to provide guidance for selecting appropriate technologies or combinations for specific applications.

WASTEWATER TREATMENT AND RECYCLING TECHNOLOGIES

Water treatment technologies are used for three purposes: water source reduction, wastewater treatment, and recycling. At present, unit operations and processes are combined to provide what are called primary, secondary, and tertiary treatment. Primary treatment includes a very preliminary physical purification process (filtration by bar screen, grit chamber, etc.). Secondary treatment deals with chemical and biological processes for treating wastewater. In the tertiary treatment process, wastewater (treated by primary and secondary processes) is converted into good quality water which can be used for different purposes such as drinking, industrial, and medicinal. In the tertiary process, up to 90 to 99% of the pollutants are removed, and water is safe for the specific use. In a complete water treatment plant, all three processes are combined to produce good and safe quality water.

Despite various advanced technologies for water treatment and reclamation, economic, effective, and rapid water treatment and reclamation on a commercial level is still a challenging problem. Prior to water treatment and reclamation, one should be aware of the qualitative and quantitative nature of water pollutants. Managing the removed pollutants (sludge) should also be kept in mind. A systematic approach to water treatment and recycling technologies involves understanding the technology which includes construction and operating cost, maintenance, and management of removed pollutants. A comparison of these wastewater treatment and reclamation technologies is presented in Table 1. A detailed literature survey of water treatment and recycling technologies has been carried out through analytical, chemical, water abstracts, and other journals, and a brief discussion of them is presented here. Water treatment and recycling technologies classified on the basis of their working principles are given below:

1. physical technologies
2. chemical technologies
3. electrical technologies
4. thermal technologies
5. biological technologies

Physical Technologies

Treatment and recycling technologies involving physical forces are known as physical technologies. These include screening, filtration and centrifugal separation, micro- and ultrafiltration, reverse osmosis, crystallization, sedimentation and gravity separation, flotation, and adsorption.

Screening, Filtration, and Centrifugal Separation. Pieces of cloth, paper, wood, cork, hair, fiber, kitchen refuse, and fecal solids in wastewater are removed by screening. The main idea of screening is to remove solid wastes from wastewater. Generally, screening is used as the very first step in a wastewater treatment plant. Screens of various sizes are used for this purpose, the size of the screen selected is based on the size of the solids in the wastewater.

Table 1. A Comparison of Wastewater Treatment and Recycling Technologies

Wastewater Technologies	Applicability[a]	Suitability[b]	Cost (US$ per Million Liters of Treated Water)
	A. Physical technologies		
Screening, filtration, and centrifugal separation	Ss & Sl IOB	RSrT	20–450
Micro- and ultra-filtration	Sl IOB	RSrT	10–400
Reverse osmosis	Sl IOB	RSrT	10–450
Crystallization[c]	Sl IO	RSrT	50–150
Sedimentation and gravity separation	Ss IOB	RSrT	2–10
Flotation	Ss IOB	RT	5–25
Adsorption	Ss & Sl IOB	RSrT	50–150
	B. Chemical technologies		
Precipitation[c]	Sl IO	RT	15–500
Coagulation	Ss & Sl I	RT	20–500
Oxidation	Sl IO	RSrT	100–2000
Ion exchange	Sl IO	RSrT	50–200
Solvent extraction	Sl OV	RSrT	250–2500
	C. Electrical technologies		
Electrodialysis	Sl IO	RSrT	10–400
Electrolysis	Sl IO	RSrT	—
	D. Thermal technologies		
Evaporation[c]	Sl & Ss IOB	RSrT	10–200
Distillation	Sl IOB	RT	10–2000
	E. Biological technologies		
Aerobic	Sl & Ss O	RT	10–200
Anaerobic	Sl & Ss O	RT	10–200

[a] Sl: soluble; Ss: suspended; I: inorganics; O: organics; V: volatiles; B: biologicals.

[b] R: reclamation; T: treatment; and Sr: source reduction.

[c] Rarely Used.

Filtration is a very simple physical process in which insoluble contaminants are removed by passing the water through a setup of pores of different sizes, depending on the presence of solid contaminants. It is used to remove suspended solids, greases, oils, and bacteria. Various types of filters such as membranes and cartridges, made of sand, gravel and other granular materials are used. The filtration technique is applicable below 100 mg/L suspended solids and 25 mg/L oil and grease. These constituents can be reduced up to 99%. Filtration is used for both water treatment and recycling. Water produced by filtration is used in adsorption, ion exchange, or membrane separation processes. Potable water is also produced by filtration. The cost of filtration varies from 20 to 450 US$ per million liters of treated water (1,2).

In centrifugal separation, suspended noncolloidal solids (up to 1 μ) are separated from water by centrifugal forces. Wastewater is placed in centrifugal devices and rotated at different speeds, and the solids (sludges) are separated and discharged. The extent of separation of suspended solids depends on their densities and the speed of the centrifuge. The applications include source reduction and separation of oils and greases. The different types of centrifuges available and in use are solid-bowl, basket type, directflow, and countercurrent flow. The cost of wastewater treatment ranges from 20 to 450 US$ per million liters of treated water (1,2).

Micro- and Ultrafiltration. Particles and other microbes from 0.04 to 1 μ are removed by microfiltration provided that the total suspended solids do not exceed 100 mg/L. The filters used are in the form of cartridges. Commercially available cartridges are made of cotton, wool, rayon, cellulose, fiberglass, polypropylene, acrylics, nylon, asbestos, and fluorinated hydrocarbon polymers. These are arranged in as tubular, disc, plates, spiral, and hollow fiber forms. The life of cartridges varies from 5 to 8 years depending upon the concentration of dissolved solids. Preremoval of suspended solids is an important factor in the life of cartridges. The operating pressure in this process ranges from 1 to 3 bar. Applications include removal of solids and microbes. Water purified by this technique is used for the food and drink industries, soft drinks, pharmaceuticals, photofilm processing, swimming pools, and drinking (2,3). It has also been used as a wastewater source reduction technique.

Ultrafiltration is a low-pressure membrane separation process that removes high molecular weight materials, colloids, pyroxenes, microorganisms, and suspended solids from wastewater. Ultrafiltration membranes are manufactured from a wide variety of polymers, and minerals in the range of 0.005 to 0.10 μ. The membranes are made of polysulphonates, polyacrylonitriles, polyamides, PVDF, and zirconium oxides. To achieve the required filtration, membranes are arranged in tubular, disc, plates, spiral, and hollow fiber forms. The life of membranes varies from 5 to 8 years and may be increased as discussed above (2). The cost of treated water varies from 10 to 400 US$ per million liters.

Reverse Osmosis. Reverse osmosis (RO), also known as hyperfiltration, is a classical method of purification that came into existence since the advancement of semipermeable membranes. It has received great attention nowadays as the best water recycling technique. The separation and concentration of a dissolved species is achieved due to the hydraulic gradient across the semipermeable membrane. Pressure greater than osmotic pressure is applied for the process. The most commonly used membranes are made of cellulose, nylon, polyether, polyethyl urea, polyphenyl oxides, phenylenes, and polyamide. To achieve the required filtration, membranes are arranged in tubular, disc, plate, spiral, and hollow fiber forms. The partition coefficients of solutes between water and the membrane play an important role in removing water pollutants. The free energy of interaction between water and membrane sites is also responsible for the RO process. The pH, pressure, size, and molecular weight of the solute and time of operation are considerable factors in RO.

RO has been used as a separation and concentration technique at macro- and microlevels for removing large, nonpolar, ionic, and toxic substances. Up to 85–99% total dissolved solids (TDS), organic dissolved matter (ODM), and bacteria can be removed by this method. It has been used for treating wastewater from sanitary wastes, municipal leachates, petrochemicals, electroplating, textiles, coal, gasification, pulp and paper, steel, and electronic industries (3,4). It rejects 100% of bacteria, viruses, and other microbes, and, therefore, it is used to prepare ultrapure water for pharmaceuticals, medicines, and electronics. In addition, it has been used for source reduction. RO is today's most economical process for potable water production from saline water.

The life of RO membranes is 2–5 years, depending on the nature of the wastewater treated. The flux and the quality of the permeate may decrease over a long period of time due to membrane fouling from humic acids, bacterial slimes, or scales that may accumulate on the RO membranes. Phenols also clog the membranes. To increase the efficiency and life of RO systems, pretreatment is necessary to minimize the concentration of colloidal and dispersed solids. Physicochemical coagulation with lime has been used to minimize colloids, turbidity, dispersed oil phases, metal ions, and suspended matters. Sodium hydroxide solution (pH 9–11) has been used to clean RO membranes in case of silica and sulfate fouling (5,6). Silica can also be removed from membranes by ion retarding resins that have high affinity for strong acids, together with conversion of the weak acid [$Si(OH)_4$] into much stronger acid (H_2SiF_6). Bacterial inhibitor solutions are circulated (to check the bacterial growth) into the RO tubules or discs before stopping the process for a long period (5). Phenolics may be removed from RO membranes by circulating hydrogen peroxide solution. The cost of the process varies from 10 to 450 US$ per million liters of treated water.

Crystallization. In this process, soluble constituents are removed by raising their concentrations to the point where they start to crystallize. This is done either by evaporation, by lowering the temperature of the water, or by adding other solvents. It is useful for treating wastewater that has high concentrations of TDS, including soluble organics and inorganics. During the process, other constituents such as bicarbonate, ammonia, and sulfite may break down and may be converted into various gases and, therefore, crystallization sometimes may be used for pH control. The treated water from this process is of high quality. Crystallization is generally used for wastewater released from cooling towers, coal and gas fired boilers, paper, and dyeing plants. It is also used for source reduction. The commonly used devices for crystallization include forced circulation, draft tube baffle, surface cooled crystallizers, and fluidized suspension. The cost of the technique ranges from 50 to 150 US$ per million liters of treated water (3,7).

Sedimentation and Gravity Separation. In this process, suspended solids, grit, and silt are removed by allowing water to remain undisturbed/semidisturbed for different time periods. The suspended solids settle by gravity (1,2). The time period depends on the size and density of the solids. Various types of tanks are designed for this purpose. Some chemicals such as alum are used to adjust pH and augment the process. Gravity separation can reduce oil concentrations and suspended solids up to 99% and 60%, respectively. Generally, sedimentation is carried out prior to a conventional treatment process. It is a very useful method for treating effluents from the paper and refinery industries. Water treated in this process is used for industrial water supply, water for ion exchange, and membrane processing. The technique is also used for source reduction. The cost of treated water varies from 2 to 10 US$ per million liters.

Flotation. This technique removes suspended solids, oils, greases, and biological solids by adhering them, to air or gas bubbles (1,2,8). The solids thus adhered to gas or air bubbles form agglomerates, which in turn accumulate at the water surface and are removed. Some chemicals such as alum and activated silica help in the flotation process. Compressed air is allowed to pass through water, which helps in the flotation process. Some workers have also used electroflotation as an effective process for water treatment and recycling. Up to 75% and 99% of suspended solids and oil/grease are removed, respectively, by this process. Flotation requires water tanks of different sizes. Flotation is a common and essential component of a conventional water treatment plant. It is a very effective technique for treating wastewater from the paper and refinery industries. The cost of the operation varies from 5 to 25 US$ per million liters of treated water.

Adsorption. Adsorption (1,2,9) is a surface phenomenon defined as the increase in concentration of a particular component at the surface or interface between two phases. Adsorption efficiency depends on a number of parameters such as pH, temperature, concentration of pollutants, contact time, particle size of the adsorbent, and nature of adsorbents and pollutants. Suspended particles, oils, and greases reduce the efficiency of the process and, therefore, pre-filtration is required. It is considered a universal water treatment and reclamation process because it can be applied to remove soluble and insoluble organics, inorganics, and biological solids. Different types of adsorbents are used in the adsorption process. The most commonly used adsorbents are activated carbon, fly ash, metal oxides, zeolites, moss, biomass, and geothites. At the industrial level, pollutants are removed from wastewater by using columns and contactors filled with the required adsorbents. The extent of removal varies from 90 to 99%. Adsorption is used for source reduction, wastewater treatment, and reclamation for potable, industrial, and other purposes. The basic problems of adsorption are regeneration of columns and column life. The cost of the technique ranges from 50 to 150 US$ per million liters of treated water.

Chemical Technologies

Water treatment methods involving the use of chemicals are chemical technologies. Precipitation, coagulation, oxidation, ion exchange, and solvent extraction are the main chemical methods for wastewater treatment and reclamation.

Precipitation. Dissolved contaminants may be converted into solid precipitates by adding chemicals (2,10) that react with the soluble pollutants and form precipitates. The most commonly used chemicals for this purpose are different types of alum, sodium bicarbonate, ferric chloride, ferric sulfate, ferrous sulfate, and lime. pH and temperature are the controlling factors in the precipitation process. Precipitation is carried out in sedimentation tanks; 40 to 60% removal of pollutants by precipitation has been reported. The presence of oil and grease may cause a problem in precipitation. The applications of precipitation include wastewater treatment (from nickel and chromium plating) and water recycling. Specific applications include water softening and removal of heavy metals and phosphate from wastewater. The major problem in precipitation is managing the large volume of sludge produced. The cost varies from 15 to 500 US$ per million liters of treated water.

Coagulation. The suspended nonsettleable solids in wastewater are allowed to settle by the addition of certain chemicals in a process called coagulation (1,11). The commercially available chemicals are alum, starch, iron compounds, activated silica, and aluminum salts. In addition, synthetic cationic, anionic, and nonionic polymers are very effective coagulants but are usually more costly. pH, temperature, and contact time are the most important controlling factors in the coagulation process. In a biological treatment plant, microbes and other organics floated on the surface are removed by the addition of certain coagulants. It is the main component of a wastewater treatment plant and its application includes wastewater treatment, recycling, and removal of heavy metal ions and fluoride. The cost of the treated water varies from 20 to 500 US$ per million liters.

Oxidation. In chemical oxidation, organic compounds are converted into water and carbon dioxide or some other products such as alcohols, aldehydes, ketones and carboxylic acids which are biodegradable (1,12). Chemical oxidation is carried out by potassium permanganate, chlorine, ozone, peroxides, air, and chlorine dioxides. The rate of chemical oxidation depends on the nature of the oxidants and pollutants. pH, and temperature also play a crucial role in the rate of chemical oxidation. Ammonia, cyanide, sulfides, phenols, hydrocarbons, and some pathogens may be removed by chemical oxidation. Chemical oxidation is used for wastewater treatment and recycling for industry and irrigation. It is also a useful and effective method for source reduction. The cost of the technique ranges from 100 to 2000 US$ per million liters of treated water.

Ion Exchange. Ion exchange is a process in which ions in wastewater are exchanged with solid materials called ion exchangers (1,13). It is a reversible process and requires low energy. The ion exchangers are of two types, cation and anion exchangers, that can exchange cations and anions, respectively. Ion exchangers are resins of natural or synthetic origins that have active sites on their surfaces and, generally, are in the form of beads. The most commonly used ion exchangers are sodium silicates, zeolites, polystyrene sulfonic acid, acrylic and methacrylic resins. Ion exchange is used to remove low concentrations of inorganics and organics (up 250 mg/L). The concentration of organics and inorganics can be reduced up to 95%. Applications include the production of potable water, water for industries, pharmacy, research, and softening for boiler feed, fossil fuels, nuclear power stations, paper, and, electronic industries. It has also been used for source reduction. Pretreatment of water is required in the presence of oil, grease, and high concentrations of organics and inorganics. One million liters of wastewater are treated for 50 to 200 US$.

Solvent Extraction. Organic solvents that are immiscible with water and can dissolve water pollutants are added to wastewater to remove pollutants. The technique is called solvent extraction (14). A maximum concentration of TDS of 2000 mg/L can be reduced up to 90% by solvent extraction. The most commonly used solvents are benzene, hexane, acetone, and other hydrocarbons. The technique is effective to remove only the dissolved organics, oils, and greases in wastewater. However, certain metal ions and actinide chemicals may be removed by the method. It is also used for water treatment and recycling in chemical process plants, phenol, gasoline, and acid industries. It has also been used for water source reduction. The presence of suspended solids may cause a problem in solvent extraction and, hence, requires pretreatment. The cost varies from 250 to 2500 US$ per million liters of treated water.

Electrical Technologies

Water pollutants are removed under the influence of electric current in electrical water treatment and recycling technologies. Electrical water treatment technologies are summarized below.

Electrodialysis. In this technique, water soluble ions are allowed to pass through ion selective semipermeable membranes under the influence of an electric current (1–3,15). The ion selective membranes are made of ion exchange material. They may be cation and anion exchangers, which permit outflow of cations and anions, respectively. The process, operated either in a continuous or batch mode, has two electrodes on which an emf. is applied. To obtain the desired degree of demineralization, membranes are arranged either in parallel or series. The dissolved solids removal depends on pH, temperature, the amount of current applied, the nature of the pollutants, selectivities of the membranes, the wastewater flow rate, fouling and scaling by wastewater, and the number and configuration of stages. Applications include production of potable water from brackish water. This technique has also been used for water source reduction. A maximum concentration of 200 mg/L of TDS can be reduced by 90% by electrodialysis. Membrane fouling occurs as in reverse osmosis. Cleanup and other precautions should be taken as discussed in the reverse osmosis section. The cost of treated water varies from 10 to 400 US$ per million liters of water.

Electrolysis. The technique in which the soluble inorganics and organics are either deposited or decomposed on the surface of electrodes by an electrochemical redox reaction is called electrolysis (16). Metal ions are deposited on the electrode surface, and organics are decomposed into carbon dioxide and water or some other products. It has been used to remove turbidity and color from wastewater. This method is effective for the removal of TDS below 200 mg/L and, therefore, requires pretreatment of wastewater. The technique comprises a water tank or tanks in series with two or a series of electrodes of the required metal. The electrodes are specific with respect to the dissolved metal ions in wastewater. The most important controlling factors for this process are pH, temperature, amount of current applied, and contact time. Electrolysis as a technique for wastewater treatment is not yet developed completely and is still at the research and development stage. It has been rarely used commercially for wastewater treatment. However, its applications include treating some industrial effluents especially enriched with metal ions and some organics. It may be used as a water source reduction technique. The advantages of this technique comprise the further use of deposited metal ions without any waste management problem.

Thermal Technologies

Techniques involving the use of heat energy for water treatment and recycling are thermal technologies. The most commonly used techniques for wastewater treatment and recycling are evaporation and distillation.

Evaporation. Evaporation is a natural process and is generally used to reduce waste liquid volume. In modern development, it has been used as a water treatment method (2,3,17). The water surface molecules escape from the surface under natural conditions, and these escaped molecules are collected as pure liquid water. Mechanical evaporators have been used for water recycling. Sometimes, vacuum evaporation has been used for wastewater recycling, and these are operated by steam or electric power. Evaporation is effective for removing inorganic and organic (except volatile organics) contaminants, and it works even at very high concentrations (about 10%) of pollutants. Foaming, scaling, and fouling along with suspended solids and carbonates are the major problems in evaporation because they create maintenance problems. Evaporation applications include treating wastewater from the fertilizer, petroleum, pharmaceutical, and food processing industries. It is also used for water supply to ion exchangers and membrane processes. Water from evaporation has been used for cooling in towers and boilers. It can be used as a technique for water source reduction. The cost of water production varies from 10 to 200 US$ per million liters.

Distillation. In distillation, water is purified by heating it up to 100 °C at which liquid water vaporizes and leaves the pollutants behind (1,18). The vapors generated are cooled to liquid water. The wastewater should be free of volatile impurities. Water produced by this technique is about 99% free from impurities. Various types of boilers with multistage and double distillation are used in this process. The size of the boilers depends on the quantity of water required. Applications of distillation in water treatment and reclamation include water supplies in laboratories, pharmacy, and medicinal preparations. Distillation is effective for preparing potable water from sea and brackish water. The cost of water production varies from 10 to 2000 US$ per million liters.

Biological Technologies

Biological treatment has a reputable place in various water treatment and recycling methods (1–3,19,20). Soluble and insoluble organic pollutants are oxidized by microbes in this process. Water is circulated in a reactor that maintains a high concentration of microbes, and the microbes convert organic matter into water, carbon dioxide, and ammonia. Sometimes, the organic matter is converted into other products such as alcohol, glucose, and nitrate. Wastewater should be free of toxic organics and inorganic pollutants. The maximum concentrations of TDS, heavy metals, cyanides, phenols, and oil should not exceed 16,000, 2.0, 60.0, 140, and 50 mg/L, respectively. Biological treatment includes aerobic and anaerobic digestion of wastewater. The cost of Biological treatment varies from 10 to 200 US$ per million liters of treated water.

Aerobic Process. When air or oxygen in dissolved form is available freely to wastewater, then the biodegradable organic matter undergoes aerobic decomposition, caused by aerobic and facultative bacteria. The extent of the process depends on oxygen availability, retention time, temperature, and the biological activity of the bacteria. The rate of biological oxidation of organic pollutants may be increased by adding chemicals required for bacterial growth. The technique is effective for removing dissolved and suspended volatile and nonvolatile organics. The concentration of biodegradable organics can be reduced up to 90%. Applications include treating industrial wastewater to reduce BOD, COD, nitrogen, and phosphorous. The disadvantage of this method is the production of a large quantity of biosolids, which require further costly management.

Anaerobic Process. If free or dissolved oxygen is not available to wastewater, then anaerobic decomposition called putrefaction occurs. Anaerobic and facultative bacteria convert complex organic matter into simpler organic compounds of nitrogen, carbon, and sulfur. The important gases evolved in this process are nitrogen, ammonia, hydrogen sulfide, and methane. The applications of the anaerobic process to organic pollutant digestion are as discussed in the aerobic process.

CONCLUSION

There is a scarcity of safe and good quality water at present, and it will become more problematic in the near future. Wastewater treatment technologies differ from each other in terms of their principles, scope of application, speed, and economy. All techniques of primary and secondary treatment processes have their own importance and are essential. Therefore, no comparison can be done, whereas wastewater recycling technologies (tertiary treatment) can be compared. The feasibility of any water recycling technique at a commercial level depends on the costs of construction, maintenance, and operation. Sludge management is also an important factor in the selection of technology. Adsorption is considered the best and a universal technique, and it can be used to remove a wide variety of pollutants. It is also a rapid process with a very low cost of construction, maintenance, and operation using low cost adsorbents. Reverse osmosis is also used widely because the water quality is good but the costs of construction and maintenance are comparatively high, and it is rarely used in developing countries. Beside these two, other techniques such as micro- and ultrafiltration, ion exchange, electrodialysis, solvent extraction, and distillation are used for specific purposes, but their use is restricted at potable and industrial levels. Electrolysis as a water recycling technique is in its development stage, and hopefully it will be the best technique on a commercial scale in terms of its cost, maintenance, and speed. The advantages of this technique are a wide range of applications.

BIBLIOGRAPHY

1. Droste, R.L. (1997). *Theory and Practice of Water and Wastewater Treatment*. John Wiley & Sons, New York.
2. Nemerow, N. and Dasgupta, A. (1991). *Industrial and Hazardous Waste Treatment*. Van Nostrand Reinhold, New York.
3. Zinkus, G.A., Byers, W.D., and Doerr, W.W. (1998). Identify appropriate water reclamation technologies. *Chem. Eng. Prog.* **94**(5): 19–31.
4. Williams, A.R. (1991). The use of reverse osmosis for the purification of coal gasification liquors. In: *Effective Industrial Membrane Processes: Benefits and Opportunities*. M.K. Turner (Ed.). Elsevier Science, Barking Essex.
5. Sun, L., Perdue, E.M., and McCarthy, J.F. (1995). Using reverse osmosis to obtain organic matter from surface and ground water. *Water Res.* **29**: 1471–1477.

6. Culkin, B., Plotkin, A., and Monroe, M. (1998). Solve membrane fouling problems with high shear filtration. *Chem. Eng. Prog.* **94**(1): 29–33.
7. vander Ham, F., Witkamp, G.J., deGrauw, J., and van Rosmalen, G.M. (1998). Eutectic freeze crystallization: Application to process streams and wastewater purification. *Chem. Eng. Process* **37**(2): 207–213.
8. Sinev, I.O., Sinev, O.P., and Linevich, S.N. (1997). Apparatus of flotation treatment of natural waters and wastewater. *Izobreteniya* **26**: 369–370.
9. Gupta, V.K. and Ali, I. (2002). Adsorbents for water treatment: Low cost alternatives to carbon. *Encyclopedia of Surface and Colloid Science*. Vol. 1. A. Hubbard (Ed.). Marcel Dekker, New York, pp. 136–166.
10. Nagasaki, Y. (1998). Treatment of Organic Wastewaters by coagulation and precipitation. Jpn.Kokai Tokyo Jp. 1057967 [9857967] (Cl. C02F1/52).
11. Latifossglu, A.A., Surucu, G., and Evirgen, M. (1997). Improvement to the dewaterability of ferric sludge produced from chemical treatment of wastewaters. *Water Pollut. IV: Modelling Meas. Predicting, 4th Int. Conf.* pp. 733–742.
12. Bigda, R.J. (1995). Consider Fenton's chemistry for wastewater treatment. *Chem. Eng. Prog.* **89**: 62–66.
13. McNulty, J.T. (1984). Anion exchange resin kinetics in mixed bed condensate polishing. In: *Ion Exchange Technology*. D. Naden and M. Streat (Eds.). Ellis Norwood, Chichester.
14. Ahn, J.W. and Ahn, J.G. (1997). Solvent extraction for the treatment of industrial wastes. *Chawn Risaikring* **6**(4): 48–54.
15. Gottberg, V., Antonia, J.M., and Siwak, L.R. (1998). Electrodialysis reversal process. *Int. Desalination Water Reuse Q.* **7**(4): 33–37.
16. Coin, R.J., Niksa, M.J., and Elyanow, D.I. (1996). Wastewater treatment by electrochemistry. *Environ. Prog.* **15**: 122–127.
17. Matoba, T. and Furuishi, H. (1998). Sea Water Desalination System. Jpn. Kokai Tokyo Jp. 1052683 [9852683] (Cl. C02F1/04).
18. Bom, P.R. (1998). Method for desalination containing water, single effect or multiple - Effect distillation apparatus and modular element suitable for a single effect or multiple effect distillation apparatus. PCT Int. Appl. WO 9825679 (Cl. B01D1/26).
19. Clark, T. and Stephenson, T. (1998). The effect of chemical adsorption on aerobic biological treatment of municipal wastewater. *Environ. Technol.* **19**(6): 579–590.
20. Kato, M.T., Field, J.A., and Lettinga, G. (1997). The anaerobic treatment of low strength wastewater in UASB and EGSB reactors. *Water Sci. Technol.* **36**: 375–382.

WASTEWATER TREATMENT PROCESSES AND WATER REUSE

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TREATMENT PROCESSES

The selection of wastewater treatment processes depends on the influent characteristics, the quality of effluent required, and the cost. Treatment can be divided into these stages: preliminary, primary, secondary, and advanced treatment.

Preliminary Treatment Processes

The objective of preliminary treatment is to prepare wastewater for further treatment by removing large objects and grit from the wastewater. These materials may otherwise impede the efficiency or increase the maintenance of downstream processes. Typical preliminary treatment may include screening, grit removal, comminution, and flow equalization.

Screening. Screening removes large objects and trash that could interfere with, clog, or damage downstream equipment, such as pumps, valves, actuators, mechanical aerators, and biological filters. Bar screens typically consist of inclined steel bars spaced at equal intervals in a channel through which the wastewater flows. Large solids are removed from the wastewater by the bars, which must be cleaned either manually or mechanically. Due to their putrescible nature, screenings are usually landfilled. When designing bar screens, bar size, bar spacing, angle of inclination, and wastewater approach velocity must be considered (1).

Manually cleaned screens usually have bar spacings ranging from 1 to 2 inches, and the bars are inclined from 30° to 45° to the horizontal (1). The screens are cleaned by raking the screenings onto a sieve plate to allow for drainage.

Mechanically cleaned screens typically have bar spacings ranging from 0.5 to 1.5 inches and are inclined from 0° to 30° from the vertical (1). The screen automatically starts the cleaning process after a preprogrammed operating time but also has a high-level override.

Grit Removal. Grit consists of sand, gravel, and other non- or minimally putrescible material that may wear mechanical equipment or accumulate in process tanks. Grit has a high settling velocity and settles quickly (1). Grit chambers are frequently aerated, which keeps the light organic materials in suspension and allows the heavy grit particles to settle to the bottom of the tank to be collected (1).

Comminution. Comminutors shred materials without removing them from the wastewater. Comminutors have a bypass channel and a screening device that may be used if the comminutor must be taken out of service (1). The basic parts of a comminutor include a screen and cutting teeth on a revolving drum. The drum has slots cut into it. The teeth shred the material as it is trapped against the screen. The shredded solids then pass through the drum slots and out of the bottom opening through an inverted siphon (2). Shredded materials cause problems in downstream process units, so comminutors are not frequently installed in new wastewater treatment plants (1).

Equalization. Equalization is used in plants that have significant variations in hydraulic or organic loading. It provides relatively uniform loading throughout the day. Uniform loading increases the efficiency and reliability of downstream process units. In addition, the downstream treatment units no longer have to treat highly variable influent, so the sizes of the units may be decreased (1).

Equalization tanks may be designed either as in-line or side-line units. The sizing should be based on an influent flow hydrograph during wet weather. To prevent detained wastewater from becoming septic, a dissolved oxygen concentration of 1 mg/L must be maintained in the tank (3). Equalization tanks should be mixed to prevent solids from settling.

Primary Treatment Processes

Sedimentation. Primary sedimentation is the oldest and most widely used operation in treating wastewater (1). It removes solids to produce an effluent that is suitable for downstream biological treatment.

Solids removal is governed by retention time and surface settling rate. The surface settling rate is the volumetric flow rate over the surface area of the clarifier. Particles whose settling velocity is greater than the surface settling rate are removed from the wastewater stream. However, if the detention time is too long, the wastewater turns septic.

Clarifier design is based on the average design flow and the peak hourly flow. Flows are generally limited to 1000 gallons per day/ft^2 for design flow and 1500 gpd/ft^2 at peak hourly flow (3). The calculated settling area is based on both flows, and the larger clarifier is selected.

Secondary Treatment Processes

Activated Sludge Processes. Activated sludge is a biological process that uses microorganisms to treat wastewater in an aerobic environment. Wastewater is introduced into the reactor tank where it is mixed with microorganisms that are returned from the clarifier. This mixture of raw wastewater and return activated sludge is called mixed liquor. The microorganisms are then allowed to flocculate and settle under quiescent conditions in a clarifier; treated wastewater flows over weirs for further treatment or discharge. There are several variations on the conventional activated sludge process, including plug flow, step feed, tapered aeration, complete mix, contact stabilization, sequencing batch reactor, and extended aeration.

Plug Flow. A plug flow reactor is configured so that the wastewater flows through a long, narrow channel during treatment. It approximates flow through a pipe. In an ideal plug flow reactor, there is no longitudinal mixing of wastewater.

Step Feed. Step feed is a variation of the plug flow reactor. In this variation, the wastewater influent is introduced into the reactor at several points, rather than adding the entire influent stream at the beginning of the reactor. It provides equalization of the load over the reactor volume.

Tapered Aeration. Tapered aeration is another variation on the plug flow reactor. The reactor influent is introduced at the front end of the reactor, but the aeration pattern is different. Approximately 50% of the aeration capacity is in the first third of the reactor, where the oxygen demand is the highest, and less is supplied further down the reactor, where the demand is less.

Complete Mix. A complete mix reactor is the opposite of a plug flow reactor. All of the wastewater is completely mixed throughout the reactor. To facilitate mixing, complete mix reactors are shorter and wider than plug flow reactors. Due to the rapid mixing of the contents, complete mix reactors can tolerate shock loads better than plug flow reactors.

Contact Stabilization. Contact stabilization is a process where treatment takes place in two tanks. The wastewater is introduced into the contact tank with microorganisms. The organics are not degraded in the contact tank but are absorbed into the microbial cells. After clarification, the settled sludge is returned to a reaeration tank, where the microorganisms then degrade the organics that were absorbed during the contact process.

Sequencing Batch Reactor. A sequencing batch reactor is a variation of the complete mix reactor. Both wastewater stabilization and settling take place in the same tank in sequenced phases. Wastewater is introduced into the tank (fill phase), where it is mixed and aerated. Following a "react phase," both mixing and aeration are turned off, and the wastewater is allowed to settle quiescently (settle phase). The treated wastewater is then decanted from the top of the reactor (decant phase), and the sequence begins again.

Extended Aeration. The extended aeration process is a suspended growth system that operates in the endogenous respiration phase of microbial growth. This process requires low organic loading rates, long aeration times, and high mixed liquor concentrations. This process is commonly used in prefabricated package treatment plants for small communities.

Aeration Requirements. The dissolved oxygen concentration in the aeration tanks should be greater than 2 mg/L at all times. To supply sufficient air for treatment, all of the treatment processes except extended aeration should be designed to provide 1.1 lb of oxygen per pound of biochemical oxygen demand (BOD) oxidized. Because of the additional aeration needs of endogenous respiration, extended aeration systems require 1.5 lb of oxygen per pound of BOD oxidized. This does not include the air required for nitrification (3).

Fixed Film Processes. Fixed film processes are biological treatment processes using microorganisms attached to a support medium. As the wastewater flows over the medium, the microorganisms absorb the organics. The biofilm builds up, as wastewater is treated, and eventually sloughs off. Like activated sludge, the sloughed microorganisms are then allowed to settle under quiescent conditions in a clarifier.

In a trickling filter, the wastewater flows through a rotating arm, which distributes it over the top of the medium. To maintain proper liquid flow for efficient operation of the filter, a portion of treated wastewater must be recirculated back to the filter.

In a rotating biological contactor, microorganisms are attached to a plastic disk, which is rotated through the wastewater. When the microorganisms are submerged, they absorb organics. During the time the microorganisms are exposed to the air, they receive the oxygen that they require for treatment. Unlike trickling filters, however, no recirculation is required.

Stabilization Ponds. Stabilization ponds are typically large, lined basins, which may be aerobic, anaerobic, or facultative. Ponds are designed around a detention time measured in days, rather than hours, and are relatively shallow compared with other biological treatment processes. These design criteria mean that a large land area is required for ponds, and they are usually used only in small communities. Their advantages include low construction and operating costs.

Advanced Treatment Processes

Nitrification. Ammonia nitrogen is converted to nitrate in a two-step process. Ammonia is first converted to nitrites, and the nitrites are then converted to nitrates. This conversion is oxygen intensive. For each milligram of ammonia converted to nitrate, 4.6 mg of oxygen is required. In addition, each milligram of ammonia converted consumes 7.14 mg of alkalinity (4).

Nitrification may occur in the same tank as carbon oxidation in a single sludge process, or it may take place in a separate nitrification tank. Because nitrifying organisms have a slower growth rate than the organisms for carbon oxidation, the process requires longer detention time and longer mean cell retention time.

Biological Phosphorus Removal. Phosphorus removal can be enhanced in a biological system by first creating an anaerobic zone followed by an aerobic zone. In biological phosphorus removal, from 2.5 to 4 times more phosphorus can be removed than in a secondary treatment process (4).

To generate energy for cell growth in the anaerobic stage, phosphorus is released from the internal polyphosphates of the cell, resulting in an increase in the liquid phosphorus concentration (3). In the aerobic zone, there is a rapid uptake of the soluble phosphorus for the resynthesis of intracellular polyphosphates. More phosphorus is absorbed by the cells than was released in the anaerobic zone.

There are three major biological phosphorus removal methodologies: the Anaerobic/Oxic (A/O) process, the PhoStrip process, and the sequencing batch reactor. The A/O process is proprietary, and phosphorus removal depends on the influent ratio of BOD to P. The PhoStrip process is also proprietary. Phosphorus removal does not depend on the BOD:P ratio, but chemicals must be used to precipitate the phosphorus (4). The SBR can be designed to provide anaerobic conditions during the treatment cycle, which release phosphorus. When the reactor is then aerated, the phosphorus is absorbed from the wastewater and is incorporated into the biomass.

Denitrification. Denitrification is the removal of nitrogen from wastewater. In an anoxic environment, several species of bacteria can use nitrates, rather than oxygen, as their energy source. Denitrification converts the nitrates into nitrogen gas and additional biomass (4). The process requires a carbon source for completion. In wastewater treatment, it is common to use the wastewater itself for the carbon supply. The raw wastewater flows into an anoxic zone with return sludge and a large mixed liquor recycle. The recycle ratio is determined by the ammonia concentration and the required effluent nitrate concentration. The anoxic zone then denitrifies by using the nitrates created in the mixed liquor. Following the anoxic zone, the wastewater flows to an aerobic zone to strip nitrogen gas. The process may be repeated for additional nitrogen removal. Denitrification is normally done in a plug flow type system, an oxidation ditch, or a sequencing batch reactor (4).

Biological Dual-Nutrient Removal. Biological dual-nutrient removal is the reduction of both nitrogen and phosphorus in wastewater by biological methods. Biological dual-nutrient removal is achieved through several proprietary treatment processes, including the A^2O process, the Bardenpho process, the University of Capetown (UCT) process, and the Virginia Initiative (VIP) process (4). These processes use the aerobic process for carbon oxidation, the anoxic process for denitrification, and the anaerobic process for biological phosphorus removal, although arrangement of the processes varies. The UCT process and the VIP process are further complicated by the use of internal recycle streams.

Air Stripping. Air stripping is a method of removing volatile compounds from a solution. Air is introduced at the bottom of a packed tower. Wastewater flows down the tower from the top and contacts the air countercurrently. The driving force in air stripping is the concentration difference between the air and the wastewater. The tower medium may become fouled, resulting in high operating and maintenance costs.

Coagulation/Sedimentation. Coagulation/sedimentation uses chemicals to enhance the sedimentation of solids, precipitate pollutants, or remove phosphorus. The chemicals most commonly used in the coagulation/sedimentation process are lime, alum, iron salts, and polymers (2). Coagulation involves destabilizing colloidal particles through any of several processes, including double layer compression, charge neutralization, enmeshment, or interparticle bridging (5). The particles then aggregate and settle out.

Alum is typically used in the chemical removal of phosphorus, although iron salts may also be used. Phosphorus removal occurs by the formation of an insoluble precipitate of aluminum or iron phosphate. Alum and iron also react with hydroxyl radicals in the water, forming hydroxides in addition to phosphates.

Filtration. Filtration is the removal of wastewater solids by passing the wastewater through granular media. Some of the media that have been used include sand, anthracite coal, diatomaceous earth, perlite, and granular activated carbon. Sand filters are the most commonly used filters in wastewater treatment, although filters can also consist of multiple types of media, such as coal over sand or coal over silica sand over garnet sand (5).

Particles may be removed by interstitial straining. However, smaller particles must be transported to the surfaces of the media, where an attachment mechanism retains the particles. Transport mechanisms may include gravitation, diffusion, and interception. These processes depend on the physical characteristics of the media. The attachment mechanism may include electrostatic attraction, chemical bridging, or adsorption. These processes are functions of the coagulant and the chemical characteristics of the wastewater and media (5).

Filters are classified as slow filters, rapid filters, or pressure filters. Slow filters require a buildup of solids on the top surface of the filter through which the wastewater must pass, which requires a low application rate. This buildup strains particles from the wastewater. Rapid filters and pressure filters use the entire depth of the media and may be operated at higher loadings than slow filters.

Activated Carbon Adsorption. Adsorption is a process where molecules of a compound adhere to a solid surface. The most commonly used adsorbent in wastewater treatment is activated carbon. Activated carbon comes in two forms, powdered and granular. Powdered activated carbon (PAC) is added to the mixed liquor in the aeration tanks and is removed from the wastewater by settling. Granular activated carbon (GAC) is used in a packed bed (2).

The adsorptive capacity of the carbon is a function of the material and method used to create the activated carbon as well as the chemical properties of the compound to be adsorbed. In general, organics are completely removed until the adsorptive capacity is exhausted. At this point, the effluent concentrations increase (2). Spent activated carbon may be regenerated by heating.

Membrane Systems. Membrane processes use a semipermeable barrier that allows the water to flow through but retains the contaminants. There are several types of membrane systems in wastewater treatment, including reverse osmosis, nanofiltration, microfiltration, and ultrafiltration. All of these processes use pressure to force water through the membrane.

Ultrafiltration may be used to remove molecules that have a molecular weight of 500 or greater and have a low osmotic pressure at moderate concentrations. This includes bacteria, viruses, proteins, and clays (5). Reverse osmosis is used to separate small molecules whose osmotic pressure is high. Microfiltration and nanofiltration are membrane systems that lie between ultrafiltration and reverse osmosis.

Membrane processes are subject to fouling of membranes. These processes should be pilot tested to determine which process and membrane work best for any given application.

Disinfection Processes

Chlorination/Dechlorination. Chlorine has been used as a disinfectant for many reasons, including inactivation of a wide range of pathogens, maintenance of a residual, and cost. As chlorine dissolves in water, it forms hypochlorous acid, which dissociates into hypochlorite ions and hydrogen ions and decrease the pH. Lower pH values cause less dissociation, which is preferable, because hypochlorous acid is a much more effective disinfectant than hypochlorite. Sodium and calcium hypochlorites also form hypochlorous acid when dissolved, but they also liberate hydroxyl ions, and thus increase the pH of the wastewater. Chlorine is toxic, so dechlorination may be required, which is usually done by using sulfur dioxide to reduce the chlorine to chlorides. Sodium metabisulfite or sodium bisulfite may be used instead of sulfur dioxide in small facilities. The reactions are nearly instantaneous, and detention times are less than 2 minutes.

Ozonation. Ozone is a powerful oxidant that can disinfect wastewater using less contact time and lower dosages than other chemical methods. It has high germicidal efficiency against a wide range of organisms, and it does not leave a residual (6). Because of its instability, ozone must be generated on-site. Ozone is applied to wastewater in closed contactors. The off-gas from the contactors contains high concentrations of ozone, which must be destroyed before it is discharged to the atmosphere.

Ultraviolet Light Disinfection. Ultraviolet light is a form of electromagnetic radiation at wavelengths of 100–400 nm. Electromagnetic radiation at wavelengths from 240–280 nm inactivates microorganisms by damaging their nucleic acid (6). Ultraviolet lamps operate in much the same way as fluorescent lamps. The UV radiation is generated by passing a current through mercury vapor. The mercury lamps may be low-pressure or medium-pressure lamps. Low-pressure lamps emit most of their energy at a wavelength of 253.7 nm, which is in the optimal range. Medium-pressure lamps generate a lesser portion of their energy in the optimal range, but the intensity of the radiation is much greater than that of the low-pressure lamps, and fewer lamps are required (6).

REUSE

Types of Reuse Applications

Urban Reuse. Reclaimed wastewater may be used in an urban setting to irrigate public parks, recreation areas, and residential landscaping (7). Some water codes even consider the use of potable water for landscape irrigation as “a waste or an unreasonable use of such water” when reclaimed water is available (2). Other urban uses include fire protection, dust control for construction activities, and concrete production. The water for urban reuse activities is obtained from a dual distribution system (one for potable water and one for reclaimed water) (7). Reclaimed wastewater may also be used inside buildings for toilet flushing (2).

Industrial Reuse. Reclaimed water can be used in industrial activities, for cooling water (once-through or recycled), industrial process water (tanning, textiles, pulp and paper manufacturing), and boiler feed water. Recycled cooling water must be of higher quality than once-through cooling water because evaporation concentrates pollutants. Industrial process water quality depends on the quality of the product. Higher quality products require higher quality process water. High-pressure boilers require nearly pure water, whereas lower pressure boilers may be able to operate with less pure water (7). Potential problems in the industrial reuse of wastewater include mineral scaling and biological growth (4).

Agricultural Irrigation. Reclaimed water includes nutrients, such as nitrogen and phosphorus, which are used by plants. Reclaimed water also includes valuable trace elements that are vital to plant growth at low concentrations. Salinity is the most important factor in agricultural irrigation (7). As soil salinity increases, plants expend more energy to adjust the salt concentration within their cells, and less energy is available for plant growth. Soil salinity increases as a function of evapotranspiration (4). The ability of plants to tolerate salinity varies widely, from sensitive plants such as citrus fruits and berries to tolerant crops, such as barley and cotton. Salt is especially detrimental to plants at the germinating and seedling stages. Salinity may be decreased by leaching or the overapplication of wastewater to carry away excess accumulated salt (7).

Habitat Restoration/Enhancement and Recreational Reuse. These uses typically include wetlands, recreational impoundments, stream augmentation, and snowmaking. Wetlands serve valuable functions, such as flood attenuation, wildlife and waterfowl habitat, aquifer recharge, and water quality enhancement. Recreational impoundments can serve noncontact uses, such as water hazards on golf courses; human contact activities, such as fishing, boating, and swimming; and the manufacture of snow for skiing. The quality of reclaimed water for contact activities must be higher than that for noncontact uses (7).

Groundwater Recharge. Groundwater can be recharged by surface irrigation or subsurface injection. Subsurface injection may require a higher degree of treatment because water does not receive the benefit of additional treatment by surface soils. Groundwater recharge applications are often used to establish barriers to saltwater intrusion in coastal areas, to provide additional treatment for later reuse, to augment aquifer levels, to provide water storage, and to prevent or control the subsidence of soils (7). Other types of reuse, such as agricultural or landscape irrigation may also provide additional benefits by recharging groundwater (4).

Table 1. Suggested Treatment

Type of Use	Recommended Degree of Treatment
Urban	
Landscape irrigation, fire protection	Secondary, filtration, disinfection
Restricted access irrigation	Secondary, disinfection
Construction	Secondary, disinfection
Industrial Reuse	
Industrial cooling, once-through	Secondary
Industrial cooling, recirculated	Secondary, disinfection
Agricultural Irrigation	
Food products, not commercially processed	Secondary, filtration, disinfection
Food products, commercially processed	Secondary, disinfection
Nonfood products	Secondary, disinfection
Habitat Restoration/Recreational	
Recreational impoundments	Secondary, filtration, disinfection
Landscape impoundments	Secondary, disinfection
Environmental (wetlands, stream augmentation)	Secondary, disinfection
Groundwater Recharge	
Surface irrigation	Primary
Subsurface injection	Secondary
Augmentation of Potable Supplies	
Indirect reuse, aquifer spreading	Secondary, disinfection
Indirect reuse, aquifer injection	Secondary, filtration, disinfection, advanced
Indirect reuse, surface augmentation	Secondary, filtration, disinfection, advanced

Augmentation of Potable Supplies. Potable supplies may be augmented by either direct or indirect methods. Direct potable reuse is objectionable and is used only in one installation in the world, in Windhoek, Namibia, and there it is used only intermittently. Indirect reuse may involve the discharge of treated effluent into a body of water upstream of a water intake. The effluent may then be further treated by natural processes and by dilution. Indirect use may also involve applying effluent to groundwater by surface irrigation or subsurface injection, where the wastewater is further treated by the soil and aquifer before being withdrawn for potable uses (7).

Treated Effluent Characteristics. The quality of the effluent required depends on the use of the wastewater. For stream discharges or applications that are not being used for drinking water or in public contact areas, secondary treatment may be all that is required. However, for more sensitive uses, such as water that will eventually be used for potable water supplies, for high-quality industrial applications, or for uses where there will be significant human contact, advanced treatment may be required.

Note that there are no national treatment standards for reuse applications. Different jurisdictions may have different treatment requirements, depending on use. EPA has recommended degrees of treatment for various applications, as shown in Table 1 (7).

BIBLIOGRAPHY

1. Water Environment Federation and American Society of Civil Engineers. (1992). *Design of Municipal Wastewater Treatment Plants*. WEF Manual of Practice No. 8/ASCE Manual and Report on Engineering Practice No. 76, 3rd Edn.
2. Water Environment Federation. (1989). *Water Reuse*. Manual of Practice SM-3, 2nd Edn. Alexandria, VA.
3. Great Lakes-Upper Mississippi River Board of State and Provincial Public Health and Environmental Managers. (1997). *Recommended Standards for Wastewater Facilities*. Health Education Service, Inc., Albany, NY.
4. Metcalf & Eddy, Inc. (1991). *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd Edn. McGraw-Hill, Inc., New York.
5. Weber, W. J. (1971). *Physicochemical Processes for Water Quality Control*. John Wiley & Sons, New York.
6. US EPA. (1999). *Alternative Disinfectants and Oxidants Guidance Manual*. EPA 815-R-99-014.
7. US EPA. (1992). *Guidelines for Water Reuse*. EPA/625/R-92/004.

WASTEWATER RECLAMATION AND REUSE RESEARCH

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Water reclamation is the treatment of wastewater to make it reusable. Water reuse is the beneficial use of the treated water and can serve either nonpotable or potable applications (1). Nonpotable water reuse includes all water applications other than augmenting drinking water supplies. Nonpotable reuse is occurring as agricultural and landscape irrigation, recreation, wildlife habitat maintenance (stream-flow augmentation), in-building applications (such as toilet flushing), industrial cooling, and groundwater recharge. Potable water reuse refers to the use of highly treated reclaimed water to augment drinking water sources. Direct potable reuse, where reclaimed water after advanced treatment is piped directly into the potable water system, is limited to rare cases. For indirect potable reuse, reclaimed water can either be discharged into a surface water or infiltrated into the subsurface to augment, in part, a drinking water supply source. Infiltration into the subsurface can be accomplished by either direct injection into the aquifer or by surface spreading which provides additional soil–aquifer treatment (SAT) when water percolates through the subsurface. The majority of research activities in wastewater reclamation and reuse reflects the main concerns about potable and nonpotable water reuse, such as (1) protection of public health, (2) reliable treatment of wastewater to meet strict water quality requirements for the intended reuse, and (3) gaining public acceptance (1,2).

WATER REUSE RESEARCH TO PROTECT PUBLIC HEALTH

The majority of research activities in water reuse has been conducted on health effects which can be classified as direct effects, indirect effects, and issues related to the aesthetic quality of reclaimed water (3,4). Figure 1 illustrates health effects related to water reuse.

Direct and indirect health effects that might occur from consumption of pathogens (including enteric viruses, parasites, and enteric bacteria) and organic and inorganic chemicals in reclaimed water could be manifested via short-term exposure and acute effects or through chronic exposure and latent effects. These chronic effects of organic and inorganic constituents or their metabolites are of particular concern to the extent that they relate to incidences of cancer. There is also increasing concern about endocrine-disrupting compounds (EDC) and pollutants originating from pharmaceuticals and active ingredients in personal care products (PPCPs), which are present in municipal wastewater and continually introduced as complex mixtures to the aquatic environment (5,6). EDCs are exogenous agents that interfere with the production, release, transport, metabolism, binding, action, or elimination of the natural hormones in the body responsible for maintaining homeostasis and regulating developmental processes. Among compounds that have endocrine activity are both synthetic chemicals produced industrially (such as surface active agents, pesticides, plasticizers, food additives, birth control pills, herbal supplements, and cosmetics) and naturally occurring compounds (such as sex steroids, plant-produced estrogens, and heavy metals) (7). The occurrence of PPCPs in domestic effluents is reported in studies since the late 1980s (8,9). The major concern for the presence of pharmaceuticals in

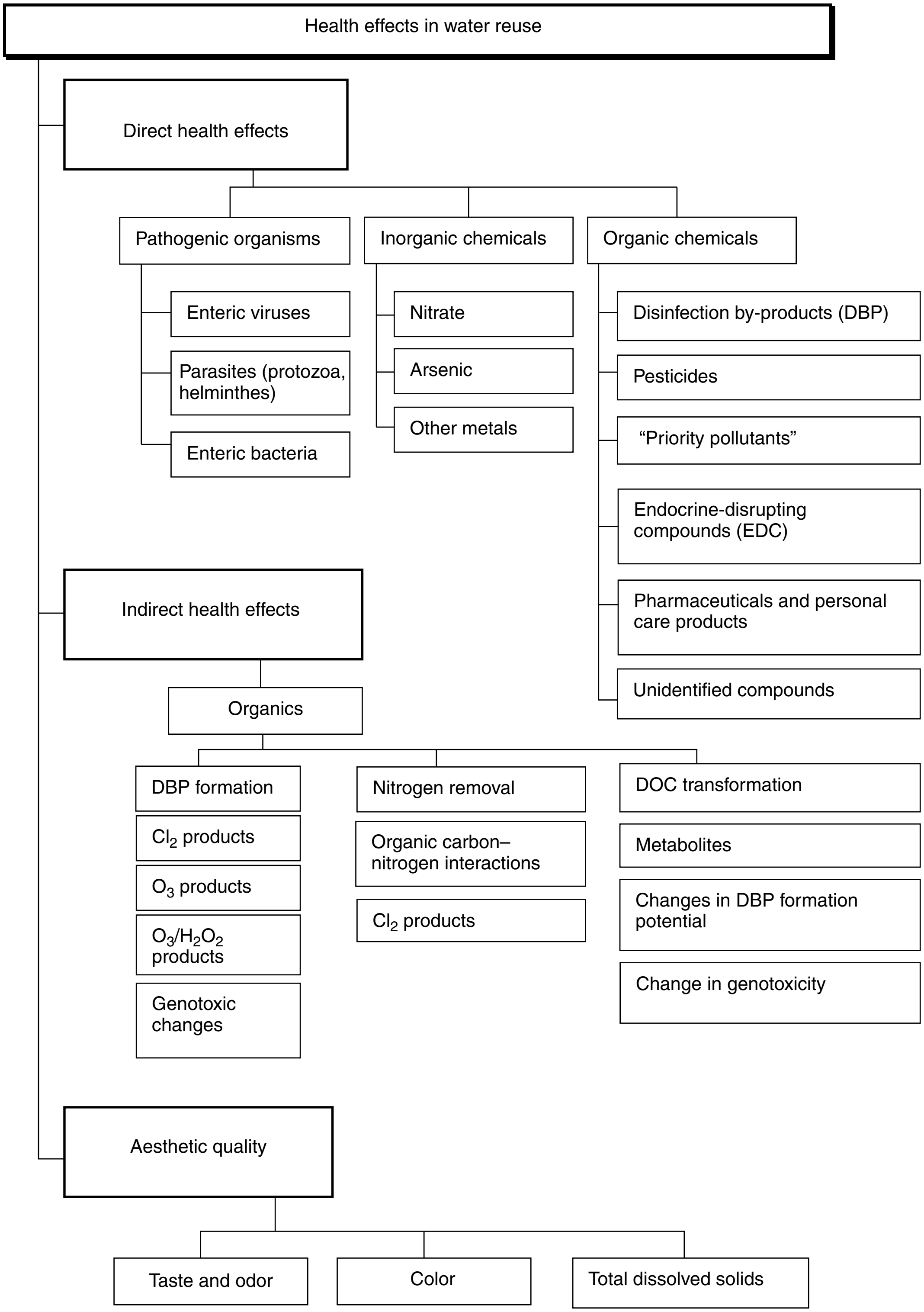


Figure 1. Research activities related to health effects in water reuse.

reclaimed water ultimately used for human consumption is not necessarily acute effects on human health, but rather the manifestation of imperceptible effects that can accumulate over time ultimately to cause truly profound changes (5). Effects might occur over long periods of time in certain populations, so changes would not be distinguishable from natural events or ecological succession. A continuous research effort is directed to unknown and unidentified organic contaminants. The toxicological risk, or safety, of these mixtures may never be known precisely. This presents an ever-present element of uncertainty for all reclaimed water projects involving potable reuse and justifies continuous monitoring and research. The aesthetic quality of reclaimed water is determined by taste and odor, color, and total dissolved solid (TDS) concentration.

Nonpotable Reuse

The main research issues in nonpotable reuse are the fate and transport of pathogens, nitrogen, and TDS during water reclamation and reuse. Today, these issues do not present a significant barrier to implementing nonpotable reuse projects, and direct nonpotable reuse today is the dominant planned reuse venue for supplementing public water supplies worldwide. Table 1 summarizes key research studies on pilot and full scale in nonpotable reuse and lists their main research objectives, locations, and references. This selection of important research studies is not complete nor does it indicate any type of ranking regarding their scientific and technical merits, but it directs the reader to important research in the field.

Enteric microorganisms are the contaminants of greatest concern in reusing reclaimed wastewater. Pathogen removal has been addressed in several research studies that focus on the efficiency of different pretreatment technologies for virus inactivation during subsequent disinfection, the survival of enteric microorganisms on food crops that have been irrigated with reclaimed water, as well as disease outbreaks from consuming contaminated foods, and the fate and transport of microorganisms in reclaimed water during artificial groundwater recharge. Recent research advances also resulted in better methods of detecting pathogens. Findings of these research studies suggest that tertiary treatment (such as coagulation/flocculation, lime clarification, dual-media filtration) and disinfection are necessary for many reuse applications to ensure pathogen reduction. Current research activities on pathogen removal address treatment plant reliability, removal of new and emerging enteric pathogens of concern, and the ability of new technologies to effect pathogen reduction (20).

For water reuse, the nonmetals ammonia, nitrite, and nitrate are of particular health significance because nitrate concentrations significantly higher than 10 mg N/L can cause methemoglobinemia in infants. Research is directed to aboveground treatment technologies and the efficiency of soil–aquifer treatment systems in removing nitrogen from reclaimed water. In the sustainable operation of local water reuse systems, the total solids concentration represents a significant challenge to the water reuse research community to develop strategies for minimizing salt buildup in local water cycles and cost-efficient treatment and disposal techniques.

Potable Reuse

Potable reuse involves a broad spectrum of potential health concerns. The major concerns are that adverse health effects could result from introducing pathogens, toxic organic chemicals, or inorganic constituents into groundwater that is consumed by the public (21). Treatment efficiency and reliability in removing pathogens are very important in potable reuse where even short-term exposure to pathogens could result in significant risk to the exposed population (22). Enteric viruses were not found in reclaimed water at field sites employing tertiary treatment but were observed in reclaimed water that had secondary treatment followed by chlorination (16). Table 2 summarizes key research studies at pilot- and full-scale potable water reuse facilities.

An assessment of health risks from potable reuse cannot be considered definitive because of limited chemical and toxicological data and inherent limitations in available toxicological and epidemiological methods. The mix of contaminants in the watershed of a reclamation facility might vary from site to site, so health effects studies

Table 1. Key Research Studies on Pilot and Full Scale in Nonpotable Water Reuse

Research Objective	Type of Water Reuse	Location	Research Study	Reference
Behavior of nitrogen and organic contaminants	Groundwater recharge	Phoenix, Arizona	Flushing Meadows project	10, 11
Virus inactivation	Irrigation Groundwater recharge Stream-flow augmentation	County Sanitation Districts of Los Angeles County, California	Pomona Virus Study evaluated different pretreatment processes for subsequent inactivation of viruses	12, 13
Virus inactivation	Storage and recovery—irrigation	Tucson, Arizona	Virus inactivation study during SAT	14–16
Efficiency of soil–aquifer treatment (SAT) in removing of pathogens and nutrients	Irrigation	Dan Region, Israel	Efficiency of SAT	17
Irrigation with reclaimed water	Irrigation	St. Petersburg, Florida	Treatment, storage, and distribution of reclaimed water for irrigation	18
Implementing nonpotable reuse	Urban and agricultural irrigation Industrial reuse Toilet flushing	Irvine Ranch Water District, California	Water quality and water distribution studies	19

Table 2. Key Research Studies on Pilot and Full Scale in Potable Water Reuse

Research Objective	Type of Water Reuse	Location	Research Study	Reference
Health effects of direct reuse	Direct potable reuse	Denver, Colorado	Direct potable reuse demonstration project	23
Health effects of chemicals and microorganisms	Groundwater recharge by direct injection into a potable aquifer	Palo Alto, California	Mutagenic activity and chemical characterization during groundwater injection	24
		Orange County, California	Water Factory 21	25, 26
Health effects of chemicals and microorganisms	Groundwater recharge by surface spreading into a potable aquifer	Montebello Forebay County Sanitation Districts of Los Angeles County, California	Health effects study Epidemiological assessment Birth outcomes study	27–29
Sustainability of soil–aquifer treatment (SAT)			Sustainability of organic carbon, nitrogen, and virus removal during SAT	16
Health effects of chemicals and microorganisms	Augmentation of surface water supplies	San Diego, California	Aqua III demonstration project	30
		Tampa, Florida	Tampa recovery project	31
Fate of trace organic compounds during advanced water treatment	Groundwater recharge by direct injection into a potable aquifer	West and Central Basin Municipal Water District, California	Removal of unidentified trace organics	32

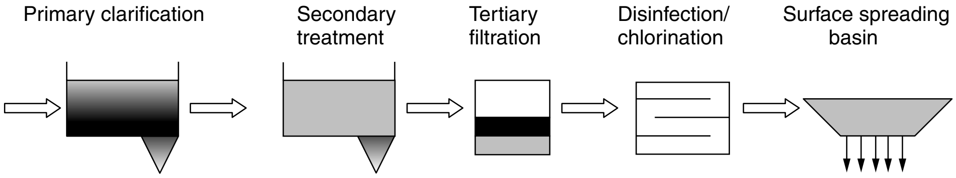
are applicable only to a specific location (4). In findings from research studies conducted at full-scale indirect potable reuse facilities, there is no indication that health risks from using reclaimed water are greater than those from using existing water supplies or that concentrations of regulated chemicals and microorganisms in product water exceeded established drinking water standards set by the U.S. EPA (23,27–29,31). The limited data and extrapolation methodologies used in toxicological assessment may present limitations and uncertainties in overall risk characterization. Similarly, epidemiological studies may suffer from the fact that many cancers have latency periods of 15 years or more. In addition, these types of studies require large populations to uncover the generally low risks from low concentrations of potential carcinogens.

The scope of inorganic chemical health issues in potable water has not changed significantly in several decades. In general, the health hazards from inorganics are well established. However, the threshold for risk protection has changed because of new information for some inorganics such as lead and arsenic. The fact that most forms of nitrogen can be readily converted to nitrate ions either in the treatment process or in soils makes managing nitrogen a significant issue in potable reuse projects.

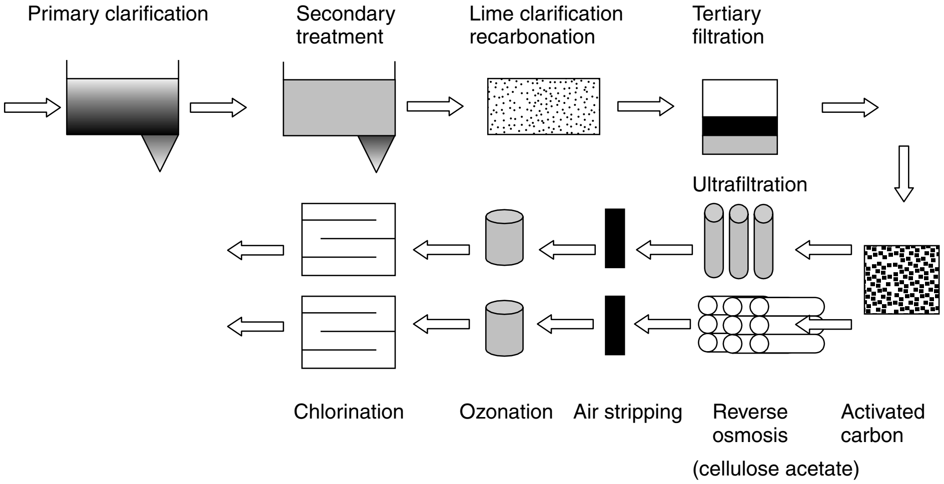
WATER REUSE RESEARCH IN WASTEWATER TREATMENT TECHNOLOGIES

Research in water reuse has contributed to significant progress in developing sound technical approaches to produce a high quality and reliable water source from reclaimed wastewater (2,33). The evolution of water reclamation technology is illustrated in Fig. 2 for water treatment processes that lead to indirect potable reuse.

Findings of research studies and the advent of new water treatment technologies have resulted in an evolution of water reclamation technologies since the first water reclamation facilities for indirect potable reuse were established in the early 1960s (Fig. 2a). Primary treatment and secondary treatment are still the basic treatment in current water reclamation facilities for removing particulate matter and degradable organic material, respectively. In the early 1970s, treatment trains were developed to improve the removal of pathogens and trace organics by adding lime clarification, granular activated carbon, and reverse osmosis (Fig. 2b,d). Since the late 1990s, the use of microporous membranes in ultrafiltration (UF) and microfiltration (MF) as a pretreatment in reverse osmosis has become the industry standard for indirect potable reuse applications (Fig. 2c,e). Disinfection, conducted over decades using chlorine, is critically reviewed by many utilities and more and more substituted by disinfection using ultraviolet light. With the proper dosage and installation, UV radiation is a proven and effective bactericide and viricide for wastewater and does not contribute to the formation of known toxic by-products (Fig. 2e). This dynamic in incorporating new unit operations in water reclamation is proceeding with the advent of membrane-coupled bioreactors that can substitute for conventional primary and secondary treatment, including tertiary filtration. Membrane bioreactors (MBR) consist of a biological reactor where suspended biomass and solids are separated by microfiltration membranes whose nominal pore sizes range from 0.1 to 0.4 μm. MBRs can operate at much higher mixed liquor suspended solids (MLSS) concentrations (15,000 to 25,000 mg/L) than conventional activated sludge processes. These (**a**) Montebello Forebay surface spreading grounds, County Sanitation Districts of Los Angeles County, California; continuous, started in 1962



(**b**) Denver potable water demonstration project, City of Denver, Colorado; initiated in 1974, completed in 1990



(**c**) Scottsdale Water Campus, City of Scottsdale, Arizona; continuous, started in 1999

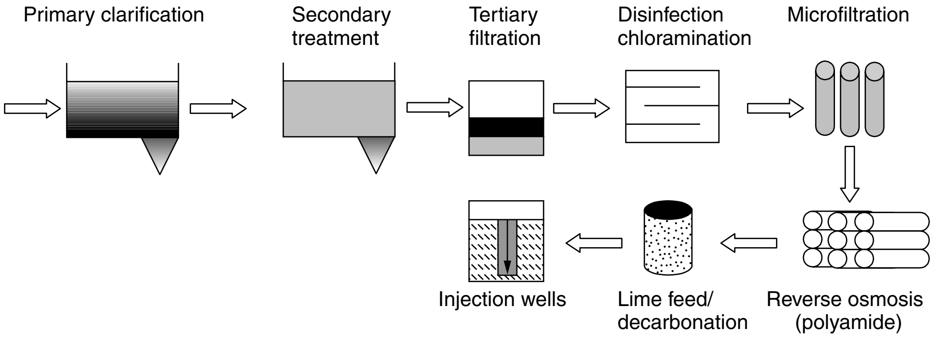


Figure 2. Evolution of water reclamation process trains leading to indirect potable reuse.

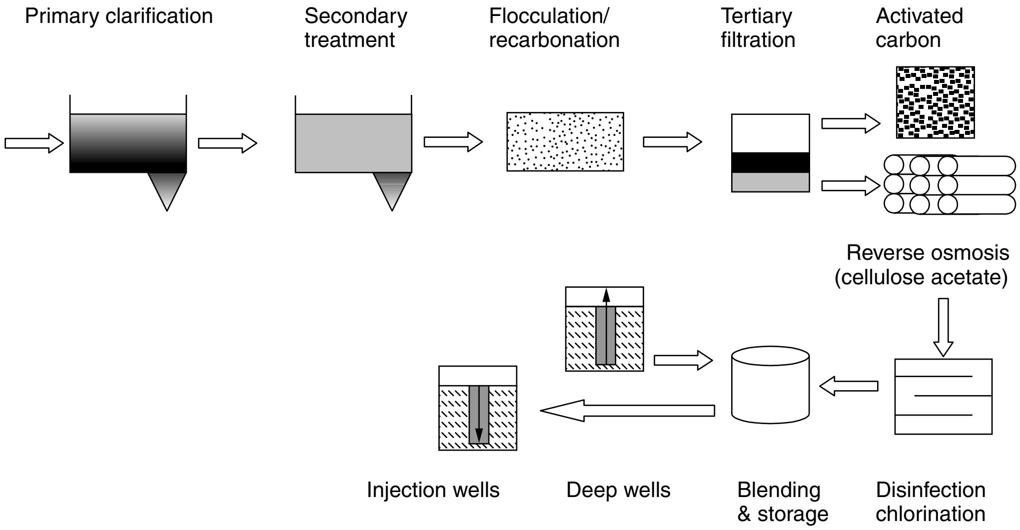
advantages are enhanced by a small footprint and high effluent quality with respect to turbidity, total suspended solids (TSS), biochemical oxygen demand (BOD), and pathogens (2).

WATER REUSE RESEARCH RELATED TO PUBLIC PERCEPTION

The ultimate success of any water reuse program is determined by its level of public acceptance. Several indirect potable reuse projects have failed to emphasize public support and resulted in project termination, although the technical and scientific evaluation was well done. Gaining public acceptance has and will initiate research programs related to human health and public involvement and education (34).

RESEARCH NEEDS IN THE FUTURE

Water quality requirements for nonpotable reuse are quite tractable, and treatment requirements are not likely to change significantly in the future, but drinking water quality standards are likely to become more rigorous. The number of contaminants to be monitored is increasing, and, for many contaminants, the maximum contaminant levels and action levels are decreasing. Thus, it is appropriate to anticipate more restrictive treatment requirements and water quality limits and (**d**) Water Factory 21, Orange County Water District; 1977



(**e**) Water Factory 21, Orange County Water District; 2002

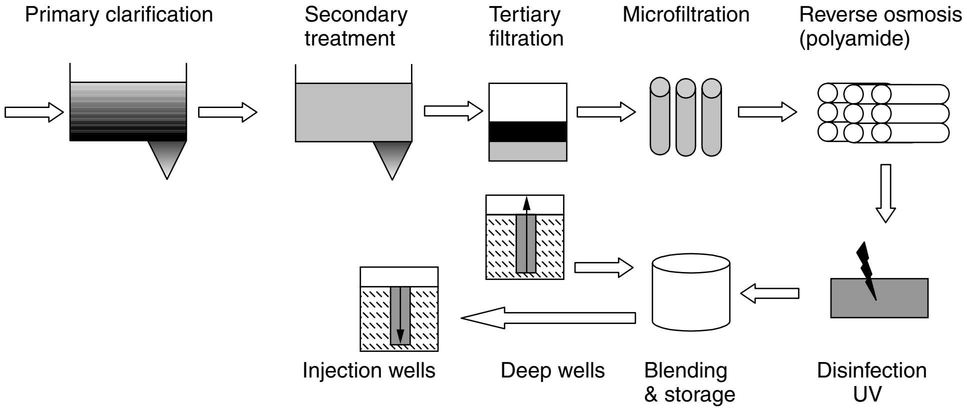


Figure 2. (*continued*).

to design facilities accordingly. Continued and future research will contribute to further progress in designing and operating water reclamation and reuse facilities. Some key topics will include assessment of health risks from trace pollutants in reclaimed water; improvement of monitoring techniques to evaluate microbiological quality; optimization of treatment trains and integration of membrane processes in producing reclaimed water; brine disposal strategies for membrane treatment processes; evaluation of the fate of microbiological, chemical, and organic contaminants; and development of surrogate parameters in combination with *in vitro* and *in vivo* assays to detect unidentified organic compounds in reclaimed water (1,4).

BIBLIOGRAPHY

1. Asano, T. (Ed.). (1998). *Wastewater Reclamation and Reuse*. Water Quality Management Library. Vol. 10. Technomic, Lancaster, PA, p. 1528.
2. Metcalf & Eddy, Inc. (2003). *Wastewater Engineering: Treatment and Reuse*, 4th Edn. Revised by G. Tchobanoglous, F.L. Burton, and H.D. Stensel, McGraw-Hill, New York.
3. Drewes, J.E., Fox, P., and Nellor, M.H. (2000). In: *Efficiency and Sustainability of Soil-Aquifer Treatment for Indirect Potable Reuse of Reclaimed Water*. I. Chorus, U. Ringelband, G. Schlag, and O. Schmoll (Eds.). Water Sanitation & Health, IWA, London, pp. 227–232.
4. National Research Council. (1998). *Issues in Potable Reuse—The Viability of Augmenting Drinking Water Supplies with Reclaimed Water*. National Academy Press, Washington, DC, p. 263.
5. Daughton, C. and Ternes, T. (1999). Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health Perspect* **107**(suppl. 6): 907–938.
6. Drewes, J.E. and Shore, L. (2001). Concerns about pharmaceuticals in water reuse, groundwater recharge, and animal waste. In: *Pharmaceuticals and Personal Care Products in the Environment: Scientific and Regulatory Issues. Symposium Series 791*. C. Daughton and T. Jones-Lepp (Eds.). American Chemical Society, Washington, DC, pp. 206–228.

7. National Research Council. (1999). *Hormonally Active Agents in the Environment*. National Academy Press, Washington, DC.
8. Richardson, M.L. and Bowron, J.M. (1985). The fate of pharmaceutical chemicals in the aquatic environment. *J. Pharm. Pharmacol.* **37**: 1–12.
9. Halling-Sørensen, B. et al. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment—a review. *Chemosphere* **36**: 357–394.
10. Bouwer, H. et al. (1980). Rapid-infiltration research—the flushing meadows project, arizona. *J. Water Pollut. Control Fed 52* **2**: 457.
11. Bouwer, E.J. et al. (1984). Organic contaminant behavior during rapid infiltration of secondary wastewater at the Phoenix 23rd Avenue Project. *Water Res.* **18**: 463.
12. County Sanitation Districts of Los Angeles County. (1977). *Pomona Virus Study—Final Report*. Whittier, CA.
13. Chen, C., Kuo, J., and Stahl, J.F. (1998). The role of filtration for wastewater reuse. In: *Wastewater Reclamation and Reuse, Water Quality Management Library*. Vol. 10. T. Asano (Ed.). Technomic, Lancaster, PA, pp. 219–262.
14. Gerba, C.P. et al. (1991). Fate of viruses in treated sewage effluent during soil aquifer treatment designed for wastewater reclamation and reuse. *Water Sci. Technol.* **24**: 95–102.
15. Powelson, D.K., Gerba, C.P., and Yahya, M.T. (1993). Virus transport and removal in wastewater during aquifer recharge. *Water Res.* **27**: 583–590.
16. Fox, P., Houston, S., Westerhoff, P., Drewes, J.E., Nellor, M., Yanko, W., Baird, R., Rincon, M., Arnold, R., Lansey, K., Bassett, R., Gerba, C., Kapiscak, M., Amy, G., and Reinhard, M. (2001). *Soil-Aquifer Treatment for Sustainable Water Reuse*. Final report. American Water Works Association Research Foundation (AWWARF), Denver, CO.
17. Kanarek, A. and Michail, M. (1996). Groundwater Recharge with Municipal Effluents, Dan Region Reclamation Project, Israel, *Proc. 18th Bienn. IAWQ Int. Conf. Water Qual.* June 23–26, Singapore, pp. 228–234.
18. Johnson, W.D. and Parnell, J.R. (1998). Wastewater reclamation and reuse in the City of St. Petersburg, Florida. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 1037–1104.
19. Young, R.E., Thompson, K.A., McVicker, R.R., Diamond, R.A., Gingras, M.B., Ferguson, D., Johannessen, J., Herr, G.K., Parsons, J.J., Seyde, V., Akiyoshi, E., Hyde, J., Kinner, C., and Oldewage, L. (1998). Irvine Ranch Water District's reuse today meets tomorrow's conservation needs. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 941–1036.
20. Yates, M. and Gerba, C. (1998). Microbial Considerations in Wastewater Reclamation and Reuse. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 627–704.
21. Crook, J. (1998). Water Reclamation and Reuse Criteria. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 627–704.
22. Tanaka, H., Asano, T., Schroeder, E.D., and Tchobanoglous, G. (1998). Estimating the safety of wastewater reclamation and reuse using enteric virus monitoring data. *Water Environ. Res.* **70**(1): 39–51.
23. Lauer, W.C. and Rogers, S.E. (1998). The demonstration of direct potable water reuse: Denver's landmark project. In: *Wastewater Reclamation and Reuse*. Vol. 10, T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 1269–1334.
24. McCarty, P.L. et al. (1980). *Mutagenic Activity and Chemical Characterization for the Palo Alto Wastewater Reclamation and Groundwater Injection Facility*. EPA-6001-81-029. U.S. Environmental Protection Agency, Washington, DC.
25. Fujita, Y., Ding, W., and Reinhard, M. (1996). Identification of wastewater dissolved organic carbon characteristics in reclaimed wastewater and recharged groundwater. *Water Environ Res* **68**(5): 867–876.
26. Mills, W.R., Bradford, S.M., Rigby, M., and Wehner, M.P. (1998). Groundwater recharge at the Orange County Water District. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 1105–1142.
27. Nellor, M.H. et al. (1984). *Health Effects Study*. Final Report, County Sanitation Districts of Los Angeles County, Whitter, CA.
28. Sloss, E.M., Geschwind, S.A., McCaffrey, D.F., and Ritz, B.R. (1996). Groundwater recharge with reclaimed water. *An Epidemiologic Assessment in Los Angeles County*. 1987–1991. Prepared for the Water Replenishment District of Southern California, Rand, Santa Monica, CA, p. 124.
29. Sloss, E.M., McCaffrey, D.F., Fricker, R.D., Geschwind, S.A., and Ritz, B.R. (1999). *Groundwater Recharge with Reclaimed Water. Birth Outcomes in Los Angeles County, 1982–1993*. Prepared for the Water Replenishment District of Southern California, Rand, Santa Monica, CA, p. 148.
30. Western Consortium for Public Health. (1997). *Total Resource Recovery Project Aqua III San Pasqual Health Effects Study Final Summary Report*. Berkeley, CA.
31. Hemmer, J. et al. (1994). Tampa Water Resource Recovery Project. *Proc. Am. Water Works Assoc/Water Environ. Fed. Water Reuse Symp*. Dallas, TX. American Water Works Association, Denver, CO, p. 557.
32. Levine, B. et al. (2000). Water quality assessment for indirect potable reuse: a new methodology for controlling trace organic compounds at the West Basin water recycling plant (California, USA). *Water Sci. Technol.* **43**(10): 249–527.
33. Joint Task Force of the Water Environment Federation and the American Water Works Association. (1998). *Using Reclaimed Water to Augment Potable Water Resources, Water Environment Federation/American Water Works Association*. Alexandria, VA/Denver, CO, p. 357.
34. Wegner-Gwidt, J. (1998). Public support and education for water reuse. In: *Wastewater Reclamation and Reuse*. Vol. 10. T. Asano (Ed.). Water Quality Management Library, Technomic, Lancaster, PA, pp. 1417–1462.

WASTEWATER RECLAMATION AND REUSE

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Because of growing population and increasing urbanization, many communities throughout the world are approaching or reaching the limits of their available water supplies. Wastewater reclamation and reuse has become an attractive option for conserving and extending available water supplies. Wastewater reclamation and reuse may also present communities an opportunity for pollution abatement when it replaces effluent discharge to sensitive surface waters.

The terminology currently used in wastewater reuse engineering is derived from sanitary and environmental engineering practice. The water potentially available for reuse includes municipal and industrial wastewater, agricultural return flows, and storm water. Of these, return flows from agriculture irrigation and storm water are usually collected and reused without further treatment. *Wastewater reclamation* involves treating or processing wastewater to make it reusable, and *wastewater reuse* or *water reuse* is the beneficial use of the treated water. Reclamation and reuse of water frequently require water conveyance facilities for delivering the reclaimed water and may require intermittent storage of the reclaimed water prior to reuse. In contrast to reuse, *wastewater recycling* or *water recycling* normally involves only one use or user, and the effluent from the user is captured and redirected back into that use scheme. In this context, the term *wastewater recycling* is applied predominantly to industrial applications such as in the steam—electric, manufacturing, and mineral industries.

The use of reclaimed wastewater where there is a direct link from the treatment system to the reuse application is termed *direct reuse*. Direct reuse provides water for agricultural and landscape irrigation, industrial applications, urban applications, and dual water systems. *Indirect reuse* includes mixing, dilution, and dispersion of reclaimed wastewater by discharge into an impoundment, receiving water, or groundwater aquifer prior to reuse, such as in groundwater recharge.

Indirect wastewater reuse, through effluent disposal to streams and groundwater basins, has been an accepted practice throughout the world for centuries. Communities that are situated at the end of major waterways have a long history of producing potable water from river water sources that have circulated through multiple cycles of withdrawal, treatment, and discharge. Similarly, riverbeds or percolation ponds may recharge underlying groundwater aquifers with treated wastewater, which in turn, is withdrawn by downgradient communities for domestic water supplies. These kinds of uses are considered unplanned indirect reuse. However, indirect reuse can also be planned, for example, the artificial groundwater recharge program in Los Angeles County, California, where reclaimed water has provided a source of water since the 1960s.

It is also important to differentiate between *potable* and *nonpotable* reuse applications. *Potable water reuse* refers to the use of highly treated reclaimed water to augment drinking water supplies. Although direct potable reuse is limited to extreme cases, it consists of incorporating reclaimed water into a potable water supply system without relinquishing control over the resource. *Nonpotable water reuse* includes all water applications other than drinking water supplies. Currently, on an international scale, direct nonpotable water reuse comprises the dominant mode of wastewater reuse for supplementing public water supplies for uses such as landscape and agricultural irrigation.

The potential health risks of wastewater reclamation and reuse are related to the extent of direct exposure to the reclaimed water and the adequacy, effectiveness, and reliability of the treatment system. The goal of each water reuse project is to protect public health without unnecessarily discouraging wastewater reclamation and reuse. Regulatory approaches stipulate water quality standards in conjunction with requirements for treatment, sampling, and monitoring. In 1992, the U.S. Environmental Protection Agency (USEPA) issued "Guidelines for Water Reuse" (1); however, specific criteria for wastewater reclamation in the United States are developed by individual states, often in conjunction with regulations on land treatment and disposal of wastewater. The World Health Organization (2) has published guidelines for reuse in agricultural irrigation. These guidelines stipulate stringent microbial water quality requirements. In recent years, many state agencies in the United States have developed their own reclamation and reuse standards. Besides microbial water quality criteria, these standards include standards for total suspended solids (TSS), biochemical oxygen demand (BOD), pH, and, in some cases, residual chlorine.

Wastewater reclamation and reuse are becoming more common and are gaining acceptance among communities and regulatory agencies. They have proven effective and successful in creating a new and reliable water supply, while not compromising public health. Nonpotable reuse is a widely accepted practice that will continue to grow. The primary drawback is cost, as these systems often require traditional water treatment facilities and a separate distribution system. The current advances in wastewater technology, especially in membrane processes, are expected to reduce the cost of wastewater reclamation and reuse in the future.

BIBLIOGRAPHY

1. USEPA. (1992). *Guidelines for Reuse Manual*. USEPA, Washington, DC.
2. WHO. (1989). *Health Guidelines for the Use of Wastewater in Agriculture and Aquaculture*. World Health Organization Scientific Group, Geneva, Switzerland.

READING LIST

Asano, T. (Ed.). (1998). *Wastewater Reclamation and Reuse*. Technomic, Lancaster, PA.

Rowe, D.R. and Abdel-Magid, I.M. (1995). *Handbook of Wastewater Reclamation and Reuse*. Lewis, Boca Raton, FL.

USEPA. (1991). *Municipal Wastewater Reuse: Selected Readings on Water Reuse*. USEPA, Washington, DC.

WASTEWATER RECLAMATION AND REUSE TREATMENT TECHNOLOGY

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The effective treatment of wastewater to meet water quality objectives for water reuse applications and to protect public health is a critical element of water reuse systems. Municipal wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter, pathogens, metals, and sometimes nutrients from wastewater. General terms used to describe different degrees of treatment, in order of increasing treatment level, are preliminary, primary, secondary, tertiary, and advanced treatment. A disinfection step for control of pathogenic organisms is often the final treatment step prior to distribution or storage of reclaimed wastewater. Wastewater reclamation, recycling, and reuse treatment systems are derived from applying technologies used for conventional wastewater treatment and drinking water treatment. The goal in designing a wastewater reclamation and reuse system is to develop an integrated cost-effective treatment scheme that can reliably meet water quality objectives.

The degree of treatment required in individual water treatment and wastewater reclamation facilities varies according to the specific reuse application and water quality requirements. The simplest treatment systems involve solid/liquid separation processes and disinfection, whereas more complex systems involve combinations of physical, chemical, and biological processes employing multiple-barrier treatment approaches for contaminant removal.

Primary treatment is the removal of particulate matter, typically by settling, with or without coagulants. In conventional wastewater treatment facilities, primary treatment includes screening and comminution for removal of large solids, grit, and sedimentation. Conventional primary treatment is effective in removing particulate matter 50 microns or larger. This process, in general, removes nearly 50% of the suspended solids and 25–50% of the biochemical oxygen demand (BOD_5) from the untreated wastewater. The removal efficiency of primary treatment processes can be increased by adding coagulants before gravity sedimentation. For most wastewater reuse applications, primary treatment alone is not adequate to meet water quality objectives.

Secondary treatment systems consist of biological treatment processes coupled with solid/liquid separation. They are intended to remove the soluble and colloidal organic matter that remains after primary treatment. Biological treatment consists of applying a controlled natural process, in which microorganisms remove soluble and colloidal organic material from the waste and are, in turn, removed themselves. To carry out this natural process in a reasonable time, the biological treatment systems are designed to maintain a large active mass of bacteria within the system. The basic principles remain the same in all biological processes, but the techniques used in their application vary widely. A useful classification divides these systems into *attached (film) growth or suspended growth processes*. Attached growth processes use a solid medium on which bacterial solids are accumulated to maintain a high population. Attached growth processes include trickling filters, rotating biological filters, fluidized beds, intermittent sand filters, and a variety of similar systems.

Suspended growth processes maintain an adequate biological mass in suspension within the reactor by employing either natural or mechanical mixing. In most processes, the required volume is reduced by returning bacteria from a secondary clarifier to maintain a high solids concentration.

Suspended growth processes include activated sludge and its various modifications, oxidation ponds, and sludge digestion systems. The effluent from conventional secondary treatment processes contains levels of suspended solids and BOD_5 ranging from about 10 to 30 mg/L. Depending on process operation, from 10% to 50% of the organic nitrogen is removed during conventional secondary treatment, and phosphorus is converted to phosphate. The sludge produced during secondary processes is treated by aerobic or anaerobic digestion, composting, or other solids processing technologies. For many wastewater reclamation and reuse systems, secondary treatment can adequately remove organic matter from wastewater. Frequently, secondary treatment is supplemented by filtration for additional removal of particles and by disinfection for microbial inactivation.

Tertiary treatment is the additional removal of colloidal and suspended solids by chemical coagulation and granular medium filtration. The advanced treatment is directed toward reduction in ammonia, organic nitrogen, total nitrogen, phosphorus, refractory organics, and dissolved solids. Tertiary and advanced treatment processes are normally applied downstream of biological treatment. Advanced treatment processes, in addition to chemical coagulation and granular medium filtration, refer to ion exchange, air stripping, chemical oxidation, adsorption, membrane treatment, and disinfection. Coagulation processes involve the addition of chemicals to wastewater to promote aggregation of particles for enhanced solid/liquid separation by sedimentation and filtration. Common coagulants used are alum (aluminum sulfate), ferric sulfate, and ferric chloride. Various types of polyelectrolytes or polymers are used in conjunction with chemical coagulants to improve process effectiveness. Chemical coagulation processes have a role in removing phosphorus, ammonia, and particulate matter.

Granular medium filtration uses a column consisting of a filter medium such as sand or anthracite. Wastewater is passed through the granular medium and particles are removed by impaction, interception, and physical straining. The filter is cleaned (this process is known as backwashing) after it reaches head-loss or turbidity breakthrough. Filters are generally used as a polishing unit and also, in some cases, as a pretreatment step for disinfection, activated carbon adsorption, ion exchange, or reverse osmosis. Filters are very effective in reducing pathogen concentrations.

Ion exchange is a chemical phenomenon in which materials in solution are removed by interchange with other ions immobilized within a solid matrix through which the flow passes. This process is used for removing nitrogen, metals, and dissolved solids.

Membrane processes include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. A membrane is a thin layer of natural or synthetic material capable of separating substances when a driving force is applied across the membrane. Reverse osmosis is used primarily to remove dissolved salts.

Nanofiltration is used to soften waters and remove color. Ultrafiltration and microfiltration are used to remove turbidity, pathogens, and other particulate matter. Membranes are normally classified by solute exclusion size, which is sometimes referred to as *pore size*. Membrane filtration works by passing water at high pressure through a thin membrane in the form of hollow fiber or spirally wound composite sheets. The contaminants are retained on the high-pressure side and frequently must be cleaned by reversing the flow and flushing the waste. Periodic chemical cleaning may be required to remove a persistent contaminant. Membrane assemblies are contained in pressure vessels or cartridges. Low-pressure membranes, in the form of either ultrafiltration (UF) or microfiltration (MF), have become more economical in both capital and operating costs and have received increased application in wastewater reuse and reclamation. Fouling of the membrane is a major problem challenging widespread application of this technology.

In recent years, the use of membrane bioreactors is proving to be an alternative to conventional biological processes. Membrane bioreactor technology combines a biological treatment process with a membrane system to provide organic and suspended solids removal. Installation within a biological reactor system typically replaces sedimentation and filtration as a means of separating mixed liquor suspended solids (MLSS) from treated effluent. Flow passes through the membranes, and solids remain in the biological treatment process. The benefit of immersed membrane technology is the amount of membrane surface area that is in contact with the process fluid. This large surface area allows operating membranes at much lower pressures.

Disinfection is an essential treatment component for almost all wastewater reclamation and reuse applications. The most common type of disinfection system in wastewater reclamation is chlorine disinfection. Ultraviolet (UV) disinfection has earned a reputation as a viable alternative to chemical disinfection processes in wastewater reclamation and reuse applications. The other technologies mentioned such as air stripping, chemical oxidation, and carbon adsorption are used in specific situations.

Water reuse for some applications, such as irrigation, is seasonal. Storage represents an important step between wastewater treatment and water reuse. Storage acts to equalize flow variations and to balance the production of reclaimed water with the use of water. Another benefit of storage is the additional residence time and treatment afforded.

Wastewater reclamation and reuse treatment technologies are drawn from currently practiced water and wastewater treatment technologies. However, some of the technologies such as membrane and ultraviolet disinfection, which are not widely used in conventional wastewater treatment plants, are gaining more viability in wastewater reuse and reclamation applications. This may be attributed to lower cost of operation and better process understanding and control of membrane and ultraviolet technologies. It may also stem from stricter regulatory standards and emphasis on multiple-barrier treatment techniques. The selection of treatment technologies for wastewater reclamation and reuse application depends on the type of reuse. For *urban reuse*, wastewater may require filtration and disinfection in addition to secondary treatment, whereas for *agricultural reuse*, secondary treatment with disinfection can meet reclaimed water quality standards. However, *indirect potable reuse* generally has to meet the strictest water quality standards. Hence, advanced wastewater treatment may be required to meet *indirect potable reuse* standards.

READING LIST

Asano, T. (Ed.). (1998). *Wastewater Reclamation and Reuse*. Technomic, Lancaster, PA.

Rowe, D.R. and Abdel-Magid, I.M. (1995). *Handbook of Wastewater Reclamation and Reuse*. Lewis, Boca Raton, FL.

USEPA. (1991). *Municipal Wastewater Reuse: Selected Readings on Water Reuse*. USEPA, Washington, DC.

USEPA. (1992). *Guidelines for Reuse Manual*. USEPA, Washington, DC.

WHO. (1989). *Health Guidelines for the Use of Wastewater in Agriculture and Aquaculture*. World Health Organization Scientific Group, Geneva, Switzerland.

SEWAGE

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When human feces and urine are diluted with flushing water or other gray water (such as from washing, bathing, and cleansing activities), it becomes sewage, domestic wastewater, or sanitary wastewater. In other words, from the standpoint of sources of generation, sewage or domestic wastewater may be defined as a combination of the liquid- or water-carried wastes from residences, institutions, and commercial and industrial establishments, together with such groundwater, surface water, and stormwater as may be present. Sewage can be classified into two types.

- *Domestic sewage or domestic wastewater*: human excrement, waterborne human excretion, or water-carried wastes from liquid or nonliquid culinary purposes, washing, cleansing, laundering, food processing, or ice production;
- *Municipal sewage or municipal wastewater*: municipal liquid waste originating primarily from residences, but may include contributions from

1. holding tanks in recreational vehicles, boats, and houseboats;
2. commercial, institutional, and industrial sources; and
3. inflow and infiltration.

SEWAGE COMPOSITION AND CONTAMINANTS

Body wastes, food waste, paper, rags, and biological cells form the bulk of suspended solids in sewage. Even inert materials such as soil particles become fouled by adsorbing organics to their surfaces. Although suspended solids are biodegradable by hydrolysis, biodegradable material in sewage is usually considered soluble organics. Soluble organics in sewage are composed chiefly of proteins (40–60%), carbohydrate (25–50%), and lipids (approximately 10%). Proteins are chiefly amino acids; carbohydrates are compounds such as sugars, starches, and cellulose. Lipids include fats, oil, and grease. All of these materials contain carbon that can be converted to carbon dioxide biologically, thus exerting oxygen demand. Proteins also contain nitrogen, and thus a nitrogenous oxygen demand is also exerted. The biochemical oxygen demand (BOD) test is therefore used to quantify biodegradable organics. All forms of waterborne pathogens may be found in sewage wastewater. These include bacteria, viruses, protozoa, and helminthes. These organisms are discharged by persons who are infected with disease. A list of contaminants commonly found in sewage, along with their sources and environmental consequences, is given in Table 1.

The quantity and composition of sewage vary widely from location to location depending on, for example, food diet, socioeconomic factors, weather, and water availability. Quantitatively, constituents of sewage may vary significantly, depending on the other kinds of wastewater and the amount of dilution from the infiltration/inflow into the collection system. The results of analyzing a typical municipal wastewater or sewage from a municipal collection system are given in Table 2. The composition of wastewater from a given collection system may change slightly on a seasonal basis, reflecting different water uses. Additionally, daily fluctuations in quality are also observable and correlate well with flow conditions. Generally, smaller systems with more homogenous uses produce greater fluctuations in wastewater composition.

Table 2. Typical Analysis Of Municipal Wastewater

	Concentration		
Constituent, mg/L	Strong	Medium	Weak
Solids, total	1200	720	350
Dissolved, total	850	500	250
Fixed	525	300	145
Volatile	325	200	105
Suspended, total	350	220	100
Fixed	75	55	20
Volatile	275	165	80
Settleable solids, mL/L	20	10	5
Biochemical oxygen demand, 5-day, 20 °C (BOD_5)	400	220	110
Total organic carbon (TOC)	290	160	80
Chemical oxygen demand (COD)	1000	500	250
Nitrogen, total as N	85	40	20
Organic	35	15	8
Free ammonia	50	25	12
Nitrites	0	0	0
Nitrates	0	0	0
Phosphorus, total as P	15	8	4
Organic	5	3	1
Inorganic	10	5	3
Chlorides	100	50	30
Alkalinity, as CaCO3	200	100	50
Grease	150	100	50

SEWAGE TREATMENT

If untreated sewage is allowed to accumulate, decomposition of the organic material it contains can lead to the production of large quantities of malodorous gases. In addition, untreated sewage usually contains numerous pathogenic or disease-causing microorganisms that dwell in the human intestinal tract. Sewage also contains nutrients, which can stimulate the growth of aquatic

Table 1. Important Wastewater Contaminants

Contaminant	Source	Environmental Significance
Suspended solids	Domestic use, industrial wastes, erosion by infiltration/inflow	Cause sludge deposits and anaerobic conditions in aquatic environment
Biodegradable organics	Domestic waste	Cause biological degradation, which may use up oxygen in receiving water and result in undesirable conditions
Pathogens	Domestic waste	Transmit communicable diseases
Nutrients	Domestic and industrial waste	May cause eutrophication
Refractory organics	Industrial waste	May cause taste and odor problems, may be caustic or carcinogenic
Heavy metals	Industrial waste, mining etc.,	Are toxic; may interfere with effluent reuse
Dissolved inorganic solids	Increase above level in water supply by domestic and/or industrial use	May interfere with effluent reuse

plants, and it may contain toxic compounds. For these reasons, the immediate and nuisance-free removal of sewage from its sources of generation, followed by treatment and disposal, is not only desirable but also necessary in an industrialized society. In the United States, it is now mandated by numerous federal and state laws. Sewage treatment is generally classified into on-site or off-site treatment systems according to nonsewered or sewered facilities.

ON-SITE SEWAGE TREATMENT SYSTEMS

They generally refer to individual septic tanks followed by soakpits. A septic tank is used to receive the wastewater discharged from individual residences and other nonsewered facilities. A septic tank followed by a soil absorption system constitutes what is known as conventional on-site sewage management system. Sludge has settled to the bottom of the septic tank over a period of years, and the liquid and surface scum layer is called septage. Septage and sludge generally require some level of treatment prior to final disposal or reuse. In many cases, septage is discharged to a municipal wastewater treatment plant and treated as a wastewater source. In separate treatment situations, the options of treatment include conventional wastewater treatment processes, conventional sludge treatment processes, land treatment, or a combination of aquatic treatment and constructed wetlands. Sludge can be treated in digesters or sludge lagoons as a liquid, or it can be dewatered and treated by land composting or land application.

OFF-SITE SEWAGE TREATMENT SYSTEMS

Off-site sewage treatment refers to the sewerage system that conveys wastewater to a chosen off-site disposal system. It is composed of a combination of unit operations and processes to reduce certain constituents of wastewater to an acceptable level. Many different combinations are possible. Municipal wastewater treatment systems are often divided into primary, secondary, and tertiary subsystems. The purpose of primary treatment is to remove solid materials from the incoming wastewater. Secondary treatment usually consists of biological conversion of dissolved and colloidal organics into biomass that can be subsequently removed by sedimentation. Contact between microorganisms and organics is optimized by suspending the biomass in wastewater or passing the wastewater over a film of biomass attached to solid surfaces. Secondary systems produce excess biomass that is biodegradable through endogenous catabolism by other microorganisms. Secondary sludges are usually combined with primary sludge for further treatment by anaerobic biological processes.

READING LIST

Crites, R. and Tchbanoglous, G. (1998). *Small and Decentralized Wastewater Management Systems*. McGraw-Hill, New York, pp. 943–950.

Peavy, H.S, Rowe, D.R., and Tchbanoglous, G. (1985). *Environmental Engineering*, International ed. McGraw-Hill, New York, pp. 209–214.

DOMESTIC SEWAGE

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CHARACTERISTICS OF DOMESTIC SEWAGE

Physical Characteristics

Fresh sewage typically has a light brown color. As it ages, oxygen is depleted, and anaerobic microorganisms begin to use other electron acceptors, including sulfates, nitrates, iron, and manganese. As sulfates are reduced, hydrogen sulfide is produced, which can combine with metals in the sewage. The color gradually changes from light brown to gray and eventually to black as a result of the metal sulfides.

The odor of fresh sewage is usually not objectionable, but as it ages, anaerobic microorganisms produce odors that are much more offensive than the odor of fresh sewage.

Odor. Some of the disagreeable compounds formed by the anaerobic decomposition of sewage include hydrogen sulfide, indole, skatole, cadaverine, and mercaptans (1).

Solids. Total solids are made up of soluble solids and suspended solids and are determined by evaporating a known volume of sewage at a temperature of 103–105 °C and weighing the residue. Total suspended solids (TSS) are determined by filtering a sample, followed by drying and weighing (in mg) the residue, and dividing by the volume of the sample (in L). Dissolved solids are the difference between the total and suspended solids. The suspended solids are further separated into settleable and nonsettleable solids. The settleable solids are those that will settle to the bottom of a cone-shaped container in a 60-minute period. The solids (total, suspended, or dissolved) can further be divided into volatile and fixed fractions. Samples are dried and then heated to 550 °C. The volatile materials are burned off, and the fixed solids are weighed. The volatile solids are presumed to be organic material, and the nonvolatile solids are presumed to be inorganic.

Temperature. The temperature of sewage is generally warmer than that of the water supply because of heat added by homes, businesses, and industrial activities. Sewage temperatures vary with the seasons and geography. In cooler climates, temperatures may vary from 7–18 °C (45–65 °F), and in warmer climates, the temperatures may vary from 13–24 °C (55–75 °F) (1).

Chemical Characteristics

Organic. The chief constituents of the organic compounds found in sewage are proteins (40–60%), carbohydrates (25–50%), and fats and oils (10%). Other compounds that may be present in small quantities include surfactants, pesticides, organic priority pollutants, and volatile organic compounds (2).

The organic strength of sewage is measured by a test called biochemical oxygen demand (BOD). The test does not directly measure the concentration of the organics, but rather measures the amount of oxygen that is used as the organic compounds are degraded by microorganisms.

Inorganic. The major inorganic constituents of sewage include alkalinity, sulfates, and metals as well as compounds of nitrogen and phosphorus. Alkalinity is a measure of buffering capacity against changes in pH and is a result of the presence of anions such as hydroxides, carbonates, and bicarbonates. Sulfur is an important element in the formation of proteins and is released when they are degraded. Metals occur naturally at low concentrations in water. Table 1 shows metal concentrations that may be found in sewage.

Small quantities of metals are vital to the biological treatment process as trace nutrients. However, at higher concentrations, metals are toxic to the treatment process.

Nitrogen. Inorganic nitrogen is in the form of ammonia, nitrites, and nitrates. Ammonia exists as both dissolved ammonia gas (NH_3) and the ammonium ion (NH_4^+). Nitrite comprises only a small portion of the inorganic nitrogen and is formed by the oxidation of ammonia. Nitrate is the most oxidized form of inorganic nitrogen in sewage treatment. Nitrate concentrations are a concern in water reuse applications because of methemoglobinemia. The drinking water standard for nitrate has been established at 10 mg/L as nitrogen.

Phosphorus. Inorganic phosphorus may be present as several orthophosphate ions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4). Phosphorus is an important nutrient for storing energy in cells. It is important for microorganisms, and phosphorus is frequently the limiting nutrient for phytoplanktonic (e.g., algae) growth in the aquatic environment. As the limiting nutrient, the growth of algae can be related to the phosphorus concentration. Excessive growth of algae can cause eutrophication of lakes and other slow moving bodies of water.

Gases. As sewage flows through the collection and conveyance system, atmospheric gases such as nitrogen, oxygen, and carbon dioxide may dissolve in the water. In addition to atmospheric gases, the organic compounds in the sewage begin to decompose, and the decomposition products, such as ammonia, hydrogen sulfide, and methane, also dissolve in the sewage (2).

Table 1. Metals Concentrations in Sewage Treatment Plant Influent[a]

	Concentration, mg/L	
Metal	Range	Average
Arsenic	0.0001–5	0.187
Chromium	0.0006–9	0.255
Copper	0.004–20	0.637
Lead	0.001–5	0.138
Mercury	0.0001–0	0.034
Nickel	0.002–7	0.294
Silver	0.0002–5	0.173
Zinc	0.024–2,027	39.4

[a] Reference 3.

Biological Characteristics

Untreated sewage is an ideal medium for microbiological organisms. It provides inorganic and inorganic nutrients that are needed for cell growth (3). Almost every type of microorganism can be found in sewage. The most abundant types include bacteria, viruses, protozoa, and helminths.

Bacteria. Bacteria are the principal microorganisms requiring the treatment of sewage. Bacteria convert carbonaceous materials into various gases and additional cell mass (2). One of the most common pathogens found in sewage is *Salmonella*. *Shigella*, the leading cause of recreational waterborne outbreaks in lakes and rivers, is also found. Some of the other bacteria that have been identified in sewage include *Vibrio, Mycobacterium, Clostridium, Leptospira, Yersinia, Escherichia coli*, and *Campylobacter* (4).

Viruses. Viruses are parasitic particles that consist of a strand of DNA or RNA. They invade living cells and redirect the cell to reproduce the virus, which accumulates within the cell. When the host cell dies, the viruses are released (2). Viruses of concern in sewage include enteroviruses, rotaviruses, reoviruses, parvoviruses, adenoviruses, and hepatitis A virus.

Protozoa. Protozoa are organisms that feed on bacteria and other microorganisms and are vital to the operation of biological treatment systems. Important protozoa in sewage treatment include amoebas, flagellates, and ciliates. There are also pathogenic protozoa in sewage. *Giardia lambia* and *Cryptosporidium* are included in this category (2).

Helminths. Sewage may contain a number of worms (helminths) that are of great concern. There are two major phyla of helminth that may be present, platyhelminthes and aschelminthes. Platyhelminthes are flatworms, including flukes and tapeworms. Nematodes are the major aschelminthes (roundworms) of concern in sewage. Of special concern are *Trichinella, Necator, Ascaris*, and *Filaria* (2).

Pathogenic Organisms. Pathogens are organisms that are highly infectious. Pathogens usually found in sewage are discharged by humans who are infected with or are carriers of a disease. These pathogens typically cause typhoid fever, diarrhea, cholera, and other diseases of the gastrointestinal tract.

Indicator Organisms. There is a large number and variety of pathogenic organisms in sewage. The time, cost, and difficulty of analyzing for all of these organisms would be excessive. To provide a level of confidence in pathogen concentrations, a substitute organism should be found for analysis. The ideal organism would be present when pathogenic organisms are present, be absent when pathogenic organisms are absent, be easy and inexpensive to analyze, and not be a pathogen itself. An organism that meets these criteria is called an indicator organism (5). The most widely used indicator organism in sewage treatment is fecal coliform bacteria.

TREATMENT TECHNOLOGY

Sewage must receive a minimum of a secondary treatment. A secondary treatment is defined as a 30-day average concentration of biochemical oxygen demand and total suspended solids not to exceed 30 mg/L, where the 7-day average does not exceed 45 mg/L. The definition also includes an 85% removal requirement for BOD and TSS. Sewage effluent that may contact humans or be indirectly used for water supply may require additional treatment. Selection of treatment technology is dependent in large part on the influent characteristics, the quality of the effluent required, and cost.

Treatment is normally classified as either physical/chemical or biological and can be broken down into several stages: preliminary treatment, primary treatment, secondary treatment, and tertiary treatment.

Preliminary Treatment Processes

Preliminary treatment is a physical process intended to remove large objects and grit from sewage (5). The removal of these materials is necessary because they could reduce the efficiency or increase the maintenance of downstream processes (6). Preliminary treatment may include the following processes: screening, grit removal, comminution, and flow equalization.

Screening. Screening removes large objects that could clog or damage downstream equipment. Screens typically consist of inclined steel bars spaced at equal intervals in a sewage channel. Common practice is to use a mechanically cleaned bar screen that has an emergency bypass channel containing a manually cleaned screen (7). Design parameters for bar screens include bar size, bar spacing, angle of inclination, channel width, and sewage approach velocity (6).

Grit Removal. Grit consists of sand, gravel, and other high specific gravity material that may abrade and wear mechanical equipment or may accumulate in treatment tanks. A common method for grit removal involves using aerated grit chambers, in which diffused air is introduced to the sewage along the bottom of one side of a rectangular chamber. This creates a rolling motion that keeps the lighter organic materials in suspension but allows the heavier grit particles to settle to the bottom of the tank, where they are removed (6).

Comminution. Comminutors are devices that shred materials without removing them from the sewage. They are typically designed with a bypass channel containing a screening device that may be used if the comminutor is removed from service. The basic parts of a comminutor include a screen and cutting teeth on a revolving drum that has slots cut into it. The cutting teeth shred the material as it is trapped against the screen. The shredded solids then pass through the drum slots and out of the bottom (7). These shredded materials can cause problems, such as clogging, in downstream process units. As a result, comminutors have fallen out of favor in the design of sewage treatment plants (6).

Equalization. Equalization is used in plants to dampen variations in hydraulic or organic loadings. Sewage flows into the unit at a variable rate but is removed at a relatively constant rate. Equalization is used to provide relatively uniform loading throughout the day and to increase the performance of downstream process units (6). Equalization tanks may be designed either as in-line or side-line units.

Equalization tanks must be aerated to prevent the contents from becoming septic and should be mixed to prevent solids from settling. Aeration equipment should be capable of maintaining a dissolved oxygen concentration of 1 mg/L (8). Mixing may be provided by diffused air systems, mechanical mixers, or both.

Primary Treatment Processes

Sedimentation. Primary sedimentation is the oldest and most widely used process in treating sewage (6). It is a physical process whose goal is to achieve solids separation.

Solids removal by sedimentation is a function of retention time and surface settling rate. The surface settling rate is defined as the volumetric flow rate over the surface area of the clarifier in units of velocity. Particles whose settling velocity is greater than the surface settling rate are removed from the sewage stream. However, if the detention time is too long, the sewage turns septic, and gas bubbles formed in the sewage reduce the efficiency of the process. A typical minimum side water depth for primary clarifiers is 10 feet. To allow for adequate settling, a minimum distance of 10 feet should separate the inlet and the outlet (8). Clarifier design is typically based on two flows, the average design flow and the peak hourly flow. The calculated size of the clarifier is based on both flows, and the larger clarifier is selected.

Secondary Treatment Processes

Activated Sludge Processes. Activating sludge is a biological treatment process using a suspension of microorganisms to treat sewage in an aerobic environment. The microorganisms are allowed to flocculate and settle under quiescent conditions, and treated sewage then flows over weirs for further treatment or discharge. Solids from the bottom of the clarifier are recycled to the reactor to provide an adequate concentration of microorganisms for treatment. The contents of the reactor, called mixed liquor, must be aerated and mixed by using either mechanical aerators or diffused air.

There are several variations of the conventional activated sludge process. These include plug flow reactors, including step feed, tapered aeration, extended aeration, and complete mix reactors, including sequencing batch reactors.

A plug flow reactor has a configuration in which the sewage flows through a long, narrow channel for treatment. It approximates flow through a pipe. In an ideal plug flow reactor, there is no longitudinal mixing of the sewage. A step feed reactor is a variation of the plug flow reactor in which the sewage is introduced into the reactor at several places. This allows more equal distribution of the organic load. Tapered aeration is another variation of the plug flow reactor. In tapered aeration, the majority of the aeration capacity is provided at the head of the reactor, where the organic load is the highest, and less aeration is provided where the organic load is lower. Extended aeration is a treatment process requiring long detention times (typically greater than 24 hours) and low organic loadings. Extended aeration is commonly available in package-type treatment plants and is economical for small treatment plants.

A complete mix reactor is the opposite of a plug flow reactor. All of the sewage is completely mixed in a short, wide reactor. Due to rapid and complete mixing of the reactor contents, complete mix reactors can tolerate shock loads better than plug flow reactors. A sequencing batch reactor (SBR) is a variation of the complete mix reactor; stabilization, settling, and equalization take place in the same tank, eliminating the need for a clarifier.

Aeration Requirements. The dissolved oxygen concentration in aeration tanks should be greater than 2 mg/L at all times. Treatment processes (except extended aeration) should be designed to provide 1.1 lb of oxygen per pound of BOD treated. Extended aeration systems generally require 1.5 lb of oxygen per pound of BOD treated. These aeration requirements do not include the aeration capacity needed for nitrification. If nitrification is required, an additional 4.6 lb of oxygen per pound of ammonia nitrogen is required (8).

Fixed Film Processes

Trickling Filters. Trickling filters are a fixed film process where the microorganisms are attached to a stone or plastic medium. The sewage flows through a rotating arm, which distributes it over the medium. As the sewage flows over the medium, the microorganisms absorb organics from the sewage. When the sewage is not being applied to that specific section of the medium, air flows through the filter, providing the oxygen that the microorganisms need for respiration.

Sewage is recirculated back to the filter to maintain a proper application rate for efficient operation of the filter, to equalize the organic loading to the filter, and to prevent the microorganisms from drying out.

Rotating Biological Contactors. Rotating biological contactors (RBCs) are another version of the fixed film process. The microorganisms are attached to a plastic disk, which is partially submerged and rotated through the sewage. When the microorganisms are submerged, they absorb organics. During the time the microorganisms are exposed to the air, they receive the oxygen that is required for treatment. Treatment efficiency is a function of the surface area of the disks, more surface area provides greater treatment. Unlike trickling filters, no recirculation is required for rotating biological contactors.

Stabilization Ponds. Stabilization ponds are large, lined basins, that may be aerobic, facultative, or anaerobic. Ponds use detention time measured in days, rather than hours, and are typically relatively shallow compared with other biological treatment processes. Thus, a large land area is required for ponds, and they are usually used only in small communities. Their advantages include low construction and operating costs.

Aerobic ponds may be aerated mechanically or naturally. Natural aeration is by atmospheric diffusion and production of oxygen by algae. Facultative ponds have several stratified layers—an upper, aerated section; a lower, anaerobic section; and an intermediate section consisting of both aerobic and anaerobic processes. Anaerobic ponds may be up to 30 feet deep and are used for treating high strength (typically industrial) waste. Deep ponds maximize anaerobic conditions.

Tertiary Treatment Processes

Nitrification. Ammonia nitrogen is converted to nitrate in a two-step process, in which ammonia is first converted to nitrites and the nitrites are then converted to nitrates. The rate-limiting step is the conversion of ammonia to nitrite. Nitrification can co-occur with carbon oxidation, or it may take place in a separate nitrification tank. The reaction rate is slower and, therefore, requires a longer detention time than carbon oxidation. Nitrifying organisms have a slower growth rate than the organisms for carbon oxidation, and the process requires a longer mean cell residence time (sludge age).

Biological Phosphorus Removal. Biological phosphorus removal can be enhanced in a two-step process. The first step takes place anaerobically. The microorganisms release phosphorus to generate energy for the uptake of organics. The second step is aerobic. In this step, the microorganisms absorb large amounts of phosphorus to replace the phosphorus that was lost in the anaerobic step, as well as to store additional energy for the next "feast or famine" feeding cycle.

There are three major biological phosphorus removal methodologies—the Anaerobic/Oxic (A/O) process, the PhoStrip process, and the sequencing batch reactor (2). Both the A/O process and the PhoStrip process are proprietary. Phosphorus removal in the A/O process is dependent on the BOD:P ratio; the PhoStrip process is independent of this ratio. The PhoStrip process does require additional chemicals for phosphorus removal, however. The sequencing batch reactor may be cycled to achieve biological phosphorus removal but usually is used for smaller flows and with more limited design data.

Denitrification. Denitrification is the removal of the inorganic nitrogen from sewage. Several species of bacteria can use nitrates, rather than oxygen, as their energy source. These bacteria convert the nitrates into nitrogen gas (2).

In the denitrification process, raw sewage flows into an anoxic zone with return sludge and return mixed liquor from an aerobic zone. The anoxic zone denitrifies by using the nitrates in the mixed liquor. Following the anoxic zone, the sewage flows to an aerobic zone where nitrates are created. The nitrates are then recycled to the anoxic zone for removal. Denitrification is normally done in a plug flow type system or in an oxidation ditch, although a sequencing batch reactor may be programmed for denitrification (2).

Biological Dual Nutrient Removal. Biological dual nutrient removal is the reduction of both nitrogen and phosphorus from sewage by microorganisms. Several proprietary treatment processes, including the A^2/O process, the Bardenpho process, the University of Capetown (UCT) process, and the Virginia Initiative Plant (VIP) process, have been developed for dual nutrient removal (2).

These processes are a combination of the denitrification process and the biological phosphorus removal process. The proprietary systems may use from three to five stages to achieve the desired nutrient removal, but all have the use of an anaerobic zone in common, followed by an anoxic zone, followed by an aerobic zone. Some of the processes may use two anoxic zones and/or two anaerobic zones with different recycle streams to achieve greater nutrient removal, but the treatment principles are the same.

Coagulation/Sedimentation. Coagulation/sedimentation requires chemical addition to enhance the sedimentation of solids, precipitate pollutants, or remove phosphorus. The chemicals most commonly used are lime, aluminum salts, ferric salts, and polymers (7).

Chemical phosphorus removal occurs by the addition of chemicals to the sewage, which create an insoluble phosphate precipitate. Alum is frequently used in the chemical precipitation of phosphorus, although iron salts may also be used. Alum also reacts with hydroxyl radicals in the water, forming aluminum hydroxide, in addition to aluminum phosphate. Iron (III) reacts in the same manner.

Filtration. Filtration is the removal of solids by passing the sewage through a bed of granular media. Although the most commonly used filters are composed of sand, filters may also consist of multiple types of media, such as coal over sand or coal over silica sand over garnet sand (9). Filters may be classified as slow filters, rapid filters, or pressure filters. Slow filters require a buildup of a biological mat on the upper surface of the filter, which provides greater treatment, but requires a low application rate, and therefore requires a larger area. Rapid filters and pressure filters depend on the entire depth of the media for filtration and may be operated at higher loading rates than slow filters, although backwashing of the media is required.

Activated Carbon Adsorption. Adsorption is a process by which a compound adheres to a solid surface. In sewage treatment, activated carbon is the most commonly used adsorbent. Activated carbon comes in two forms, powdered and granular. Powdered activated carbon (PAC) is applied in slurry form at the head of the aeration tanks and is removed in the final clarifiers. Granular activated carbon (GAC) is used in a filter bed (7). Carbon adsorption is used only where highly treated effluent is required.

Membrane Systems. Membrane processes involve the use of a semipermeable barrier. The membrane allows the water to flow through and retains the contaminants. There are several types of membrane systems in sewage treatment, including reverse osmosis, nanofiltration, microfiltration, and ultrafiltration. All of these processes require pressure to force water through the membrane. Ultrafiltration requires the least pressure, whereas reverse osmosis requires the greatest pressure. Membrane processes are subject to fouling of the membranes. These processes should be pilot tested to determine which process and membrane will work best. Like carbon adsorption, membrane processes are used when only high-quality effluent is required.

Disinfection Processes

Chlorination/Dechlorination. Chlorine has been used as a disinfectant for sewage for several reasons, including inactivation of a wide range of pathogens, maintenance of a residual, and economy. There are several forms of chlorine that may be used: gaseous chlorine, sodium hypochlorite, and calcium hypochlorite. Chlorine is toxic to aquatic life, so the recent trend has been to dechlorinate the sewage before discharge to the receiving stream, which is usually done by using sulfur dioxide to reduce the chlorine to chlorides. Sodium metabisulfite or bisulfite may be used as a substitute for sulfur dioxide in small facilities. Reaction times are nearly instantaneous, and detention times are usually less than 2 minutes.

Ozonation. Ozone is a very powerful oxidant. It can inactivate sewage pathogens with less contact time and a lower dosage than other disinfection methods. It is effective against a wide range of organisms, and it does not leave a toxic residual (10). Ozone must be generated on-site because it is unstable. Ozone is generated by corona discharge, which consists of passing clean, dry air or oxygen through electrodes, which are separated by a dielectric and a gap.

Ultraviolet Light Disinfection. Ultraviolet radiation whose wavelengths are in the range of 240–280 nm inactivate microorganisms by causing damage to their DNA (10). Ultraviolet lamps operate in the same way as fluorescent lamps—the radiation is generated by passing an electrical current through ionized mercury vapor. The mercury lamps may operate at low or medium pressures. Low-pressure lamps emit the majority of their energy at 253.7 nm, which is in the optimal range for inactivation. Medium-pressure lamps generate a smaller portion of their energy in the 240–280 nm range, but the intensity of their light is much greater. Therefore, fewer medium-intensity lamps are required for the same amount of disinfection (10).

BIBLIOGRAPHY

1. Linsley, R.K. and Franzini, J.B. (1979). *Water Resources Engineering*, 3rd Edn. McGraw-Hill, New York.
2. Metcalf & Eddy, Inc. (1991). *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd Edn. McGraw-Hill, New York.
3. Water Environment Federation. (1994). *Wastewater Biology: The Life Processes*. Alexandria, VA.
4. US EPA. (1992). *Guidelines for Water Reuse*. EPA/625/R-92/004.
5. Sincero, A.P. and Sincero, G.A. (1996). *Environmental Engineering: A Design Approach*. Prentice-Hall, Upper Saddle River, NJ.
6. Water Environment Federation and American Society of Civil Engineers. (1992). *Design of Municipal Wastewater Treatment Plants*. WEF Manual of Practice No. 8/ASCE Manual and Report on Engineering Practice No. 76, 3rd Edn.
7. Water Environment Federation. (1989). *Water Reuse, Manual of Practice SM-3*, 2nd Edn. Alexandria, VA.
8. Great Lakes-Upper Mississippi River Board of State and Provincial Public Health and Environmental Managers. (1997). *Recommended Standards for Wastewater Facilities*. Health Education Service, Inc., Albany, NY.
9. Weber, W.J. (1971). *Physicochemical Processes for Water Quality Control*. John Wiley & Sons, New York.
10. US EPA. (1999). *Alternative Disinfectants and Oxidants Guidance Manual*. EPA 815-R-99-014.

SOLIDIFICATION/STABILIZATION OF HAZARDOUS SOLID WASTES

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INTRODUCTION

Solidification/stabilization is an established technology that has been used for almost 20 years to treat a variety of toxic or hazardous wastes. Historically, this technology belongs to the top five source control treatment technologies, used at Superfund remedial sites, as presented in Fig. 1 (1).

Stabilization is a process by which sufficient quantities of specific additives (reagents) are added to hazardous materials to reduce the toxic nature (properties) of a waste by converting the toxic constituents into an appropriate solidified form. As a result, (a) the rate of contaminant migration into the surrounding environmental media is minimized, and (b) the level of toxicity is substantially reduced, as determined by the application of the appropriate leaching tests, such as TCLP. The procedure of solidification/stabilization has shown considerable promise, and it is commonly used for the fixing different waste types. The wide use of stabilization for treating (mainly) inorganic-laden wastes derives primarily from

1. the lack of better alternatives; for example, toxic metals do not biodegrade and they do not change in atomic structure/properties, when incinerated.
2. the well-defined physicochemical mechanisms taking place, such as precipitation and adsorption (2).

SOLIDIFICATION/STABILIZATION TECHNOLOGY

Solidification and stabilization (denoted hereafter as S/S) waste treatment processes involve mixing specialized additives or reagents with hazardous waste materials to reduce, by physical or chemical means, the solubility or mobility of contaminants in the surrounding environmental matrix. Solidification and stabilization are closely related; both use several chemical, physical, and thermal processes or an appropriate combination of them, to detoxify hazardous wastes.

The term “solidification/stabilization” refers to a general category of processes, that are used to treat a wide variety of hazardous (or toxic) wastes, including mostly solids, but also liquids. Nevertheless, solidification and stabilization are considered distinct technologies.

Solidification refers to processes that encapsulate a waste to form a solid material and to restrict the migration of contaminant by decreasing the available surface area, which is exposed to leaching, when contacting liquids and also by coating the waste with low-permeability materials. Solidification can be accomplished by a chemical reaction between the hazardous waste and the binding (solidifying) reagents or by the application of mechanical processes (e.g., compaction). The solidification of fine solid waste particles (i.e., those whose diameters are below 100 μm) is referred to as *microencapsulation*, whereas

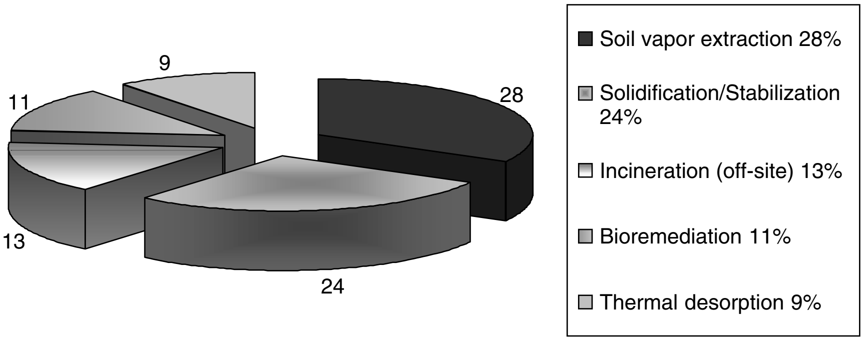


Figure 1. The top source control treatment technologies used at Superfund remedial sites.

the solidification of a large block or container of waste is referred to as *macroencapsulation*.

Stabilization refers to processes that involve chemical reactions, which reduce the leachability of the product (stabilized waste). Stabilization immobilizes the hazardous materials or reduces their solubility through appropriate chemical reactions. The physical nature of the waste may or may not be changed by this process.

Solidification refers to processes that encapsulate the waste in a monolithic solid, which has sufficient structural integrity. The encapsulation may be that of compacted fine waste particles, or of a large block, or container of wastes. Solidification does not necessarily involve a chemical interaction between the waste and the solidifying reagents, but the binding of waste in the product (monolith) may be mechanical. Migration of contaminants is restricted by the large decrease in surface area, which is exposed to eventual leaching, and by isolating the waste within an impervious capsule.

Stabilization refers to processes, which reduce the risk posed by a waste, through the conversion of contaminants into a less soluble, immobile, or less toxic form, whereas the physical nature of the waste may not be necessarily changed. Phosphates, sulfides, carbonates, and several other materials have been used as appropriate treatment reagents.

In many instances, stabilization takes place exclusive of solidification. A stabilized product should have low leaching characteristics. Many of the reagents used for the S/S method can also be used in other chemical treatment (oxidation) processes, such as in dechlorination of liquid wastes. S/S systems can be used to treat contaminated soil or wastes in place, or they can be employed to treat excavated wastes externally, preparing them for subsequent disposal (3).

Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as *fixation*, usually uses a chemical reaction to convert the hazardous constituents of the waste to a less mobile form. The general approach for S/S treatment processes involves mixing or injecting treatment agents into the contaminated soils. Inorganic binders, such as cement, fly ash, or blast furnace slag, as well as organic binders, such as bitumen, have been used to form a crystalline, glassy, or polymeric framework around the waste.

The dominant mechanism by which metals are immobilized in the absence of anions such as phosphates, carbonates, halides, or sulphates, is the precipitation of respective hydroxides within the solid matrix. S/S technologies are not useful for certain forms of metal contamination, such as species that exist as anions [e.g., Cr(VI) or arsenic], or for metals whose hydroxides are very soluble (e.g., mercury).

The S/S technology may not be applicable at polluted sites, containing wastes that include organic compounds, especially when volatile organic contaminants are present. The application of mixing and heating processes, associated with the hydration of binders, may release organic vapors. Pretreatment, such as air stripping or incineration, may be used to remove the volatile organics during preliminary treatment and to prepare the waste for the S/S of residues. The chemical composition of the contaminated matrix, the amount of water present, and the ambient temperature also affect the application of S/S technologies. Some factors can interfere with the effectiveness of the S/S process by inhibiting bonding of the waste to the binding material, retarding the setting of the mixtures, decreasing the stability of the matrix, or reducing the strength of the solidified products.

Cement-based binders and stabilizers are commonly used materials, when implementing S/S technologies (4). Portland cement, a mixture of Ca silicates, aluminates, alumino ferrites and sulfates, is an important cement-based material. Pozzolanic materials, which consist of small spherical particles, formed by coal combustion in lime and cement kilns, such as fly ash, are also commonly used for S/S. Pozzolans exhibit cement-like properties, especially when their silica content is relatively high. Portland cement and pozzolans can be used alone or together to obtain optimal stabilization properties for a particular waste or polluted site (5).

Organic binders may also be used to treat metals by polymer microencapsulation. This process uses organic materials, such as bitumen, polyethylene, paraffins, waxes, and other polyolefins, as thermoplastic or thermosetting resins. For polymer encapsulation, the organic materials are heated and mixed with the contaminated matrix at elevated temperatures (120–200 °C). The organic materials polymerize, agglomerate the waste, and as a result, the waste matrix is encapsulated (5). The organics are volatilized and collected, and the treated material is extruded for disposal or possible reuse (e.g., as paving material).

The contaminated material may require a certain extent of pretreatment to separate rocks and other debris and to dry the feed material. Polymer encapsulation requires more energy and more complex equipment than cement-based S/S operations. Bitumen (asphalt) is the cheapest and most common thermoplastic binder (5). S/S is achieved by mixing the contaminated material with appropriate quantities of binder/stabilizer and with water. The mixture sets and cures to form a solidified matrix, which contains the hazardous constituents. The cure time and handling characteristics of the mixture and the final properties of the hardened cement depend on the specific composition of the binder/stabilizer used (i.e., amount of cement, pozzolan, water, etc.).

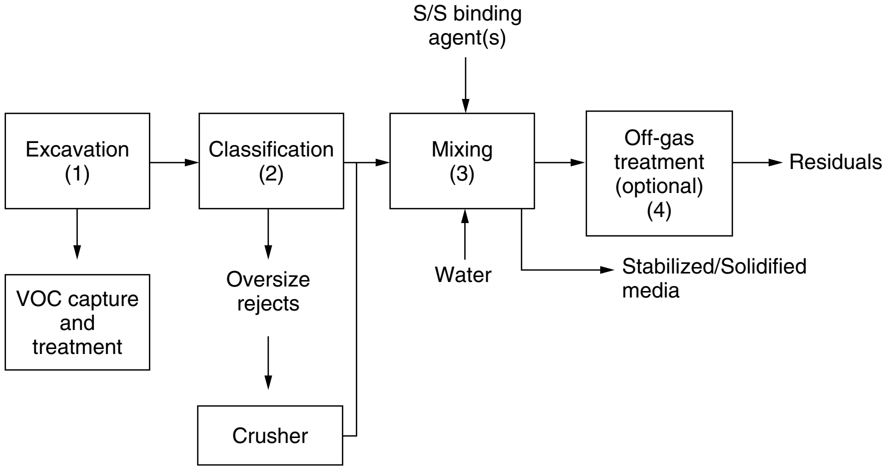
Vitrification is the process of converting solid materials into a glass-like substance. This process is increasingly being considered for treating various toxic or hazardous wastes. The mobility of metal contaminants can be highly decreased by the application of high temperatures to the contaminated waste, which results in the formation of vitreous material, usually as oxide solids. During this process, the increased temperature may also cause the volatilization and/or destruction of organic contaminants or of volatile metal species (such as Hg), which must be carefully collected for further treatment or disposal. Most contaminated soils can be treated by vitrification, and a wide variety of inorganic and organic contaminants can be targeted. As a stabilization process, vitrification may immobilize inorganics by incorporating them into the glass structure or by encapsulating them within the product (glass). Vitrification may be performed *ex situ* or *in situ*, although the *in situ* processes are preferred, due to lower energy requirements and cost. The performance and characteristics of vitrification make it the focal point of treatment systems applied to high-level radioactive waste (HLW) around the world (6).

Ex situ S/S processes can be easily applied to excavated soils because the necessary mechanical methods are available to provide vigorous mixing, which is needed to combine the binder/stabilizer with the contaminated material. Pretreatment of a solid waste may be necessary to screen and crush large rocks and debris. Mixing can be performed via *in-drum, in-plant*, or whole area mixing processes. In-drum mixing may be preferred for treating small volumes of wastes or for toxic wastes. In-plant processes use rotary drum mixers for batch processes or pug mill mixers for continuous treatment. Larger volumes of wastes may be excavated and moved to a contained area for area mixing. This process involves layering contaminated material with the stabilizer/binder and subsequent mixing with a backhoe or similar equipment. Mobile, as well as fixed treatment plants are available for *ex situ* S/S treatment. Smaller pilot-scale plants can treat up to 100 tons of contaminated waste or soil/day; larger portable plants typically process 500 to over 1000 tons/day.

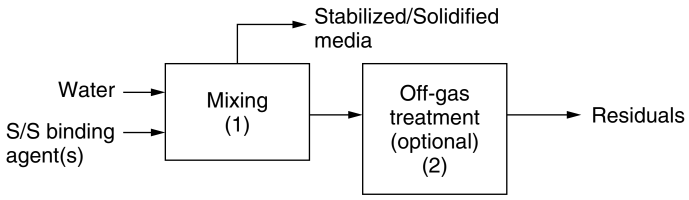
S/S techniques are also available to mix binder/stabilizer with the waste or contaminated soil *in situ*. *In situ* S/S technology is less labor- and energy-intensive than *ex situ* processes, which require excavation, transport, and disposal of the treated material. The *in situ* S/S method is also preferred, when volatile or semi-volatile organics are present in a waste because otherwise the excavation would expose these contaminants to the air. However, the presence of bedrock, large boulders, cohesive soils, oily sands, and clays may preclude the application of the *in situ* S/S method at certain sites. It is also more difficult to provide uniform and complete mixing, when applying *in situ* processes. The binder may be mixed with the contaminated matrix using in-place mixing, vertical auger mixing, or injection grouting. In-place mixing is similar to *ex situ* area mixing, except that the waste or soil is not excavated prior to treatment.

The *in situ* process is useful for treating surface or shallow contamination and involves spreading and mixing binders with the waste, using conventional excavation equipment, such as draglines, backhoes, or clamshell buckets. Vertical auger mixing uses a system of augers to inject and mix the binding reagents with the waste. Larger (2–4 m diameter) augers are used for shallow drilling (depths of 3–13 m) and can treat 400–800 m^3/day. Deeper applications of S/S methods (up to 50 m deep) can be achieved by using ganged augers (up to 1 m in diameter each), which can treat 100–300 m^3/d. Finally, injection grouting may be performed to inject the binder, containing suspended or dissolved reagents, into the treatment area under pressure. The binder permeates the surrounding soil and cures in place (7).

The main generic elements of typical S/S are presented in Fig. 2.



Ex situ S/S process



In situ S/S process

Figure 2. Generic elements of typical S/S processes.

KEY FEATURES OF S/S PROCESSES FOR BEST MANAGEMENT PRACTICES (BMPs)

The key features of S/S processes for BMPs are briefly presented in the following:

- This process requires the mixing of reagents, either on- or off-site.
- As a result of S/S application, contaminants are immobilized.
- Similarly to other immobilization technologies, S/S does not destroy inorganic wastes but may alter or change organic wastes.
- Stabilization can be combined with encapsulation or other immobilization technology.
- The application of S/S may increase the total volume of materials, which must be handled as waste for disposal.
- The wastes treated by the S/S method may be amenable to further reuse, following this treatment.
- Field application may involve the installation of any or all of the following:
  - a) auger type drilling and mixing equipment for *in situ* applications.
  - b) dust collection systems.
  - c) volatile emission control systems.
  - d) bulk storage tanks.

CROSS-MEDIA TRANSFER POTENTIAL OF POLLUTANTS AFTER S/S

There is a certain potential for the cross-media transfer of pollutants, after S/S:

1. There is always a risk of inaccurate site characterization, which has to be considered during the application of technology for treating soils. The solid material encountered at the remedial site may not be similar to the soils studied during laboratory treatability or pilot-scale tests. Additional contaminants may be encountered, whereas the percentage of the fine-grained fraction may be significantly different from that expected. These factors may lead to long-term storage or generation of a high volume of residuals that increases the potential for cross-media transfer of pollutants.
2. Also, during remediation, implementation, including staging and site preparation (e.g., clearing, grubbing), drilling, well installation and trenching operations, mobilization and demobilization of equipment, excavation, transport of materials across the site, and certain treatment activities, there is high potential for fugitive dust emissions due to the movement of equipment at the site. In addition, these activities can enhance the volatilization of VOCs (volatile organic compounds), SVOCs (semivolatile organic compounds), and of other potentially hazardous materials into the atmosphere.
3. During pretreatment operations, such as excavation, storage, sizing, crushing, dewatering, neutralization, blending, and feeding, there is the potential for dust and VOC emissions from the contaminated media (solid or liquid wastes).
4. The migration of contaminants to uncontaminated areas may occur during mobilization or demobilization.
5. VOC and SVOC emissions tend to increase during periods of hot and dry weather.
6. Leaching of contaminants to neighboring surface waters can occur from uncovered stockpiles and from excavated pits.
7. Improper handling and disposal of residues, such as sediment/sludge residuals or postwashing wastewaters, may allow contaminants to migrate into and pollute uncontaminated areas.
8. The posttreatment discharge of wastewater produced, when improperly managed, can also cause migration of contaminants.

Additional concerns for the application of S/S technology include

1. The leaching of contaminants or excess reagents to groundwaters from the treated wastes, which are disposed of on-site.
2. The long-term degradation of the stabilized mass, creating a potential for release of solidified hazardous constituents, reagents, VOCs, etc. from the treated waste.

WASTE CHARACTERISTICS THAT MAY INCREASE THE LIKELIHOOD OF CROSS-MEDIA CONTAMINATION FROM THE APPLICATION OF S/S TECHNOLOGIES

The effectiveness of S/S applications can be compromised and provoke cross-media contamination under certain conditions, which are identified in the following (8). However, some of these limitations might be overcome with various technology-specific modifications and variations.

1. The main physical mechanisms that can interfere the effective application of S/S process include
   - a. Incomplete mixing due to the presence of high moisture or organic chemical content, resulting in only partial wetting or coating of the waste particles with the stabilizing and binding agents and aggregation of untreated waste into lumps.
   - b. Disruption of the gel structure of the curing cement or pozzolanic mixture by hydrophilic organics in the waste soil to be treated.
   - c. Undermixing of dry or pasty wastes.
2. The main chemical mechanisms that can interfere with the S/S process include
   - a. chemical adsorption
   - b. precipitation
   - c. nucleation

Additional factors, which can interfere with the S/S/process include

a. the precise tailoring of waste composition to the S/S process used.
b. The treatment of waste containing oil and grease in moderate to high concentrations.

APPLICATION AND PERFORMANCE OF S/S

Types of Applications

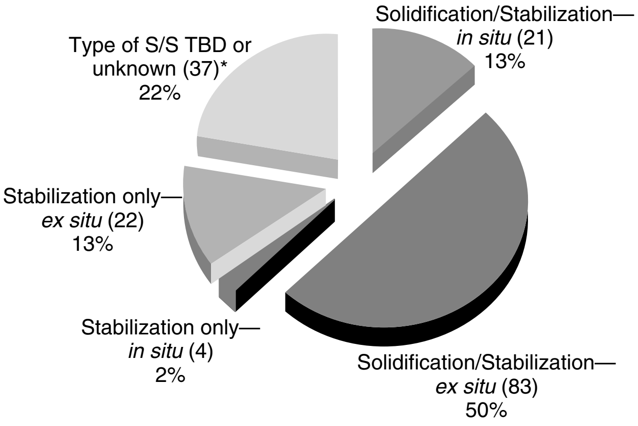
The majority of S/S projects at Superfund remedial sites are *ex situ* applications, where inorganic binders and additives were used to treat metal-containing waste. Organic binders were used for treating specialized wastes, such as radioactive wastes, as well as those containing specific hazardous organic compounds. The S/S method was used to treat wastes containing mainly organic contaminants in a small number (6%) of the total number of projects.

Performance

Most performance testing for S/S waste products has been conducted after curing was completed, whereas only limited data are available on long-term performance of S/S at Superfund remedial sites. The available performance data for the behavior of metals in these projects showed that S/S can meet established performance goals. Also, only limited data were available on the behavior of organics; however, the S/S process met the established performance goals for several projects.

SPECIFIC TYPES OF S/S APPLICATIONS

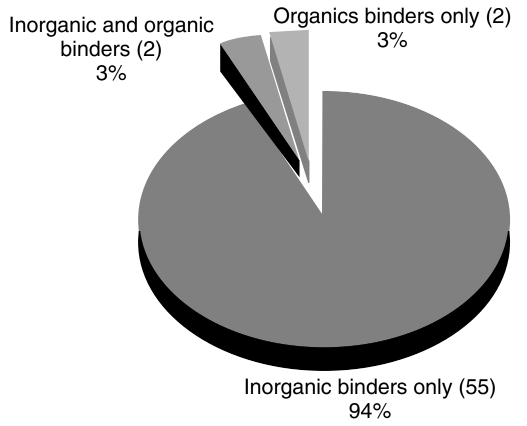
Figure 3 shows a breakdown of S/S projects by specific application type, which include *ex situ* S/S, *in situ* S/S, *ex situ* stabilization only, and *in situ* stabilization only. A specific type of S/S application was identified for 88% of the completed projects. S/S (*in situ* and *ex situ*) represents 63% of the S/S projects, compared to 15% for stabilization only (*in situ* and *ex situ*).



* Includes 3 *in situ* projects.

Note: The number of projects by type is shown in parentheses. TBD= (still) to be determined.

Figure 3. S/S projects by type. Total number of projects: 167.



Note: Inorganic binders consist of cement, fly ash, lime, soluble silicates, or sulfur. Organic binders consist of asphalt, organophilic clay, or activated carbon.

Figure 4. Binder materials used for S/S projects. Total number of projects: 59.

Figure 4 shows the types of binders used for S/S projects at Superfund remedial sites, including inorganic binders, organic binders, and appropriate combinations of organic and inorganic binders. Many of the binders used included one or more proprietary additives. Specific examples of inorganic binders included cement, fly ash, lime, soluble silicates, and sulfur-based binders; organic binders included asphalt, epoxide, polyesters, and polyethylene. More than 90% of the S/S completed projects used inorganic binders. In general, inorganic binders are less expensive and easier to use than organic binders, which are generally used to solidify radioactive wastes or other specific hazardous organic compounds.

COST DATA

Information about the cost of using S/S to treat wastes at Superfund remedial sites was available for 29 completed projects. The total costs for S/S projects ranged from \$75,000 to \$16 million, including the cost of excavation, treatment, and disposal (for *ex situ* applications). The cost per m^3 of treated waste ranged from \$10 to approximately \$1500/m^3. The average cost/m^3 for these projects was \$340, including two projects with relatively high costs (approximately \$1500/m^3). Excluding those two projects, the average cost was \$250/m^3 (1).

Additional information (3,4) indicates that the cost of *in situ* S/S can range from as little as \$25 to \$50/m^3 to as much as \$120 to \$250/m^3, depending on the volume to be treated, the structure of the soil (porosity), the treatment depth, the specific type of main contaminant to be stabilized/solidified, and the desired posttreatment objectives (leachability, permeability, or bearing ratio). The low end of the cost range would apply to solidifying, whereas the high end would apply to treating high concentrations of contaminants at great depths. Typical costs for application at a hazardous waste site, consisting of sands to silts, at a depth up to 9 m, has been estimated at around \$90 to \$120/m^3; around 20% would be the cost of reagent/additive.

BIBLIOGRAPHY

1. US EPA. (2000). *Solidification/Stabilization Use at Superfund Sites*. EPA Report 542-R-00-010. Cincinnati, OH.
2. LaGrega, M.D., Buckingham, P.L., and Evans, J.C. (1994). *Hazardous Waste Management*. McGraw-Hill, New York.
3. US EPA. (1997). *Recent Developments for in situ Treatment of Metal Contaminated Soils*. Office of Solid Waste and Emergency Response, Technology Innovation Office, Washington, DC.
4. US EPA. (1997). *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb*. Engineering Bulletin, EPA Report 540/S-97/500. Cincinnati, OH.
5. US EPA. (1989). *Stabilization/Solidification of CERCLA and RCRA Wastes*. EPA Report. Cincinnati, OH.
6. US EPA. (1992). *Vitrification Technologies for Treatment of Hazardous and Radioactive Waste*. Handbook. Cincinnati, OH.
7. Evanko, C.R. and Dzombak, D.A. (1997). *Remediation of Metals-Contaminated Soils and Groundwater*. Technology Evaluation Report, GWRTAC.
8. US EPA. (1997). *Best Management Practices (BMPs) for Soil Treatment Technologies, Suggested Operational Guidelines to Prevent Cross-Media Transfer of Contaminants During Cleanup Activities*. EPA Report 530-R-97-007. Cincinnati, OH.

WASTEWATER TREATMENT—SMALL SCALE

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Small wastewater treatment plants are defined as those to which fewer than 2’000 people are connected or those whose flow is less than 200 m^3/d. These are treatment plants for small communities, villages, institutions, hotels, and camping resorts.

There are a tremendous number of small wastewater treatment plants worldwide. Small treatment works are needed mainly in rural areas to treat municipal wastewater. However, technologies to treat wastewater from industry are also important. The separate treatment of wastewater from certain processes provides opportunities to reuse water and to reduce the overall consumption of freshwater.

In rural areas and also in large cities that are not yet provided with sewers, sanitation requirements can be met at a reasonable price and on a reasonable timescale by constructing small but highly compact and efficient plants to serve clusters of dwellings.

Small wastewater treatment plants are required to satisfy very different needs which can be integrated into infrastructures at very different stages of development and sophistication. Engineers are called upon to provide technologies that are reliable, easy to operate and control, and tolerant of variations in the influent. The task is difficult and needs an interdisciplinary approach that takes into account local conditions.

REQUIREMENTS FOR SMALL WASTEWATER TREATMENT PLANTS

Rural areas have some general characteristics:

- small communities, groups of houses, and also single houses sometimes where large distances are between them,
- low population density; and
- primarily agricultural use and only little industry.

These properties result in

- highly fluctuating wastewater flows, and
- high concentrations of wastewater constituents with high fluctuations.

Additionally only few trained personnel are available to operate wastewater treatment plants. As a result, some general requirements for small wastewater treatment plants in rural areas can be formulated:

- simplicity of technology,
- simple operation and maintenance,
- high robustness,
- large volume to buffer the high fluctuations of flow and concentrations,
- high stability, and
- low surplus sludge production.

TREATMENT METHODS

Wastewater treatment alternatives (for small communities) can be broadly subdivided into the following categories that represent the basic approaches to wastewater conveyance, treatment, and/or disposal (1):

- *Natural systems* use soil as a treatment and/or disposal medium, including land application, constructed wetlands, and subsurface infiltration. Some sludge and septage handling systems, such as sand drying beds, land spreading, and lagoons, are included.
- *Conventional treatment systems* use a combination of biological, physical, and chemical processes and employ tanks, pumps, blowers, rotating mechanisms, and/or mechanical components as part of the overall system. These include suspended growth, fixed growth, and combinations of the two. This category also includes some sludge and septage management alternatives, such as digestion, dewatering, and composting systems and appropriate disposal.
- *Alternative collecting systems* that use lightweight plastic pipe buried at shallow depths that have fewer pipe joints and less complex access structures than conventional gravity sewers. These include pressure, vacuum, and small-diameter gravity sewer systems.
- *Alternative treatment systems* use source control and separating systems. Wastewater can be separated

into blackwater—waste from toilets—and graywater—the part of the wastewater which is not mixed with excreta (from kitchens, bathrooms, and laundries). Blackwater can further be separated into urine (yellowwater) and feces (brownwater).

Depending on the local situation, different requirements arise for the treatment of organic matter, nutrients, and pathogens. In principle, all treatment methods that are used for large-scale wastewater treatment can be applied in small wastewater treatment plants. However, treatments that meet the special requirements of small systems should be favored.

Table 1 summarizes treatment alternatives to fulfill different effluent requirements. In many countries, systems for partial treatment combined with chemical precipitation are the only treatment and may serve as pre-treatment for additional future treatment steps. It is well understood that, in most cases, the relatively low removal rates in primary clarifiers and septic tanks do not comply with treatment goals and that septic tanks, especially, are perfectly suited for pre-treatment in infiltration systems and constructed wetlands. Although construction and operation of anaerobic pre-treatment is simple, only appropriate sludge control, it has been shown, guarantees settling of solids and partial hydrolysis by methanogenic fermentation. In all other treatment systems, biochemical oxidation is the most important process and determines, to a great extent, the size and costs of the treatment system.

Pathogen removal in nitrifying systems is generally higher than that in nonnitrifying systems. If very low microbial contamination is required, disinfection methods have to be applied.

Table 2 classifies treatment systems as low and high rate systems. In low rate systems, only lower hydraulic and contaminant loading rates can be applied, oxygen transfer is limited to natural diffusion and convection processes, the biomass concentration is lower, and therefore the specific volume and area requirements are higher. However, they are easier to operate and maintain and require, therefore, less skilled personnel.

The advantages of using natural systems are their "low-tech/no-tech" nature, which means that these systems

Table 1. Treatment Alternatives to Fulfill Different Effluent Requirements[a]

Treatment Requirement	Treatment Alternatives
Partial treatment (pre-treatment)	• Primary clarifier • Septic tank • Imhoff tank • Anaerobic pond • Surface-flow constructed wetlands
Physicochemical treatment	• Chemical precipitation combined with partial treatment one- or two-stage (+flocculation)
Complete organic matter removal	• Nonaerated and aerated pond • Rotating biological contactor • Trickling filter • Biofilter • Moving bed reactor • Subsurface horizontal-flow constructed wetlands • (Activated sludge)
including phosphorus removal	• Chemical precipitation in combination with most other technologies
including nitrification	• Extended aeration • Sequencing batch reactors (SBR) • Rotating biological contactor • Trickling filter • Biofilter • Moving bed reactor • Subsurface vertical-flow constructed wetlands • Sand infiltration
including denitrification	• Activated sludge • Sequencing batch reactors (SBR) • Rotating biological contactor • Trickling filter • Biofilter • Moving bed reactor • Subsurface-flow constructed wetlands
Pathogen removal	• Activated sludge, sequencing batch reactors (SBR) • Soil infiltration • Subsurface vertical-flow constructed wetlands • Disinfection (UV, chlorine, ozone)

[a] References 2 and 3.

Table 2. Low and High Rate Treatment Systems[a]

Low Rate Systems				High Rate Systems
• Sand infiltration • Soil infiltration • Constructed wetlands • Ponds				• Conventional activated sludge systems • Sequencing batch reactors (SBR) • Rotating biological contactor • Trickling filter • Biofilter • Moving bed reactor • Extended aeration
low	←	loading rates	→	high
low	←	oxygenation rates	→	high
low	←	oxidation rates	→	high
low	←	biomass concentration	→	high
high	←	volume and area requirements	→	low
low	←	skilled control	→	high

[a] Reference 2.

are relatively easy to construct and operate; and their low costs (especially operating costs), which makes them attractive to communities with a limited budget. However, their simplicity and low cost may be deceptive in that the systems require frequent inspections and constant maintenance to ensure smooth operation (low maintenance does not mean no maintenance).

Mainly because of the land requirements for natural systems, many communities prefer technical systems, which tend to require less land and permit better control of the operation. However, these systems generally are high cost and require more skilled personnel to operate them. The disadvantages generally relate to the cost of construction and ease of operation. Mechanical systems can be costly to build and operate because they require specialized personnel. Generally, the complexity and cost of wastewater treatment technologies increase with the quality of the effluent produced.

Table 3 compares the specific reactor area and volume of systems used in small wastewater treatment plants. Additionally, the capability of the systems to nitrify is shown.

All systems described can be used for decentralized or 'on-plot' treatment and centralized or 'off-plot' treatment. For decentralized solutions, safe disposal of excreta takes place on or near a single household or a small settlement. Centralized solutions collect excreta from individual houses and carry them away from the plot to be treated off-site. The selection of the most appropriate sanitation system is influenced by ecological, technical, social, cultural, financial, and institutional factors.

COSTS

The costs of a wastewater treatment plant can be subdivided into investment and operating costs. To include the payback of the investment, the investment costs are transformed into yearly costs (using an economical interest rate; 3.5% is used in the examples given below). In the examples, the assumed lifetime of the treatment system (SBR and constructed wetland) is 20 years; for the sewer system, a lifetime of 40 years is assumed.

Table 4 compares specific investment, operating, and yearly costs of a technical treatment system (SBR) and a constructed wetland (subsurface vertical-flow, intermittently loaded). Additionally, two sizes of the treatment plant are compared, 100 and 500 PE (people equivalent). Both treatment systems have to fulfill the same effluent requirements (nitrification); the same sewer line configuration is used in both cases. The investment and operating costs for the sewer are estimated at about $1500\ \mathrm{EUR} \cdot \mathrm{PE}^{-1}$ and $5\ \mathrm{EUR} \cdot \mathrm{PE}^{-1} \cdot \mathrm{yr}^{-1}$, respectively. The investment costs for the two treatment systems are similar; specific costs increase as plant size decreases. However, the constructed wetland system shows lower operating and therefore lower yearly costs.

Seven different treatment scenarios for individual solutions for wastewater treatment of a single house (5 PE) are compared:

1. *Technical treatment system*: A conventional technical treatment system is used, and the effluent is discharged.

Table 3. Specific Reactor Area and Volume of Systems Used in Small Wastewater Treatment Plants[a]

System	Area/PE, m^2	Volume/PE, m^3	Contact Time	Nitrification
Nonaerated pond	10	10–15	>20 d	—
Soil infiltration	4–20	7–12	—	+
Surface-flow constructed wetland	5–10	5–15	>10 d	—
Aerated pond	3	4–7	>3–6 d	±
Subsurface horizontal-flow constructed wetland	4–8	3–5	1–4 d	—
Buried sand filter	4–6	4–6	1 h–7 d	+
Subsurface vertical-flow constructed wetland	2–5	1–3	1–3 d	+
Nitrifying trickling filter	0.17–0.3	0.45–0.6	6–10 min.	+
Extended aeration	0.12–0.25	0.35–0.6	1–3 d	+
Sequencing batch reactors (SBR)	0.1–0.2	0.3–0.5	1–3 d	+
Nitrifying rotating biological contactor	0.1–0.18	0.17–0.25	10–20 h	+
Nonnitrifying trickling filter	0.05–0.08	0.13–0.18	3–6 min	—
Nonnitrifying rotating biological contactor	0.04–0.07	0.07–0.13	8–15 h	—
Nitrifying biofilter	0.005–0.01	0.02–0.03	30–50 min.	+
Nonnitrifying biofilter	0.005–0.01	0.013–0.03	20–40 min.	—

[a] Reference 2, revised.

Table 4. Comparison of Specific Investment, Operating, and Yearly Costs for a Technical Treatment System (SBR) and a Constructed Wetland[a]

System		SBR		Constructed Wetland	
Size of the Treatment Plant	PE	500	100	500	100
Investment costs	$EUR \cdot PE^{-1}$	430	770	420	690
Operating costs	$EUR \cdot PE^{-1} \cdot yr^{-1}$	22	44	15	36
Yearly costs	$EUR \cdot PE^{-1} \cdot yr^{-1}$	128	174	120	160

[a] Reference 4, modified.

2. *Constructed wetland*: A constructed wetland system is used instead of the technical solution. The effluent is discharged.
3. *Cesspit and disposal* of cesspit waste: All wastewater is collected in a cesspit, and the cesspit waste is disposed of periodically at a wastewater treatment plant.
4. *Cesspit and agricultural use* of cesspit waste: The same as No. 3, but the cesspit waste is used in agriculture.
5. *Cesspit for blackwater (disposal* of cesspit waste) and constructed wetland for *graywater treatment*: Blackwater and graywater are separated. Only blackwater is collected in the cesspit and disposed of periodically. Graywater is treated using a constructed wetland.
6. *Cesspit for blackwater* (*agricultural use* of cesspit waste) and constructed wetland for *graywater treatment*: The same as No. 6, but the cesspit waste is used in agriculture.
7. *Urine separation* (agricultural use of urine and feces) and constructed wetland for graywater treatment: Separation of urine and feces; both are used in agriculture. Graywater is treated using a constructed wetland.

Table 5 compares the investment, operating, and yearly costs for different treatment scenarios.

The constructed wetland system has yearly costs lower than to the conventional technical treatment system. When all wastewater is collected in a cesspit, the yearly costs of the scenario for agricultural use of the cesspit waste are only about 75% of the yearly costs when disposing of the waste at a wastewater treatment plant. However, all scenarios using source separation have the lowest operating and yearly costs. Separating toilet water from graywater leads to a tremendous reduction of the volume that has to be collected, and, therefore, the operating and also the yearly costs drop drastically. Urine separation has the lowest costs and, additionally, closes water and nutrient cycles on a local scale. Therefore, it is a promising system toward more ecologically sound sanitation.

SUMMARY

Wastewater treatment plants for small communities, groups of houses, and also single houses have to handle special wastewater characteristics such as highly fluctuating wastewater flows and high concentrations of wastewater constituents (and additionally with high fluctuations). Therefore, treatment systems for small-scale applications should have high process robustness and stability and a large buffer volume. Additionally, they should have simple technology, they should be easy to operate and maintain, and should have low surplus sludge production.

Table 5. Comparison of Investment, Operating, and Yearly Costs for the Treatment Alternatives for a Single Household with 5 PE[a]

Scenario System[b]		1 Technical System	2 CW	3 CP	4 CP	5 CP (BW)	6 CP (BW)	7 US
Disposal of cesspit waste				WWTP	AU	WWTP	AU	AU
Separation of black-/graywater		No	No	No	No	Yes	Yes	Yes + US
Graywater treatment						CW	CW	CW
				Investment costs				
Treatment unit	$EUR.PE^{-1}$	1450	1450	1780	1780	1120	1120	1160
Sewer	$EUR.PE^{-1}$	350	350	230	230	410	410	290
				Operating costs				
Treatment unit	$EUR.PE^{-1}.yr^{-1}$	240	170	370	230	160	130	90
Sewer	$EUR.PE^{-1}.yr^{-1}$	5	5	5	5	5	5	5
Yearly costs	$EUR.PE^{-1}.yr^{-1}$	**362**	**292**	**468**	**336**	**246**	**208**	**192**

[a] Reference 4, modified.

[b] CW: constructed wetland; CP: cesspit; CP(BW): cesspit only for blackwater; WWTP: wastewater treatment plant; AU: agricultural use; US: urine separation.

Different requirements for treatment efficiency arise, depending on the local situation. Several treatment methods can be used to meet these requirements. The selection of the most appropriate sanitation system is influenced by ecological, technical, social, cultural, financial, and institutional factors.

For a small wastewater treatment plant, especially, low operating costs are essential. It was shown that for single households, solutions with source control separating at least blackwater and graywater yield significantly lower costs compared to solutions where the different types of wastewater are mixed and, therefore, a large volume has to be treated.

BIBLIOGRAPHY

1. Lens, P., Zeeman, G., and Lettinga, G. (Eds.). (2001). *Decentralized Sanitation and Reuse-Concepts, Systems and Implementation*. IWA Publishing, London, UK.
2. Boller, M. (1997). Small wastewater treatment plants—a challenge to wastewater engineers. *Water Sci. Technol.* **35**(6): 1–12.
3. US EPA. (2002). *Onsite Wastewater Treatment Systems Manual*. Report No. EPA/625/R-00/008. US EPA, Cincinnati, OH.
4. BMLFUW. (2002). Kosten-Nutzen-Überlegungen zur Gewässerschutzpolitik in Österreich mit besonderer Berücksichtigung des ländlichen Raumes (Cost-benefit analysis of water pollution control in Austria with a special focus on rural areas). *Schriftenreihe des BMLFUW*. Vienna, Austia [*in German*].

READING LIST

Lange, J. and Otterpohl, R. (2000). *Abwasser—Handbuch zu einer zukunftsfähigen Wasserwirtschaft* (*Wastewater—Manual for sustainable water management*), 2nd Edn. MALLBETON-Verlag, Donaueschingen-Pfohren, Germany [*in German*].

Watanabe, Y. (Ed.). (1997). Small wastewater treatment plants III. *Water Sci. Technol.* **35**(6).

Wilderer, P.A. and Deininger, A. (Eds.). (2000). Small wastewater treatment plants IV. *Water Sci. Technol.* **41**(1).

MICROBIAL FOAMING AND BULKING IN ACTIVATED SLUDGE PLANTS

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BACKGROUND

Microbial foaming and bulking are among the most frequent and widespread problems in activated sludge (AS) wastewater treatment plants (WWTPs). Bulking has plagued AS plants almost since their inception nearly a century ago, whereas microbial foaming was not documented until around 30 years ago. Both problems are associated with the excessive growth of various filamentous bacteria, although the mechanisms by which they form are not fully understood. Initial attempts to identify these bacteria shifted attention from engineering aspects to the microbiological activities fundamental to the activated sludge process. Subsequently, filament identification keys and abundance scales became routine tools for monitoring filamentous populations in activated sludge. More recently, molecular biological techniques have enabled more detailed and precise study of the diversity and ecology of bacterial communities associated with foaming and bulking.

CURRENT REGULATION OF WASTEWATER TREATMENT

Within the European union, treated effluents must comply with the standards set out in the EU Urban Wastewater Treatment Directive (1). The Directive states the minimal standards for the treatment and disposal of wastewater and waste sludge via WWTPs. These standards include the maximum biological oxygen demand (BOD; 20 mg/L) and level of suspended solids (SS; 30 mg/L), known as the 20:30 standard, allowed in treated effluents (2). In AS plants, the quality of the final effluent is governed by factors that affect both biological oxidation in the aeration basins and sludge separation in the final clarification tanks.

FOAMING AND BULKING ARE SLUDGE SEPARATION PROBLEMS

Central Role of Activated Sludge Floc

Activated sludge is comprised of three-dimensional aggregate structures, known as flocs, that contain microorganisms and abiotic matter. The structure of these flocs, including firmness, shape, and size determines the settling and compacting characteristics of the sludge solids. In 'healthy' flocs, filamentous bacterial growth creates a framework onto which other floc-forming bacteria can attach, and provides the strength required for the floc to remain intact in the turbulent environment of the aeration basin (3). However, excessive growth of various types of filaments can alter floc structure and interfere with the separation and recycling of sludge solids; this is observed in both microbial foaming and bulking.

Mechanism of Foam Formation

Microbial foam manifests on the surfaces of activated sludge aeration tanks as a dense, frothy, grey-brown, viscous scum, often described as having a 'chocolate mousse' appearance (Fig. 1). The majority of microbial foams are extremely stable and persistent and can accumulate to depths of more than a meter (4).

Foams consist of aggregates of air bubbles in liquid, flocs, and large numbers of filamentous bacteria, which selectively accumulate on the surface of mixed liquor

Figure 1. Microbial foam on the surface of (**a**) a mechanically agitated aeration basin and (**b**) a final clarifier, where it has partially dried out placing the tank out of operation.

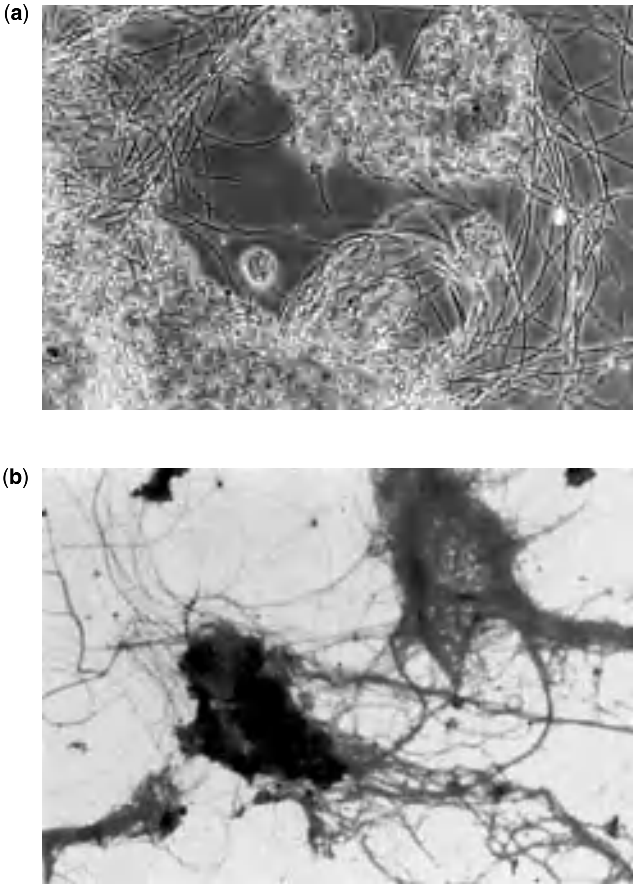

Figure 2. Microscopic examination of bulking activated sludge: (**a**) wet mount preparation viewed under phase contrast (×330 magnification) showing excessive growth of Eikelboom type 021N extending into the bulk phase and bridging adjacent flocs and (**b**) Gram-stained preparation viewed under bright-field (× 330) showing 021N filaments stained gram-negative forming large entangled knots (upper right) and surrounding the flocs (lower left).

by flotation. It is thought that excessive growth of hydrophobic bacteria in the mixed liquor renders flocs hydrophobic and hence amenable to attachment to air bubbles that are introduced to the mixed liquor by aeration. Large open flocs, it is thought, require only a few hydrophobic sites to adhere to air bubbles (5). The air bubble–floc aggregates have a lower density than water and rapidly rise to the surface of aeration basins where they accumulate. Hydrophobic solids stabilize the foam by bridging the bubble lamellae, preventing liquid drainage and subsequent breakdown.

Microbial Bulking

Bulking is caused by extensive and uncontrolled growth of various filamentous bacteria, both within and extending from the confines of flocs into the bulk liquor (Fig. 2). This results in a diffuse, open floc structure and interfloc bridging that can interfere with the settling and compaction of sludge solids in the final clarifiers. The supernatant is usually clear because bulking flocs filter out suspended particles (6). Although a blanket of scum may appear on the mixed liquor surface, bulking sludge is generally less easy to detect visually than foam. Several empirical methods have been devised and are widely used in the wastewater industry to monitor sludge characteristics and diagnose bulking. These include the diluted sludge volume index (DSVI; 7) total extended filament length (TEFL), and subjective filament abundance scales (4,8).

Problems Caused by Foaming and Bulking

Foaming and bulking lead to a number of problems that may compromise operational efficiency and effluent quality and have inevitable financial and regulatory repercussions:

- Overflow of foam or blanket scum to the final clarifiers may lead to increased BOD and SS levels in the final effluent.
- Loss of solids means increased substrate-loading rates per unit of sludge in the aeration basins.
- Poor sludge settling and compaction caused by bulking affects the dewatering characteristics of waste activated sludge.

- Thick foams inhibit mixing and oxygen transfer at the surfaces of mechanically aerated basins, thereby restricting biological oxidation.
- Spillage of foam onto plant walkways can create hazardous working conditions, limit access to sections of the treatment unit, and create cleaning and odor problems.
- Release of poorly clarified effluent to receiving waters may disperse enterobacteria and viruses that are pathogenic to humans or animals.
- Pathogens may be carried in aerosols arising from windblown scum, which may be inhaled or ingested by plant workers or local inhabitants (9).

PREVENTION AND CONTROL OF FOAMING AND BULKING

There are no definitive procedures for preventing and controlling either foaming or bulking. Most proposed measures are derived from experiences within one plant or laboratory scale system or from questionnaire-based surveys and hence not universally applicable (4,10–12). Chemical treatment methods, such as chlorine or hydrogen peroxide dosing, are only temporary measures; these oxidants are nonselective; therefore, organisms that are beneficial to the AS process may also be adversely affected. Antifoaming agents, bioadditives containing enzymes, microorganisms and nutrients, coagulants and iron salts, used to treat foams, vary in success but are generally not cost-effective. Filaments implicated in foaming and bulking are considered slow growers and may be washed out of the AS system by reducing the sludge age or mean cell residence time (MCRT). This approach is usually not suitable in plants where nitrification is essential because the MCRT necessary for nitrifying bacteria exceeds that required to washout filaments. Selector technology is an engineering approach, whereby modified or additional bioreactor tanks impose environmental conditions that place undesirable filaments at a competitive disadvantage to other floc-formers (13,14). However, selector tanks are not effective against all foaming or bulking filament types as these can vary considerably in their metabolic activities.

BACTERIA INVOLVED IN FOAMING AND BULKING

Filament Identification Schemes

Eikelboom (15) published the first key recommended for identifying filaments in activated sludge. In this scheme, filaments were identified by taxonomic name or given a morpho-type number and assigned to groups based on morphology, staining properties, example, Gram's stain, and the occurrence of cell inclusions, example, sulfur granules, determined by microscopy. This artificial classification, used in conjunction with filament abundance scales, has enabled comparative studies of filament composition and floc structure in AS plants in different regions of the world, under different plant operating conditions, and during bulking and foaming episodes. Microscopic examination is relatively simple and inexpensive, and regular monitoring can provide an early indication of foaming and bulking (16,17). Several additional schemes are available for filament identification (4,8,18), including color posters (19) and computer software formats (20).

The Usual Suspects

Numerous foaming and bulking plants have been surveyed worldwide to establish the relative abundance of different filament types. The same filaments are often reported in different geographical regions, though their relative abundance may vary, and several filaments occur in both foaming and bulking sludges. Foaming was originally attributed to gram-positive branched filaments identified as members of the genus *Nocardia* (21). Subsequent studies have reported many other species related to *Nocardia* in foams, including nonfilamentous types; these organisms are phylogenetically related and are termed collectively mycolic acid-containing actinomycetes (22,23). The gram-positive, unbranched filament *Microthrix parvicella* (24) has also been reported in foaming AS plants in many parts of the world (Fig. 3).

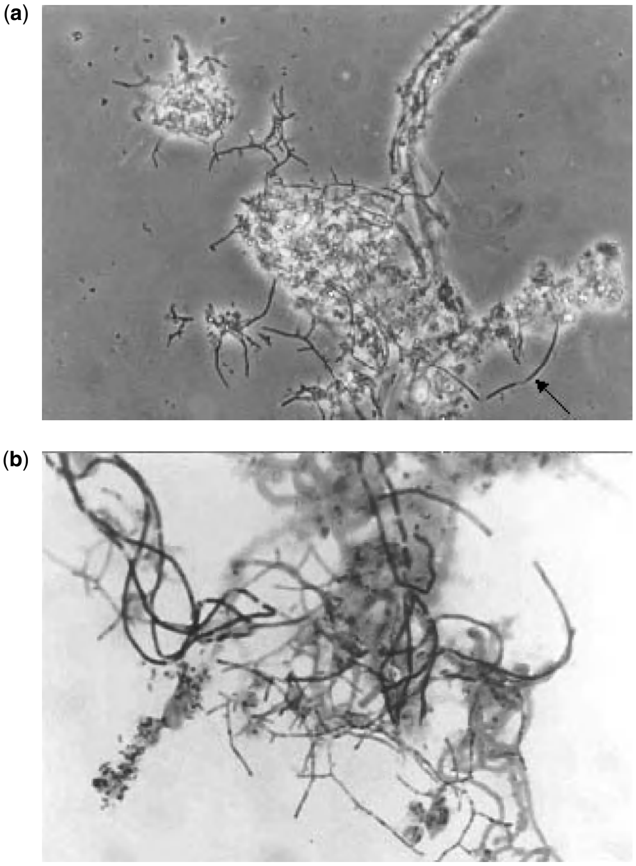

Figure 3. Microscopic examination of foaming activated sludge: (**a**) Wet mount preparation viewed under phase contrast (× 1000 magnification) and (**b**) Gram-stained preparation viewed under bright-field (× 1250). The dominant filaments are the spaghetti-like *Microthrix parvicella* with empty sections in trichome (arrow) and right-angled branched filaments with irregular staining patterns identified as mycolic acid-containing actinomycetes.

Other dominant filaments include *Halisocomenobacter hydrossis*, *Nostocoida limicola*, *Sphaerotilus* spp., and Eikelboom types 1863, 0092, 0041, and 0675 (13).

Filaments regularly associated with bulking in various parts of the world include *H. hydrossis*, *M. parvicella*, *Nocardia* spp., *N. limicola*, *Sphaerotilus natans, Thiothrix* spp., and types 021N, 1701, 0041, 0092, and 0675 (4,16). Geographical variations in filament populations may reflect differences in climate, wastewater composition, plant design, and operating conditions.

Isolation and Characterization of Filaments

Filament identification schemes provide a simplified view of the bacterial communities in activated sludge. Few bacteria can be accurately identified using only microscopy. Selective isolation studies, whereby dilutions of activated sludge or individual filaments extracted by micromanipulation are plated onto various nutrient media (23,24), enable the cultivation of bacteria in the laboratory for further characterization and identification. Studies that examine the genetic, phenotypic, and physiological traits of such organisms reveal that filaments with identical morphologies may be only distantly related in evolutionary terms and have quite different metabolic requirements (25,26). This, in turn, has profound implications for the development of engineering strategies to the control foaming and bulking organisms.

FACTORS AFFECTING THE GROWTH OF FOAMING AND BULKING ORGANISMS

Plant operating parameters, including mode of aeration, feed to mass ratio, and sludge retention time or MCRT, reportedly influence the proliferation of particular filament types (4). The composition of influent wastewater, substrate concentrations, and abiotic factors such as dissolved oxygen concentration, ambient temperature, mixed liquor pH, and redox potential are also important. The growth rates of bacteria and hence their ability to remain within the AS system also depend on their nutrient requirements and metabolic versatility. Mycolic acid-containing actinomycetes provide a good example because they can metabolize a diverse range of substrates. Many members of this group also produce biosurfactants (27,28), which aid foam stabilization and provide selective access to oils and fats prevalent in wastewater (29), which gives them a competitive advantage over many other bacteria.

MOLECULAR BIOLOGICAL TOOLS

Molecular biological techniques developed in the last decade are providing new insights into the complexity, dynamics, and ecophysiology of bacterial populations implicated in foaming and bulking. Fluorescent *in situ* hybridization (FISH) enables detecting and enumerating of particular phylogenetic groups of bacteria in activated sludge, irrespective of their morphology (30). Fluorescent-labeled nucleic acid probes can be designed to target cells of the whole bacterial community or at different phylogenetic levels down to individual species or even subspecies (31–33). Quantitative microautoradiography (QMAR) used together with FISH, allows *in situ* measurement of the uptake of specific radiolabeled substrates by individual bacterial cells that belong to particular phylogenetic groups (34). Information on the substrate utilization kinetics of different filamentous bacteria will help us to understand why they predominate in bulking or foaming AS plants and the operating conditions under which this occurs.

EXAMPLE: MONITORING FOAM-FORMING BACTERIA USING FISH

The micrograph image in Fig. 4a shows an example of FISH using two fluorescent-labeled probes. The technique involves fixation of an activated sludge sample to preserve the bacterial populations present, followed by permeabilization of the cells to allow the probes to enter and hybridize with target nucleic acid sequences. Treated samples are mounted on microscope slides and viewed by epifluorescence microscopy using a confocal laser scanning microscope (CLSM). Images of randomly selected fields of view can be captured, and the cells in a known volume

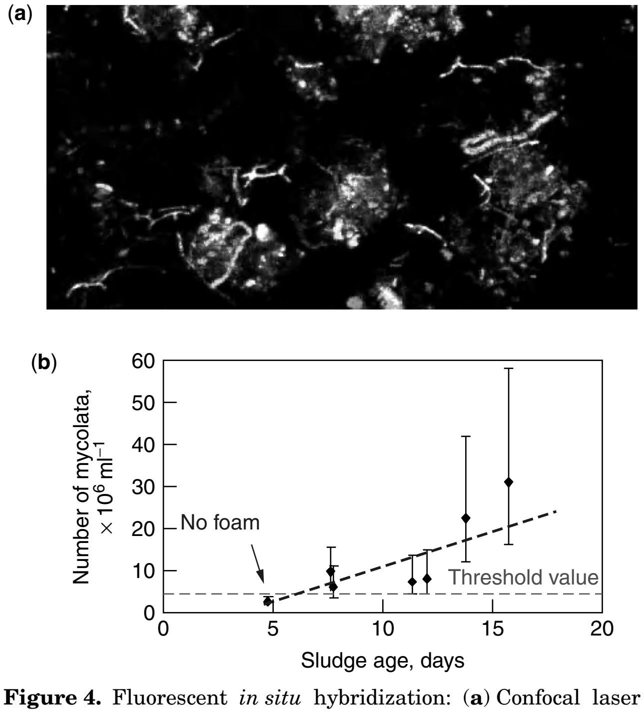

Figure 4. Fluorescent *in situ* hybridization: (**a**) Confocal laser scanning micrograph of activated sludge taken from a foaming WWTP. The sample is hybridized with two nucleic acid probes, a eubacterial-specific probe (Bact338) labeled with fluorescein isothiocyanate (FITC), which fluoresces green, and a mycolata-specific probe (Myc657) labeled with tetrarhodamine isothiocyanate (TRITC), which fluoresces red. Only bacterial cells that hybridize with both probes and appear yellow-orange in color are mycolata (mycolic acid-containing actinomycetes). (**b**) Plot showing the relationships between sludge age, numbers of mycolic acid-containing actinomycetes determined using quantitative FISH and foaming in an AS reactor. The error bars indicate 95% confidence intervals (courtesy of R. J. Davenport, unpublished data; 2003).

of activated sludge calculated using computer software. FISH has been used to monitor changes in the abundance of mycolic acid-containing actinomycetes in an AS plant operated at different sludge ages. The graph in Fig. 4b shows that a significant rise in the numbers of these organisms occurs with increasing sludge age and that there is a threshold in numbers that triggers foaming (32).

BIBLIOGRAPHY

1. European Commission Council Directive. Official Journal L135. (1991). Urban Waste Water Treatment Directive 91/271/EEC. EEC, Brussels, Belgium.
2. Gray, N.F. (1989). *Biology of Wastewater Treatment*. Oxford University Press, Oxford, UK.
3. Li, D-H. and Ganczarczyk, J.J. (1990). *Biotechnol. and Bioeng.* **35**: 57–65.
4. Jenkins, D., Richard, M.G., and Daigger, G.T. (1993). *Manual on the Causes and Control of Activated Sludge Bulking and Foaming*, 2nd Edn. Lewis, Boca Raton, FL.
5. Lemmer, H., Lind, G., Müller, E., Schade, M., and Ziegelmayer, B. (2000). *Acta Hydrochima et Hydrobiologica* **28**: 34–40.
6. Blackall, L.L. (1999). Bulking. In: *The Microbiology of Activated Sludge*. R.J. Seviour and L.L. Blackall (Eds.). Chapman & Hall, London, pp. 147–160.
7. Wanner, J. (1994). *Water Sci. Technol.* **29**: 193–203.
8. Eikelboom, D.H. and van Buijsen, H.J.J. (1983). *Microscopic Sludge Investigation Manual*, 2nd Edn. TNO Research Institute for Environmental Hygiene, Delft.
9. Carducci, A. et al. (2000). *Water Res.* **34**: 1173–1178.
10. Blackall, L.L., Harbers, A.E., Greenfield, P.F., and Hayward, A.C. (1991). *Water Res.* **25**: 313–317.
11. Foot, R.J., Robinson, M.S., and Forster, C.F. (1994). *Water Sci. Technol.* **29**: 213–220.
12. Pitman, A.R. (1996). *Water Sci. Technol.* **34**: 291–298.
13. Soddell, J.A. (1999). Foaming. In: *The Microbiology of Activated Sludge*. R.J. Seviour and L.L. Blackall (Eds.). Kluwer, Boston, pp. 161–202.
14. Grady, C.P.L. and Filipe, C.D.M. (2000). *Water Air Soil Pollut.* **123**: 117–132.
15. Eikelboom, D.H. (1975). *Water Res.* **9**: 365–388.
16. Eikelboom, D.H., Andreadakis, A., and Andreasen, K. (1998). *Water Sci. Technol.* **37**: 281–289.
17. Madoni, P., Davoli, D., and Gibin, G. (2000). *Water Res.* **34**: 1767–1772.
18. Wanner, J. and Grau, P. (1989). *Water Res.* **23**: 883–891.
19. Seviour, E.M., Lindrea, K.C., Seviour, R.J., and Soddell, J.A. (1997). Colour Posters to Assist in the Identification of Filamentous Bacteria and Protozoa in Activated Sludge Biomass. *Proc. 2nd Int. Conf. Microorganisms Activated Sludge Biofilm Processes*. July 21–23, Berkeley, CA, pp. 633–635.
20. de Arcaya Alvarez, J.M., Blanco, J.M., Urbano, C., and Palmer, A. (1997). A Computer Program for the Identification of Activated Sludge Microorganisms. *Proc. 2nd Int. Conf. Microorganisms Activated Sludge Biofilm Processes*. July 21–23, Berkeley, CA, pp. 67–670.
21. Lechevalier, M.P. and Lechevalier, H.A. (1974). *Int. J. Syst. Bacteriol.* **24**: 278–288.
22. Soddell, J.A. and Seviour, R.J. (1998). *J. Appl. Microbiol.* **84**: 1–13.
23. Stainsby, F.M., Soddell, J., Seviour, R., Upton, J., and Goodfellow, M. (2002). *Water Sci. Technol.* **46**: 81–90.
24. Blackall, L.L. et al. (1996). *Int. J. Syst. Bacteriol.* **46**: 344–346.
25. Seviour, E.M. et al. (1997). *J. Appl. Microbiol.* **82**: 411–421.
26. Kanagawa, T. et al. (2000). *Appl. Environ. Microbiol.* **66**: 5043–5052.
27. Lang, S. and Philip, J.C. (1998). *Antonie Leeuwenhoek* **74**: 59–70.
28. Philp, J.C. et al. (2002). *Appl. Microbiol. Biotechnol.* **59**: 318–324.
29. Soddell, J.A. and Seviour, R.J. (1996). *Water Sci. Technol.* **34**: 113–118.
30. Davenport, R.J. and Curtis, T.P. (2002). *Water Sci Technol.* **46**: 529–533.
31. Wagner, M., Amann, R., Lemmer, H., Manz, W., and Schleifer, K-H. (1994). *Water Sci. Technol.* **29**: 15–23.
32. Davenport, R.J., Curtis, T.P., Goodfellow, M., Stainsby, F.M., and Bingley, M. (2000). *Appl. Environ. Microbiol.* **66**: 1158–1166.
33. de los Reyes, F.L. and Raskin, L. (2002). *Water Res.* **36**: 445–459.
34. Nielsen, J.L., Christensen, D., Kloppenborg, M., and Nielsen, P.H. (2003). *Environ. Microbiol.* **5**: 202–211.

AQUEOUS BEHAVIOR OF ELEMENTS IN A FLUE GAS DESULFURIZATION SLUDGE DISPOSAL SITE

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FLUE GAS DESULFURIZATION PROCESS DESCRIPTION

Most conventional combustion processes emit sulfur oxides, nitrogen oxides, carbon oxides, particulate matter, and other potentially harmful pollutants into the air. Solid wastes from combustion processes or from associated control technologies present disposal and environmental health problems. Adverse water-related health and ecological effects might result when chemical compounds and metals are leached from solid residues.

Flue gas desulfurization (FGD) systems are end of process pollution abatement techniques used primarily for removing sulfur dioxide from coal-fired utility and industrial boiler combustion gases. The technology has also been successfully applied to Claus sulfur recovery unit tail gas and sulfuric acid plant tail gas streams. Sulfur dioxide (SO_2) and particulate emissions are controlled by a flue gas scrubber system. The scrubber is often designed as an integral part of the steam generation plant. It consists of a two-stage venturi-absorber scrubber module designed to treat boiler flue gas. The flue gas from the boiler enters the air quality control system through a common plenum. The gas stream is sent to the individual scrubber modules from this plenum.

The sulfur-laden flue gas first passes through an electrostatic precipitator or venturi scrubber for particulate removal and then into a multistage absorber where it contacts the absorption slurry. Scrubbed gas passes through a demister and is reheated prior to discharge to the atmosphere to provide buoyancy and prevent condensation. Sulfur dioxide removal is normally 85–90%. Up to 99% of the particulate matter is removed from the gas stream at this point (1). The particles are entrained in the liquid that drops into the bottom sump. The gases then pass through the SO_2 absorber section. The SO_2 is removed by adsorption as the gas stream is drawn through stainless steel sieve trays that are sprayed with the absorption slurry. This slurry with the absorbed SO_2 also drops into the bottom sump. The gas stream then passes through a demister section in which excess moisture and mist are removed. Then, the gases are reheated to increase the gas temperature for improved gas buoyancy and to reduce the probability of deposits on the induced air fans. Upon exiting the scrubber, the gases are sent to the stack.

Wet desulfurization processes produce large quantities of nonregenerable waste. Wet scrubbing processes may use calcium carbonate ($CaCO_3$), calcium oxide (CaO), alkaline fly ash, and sodium carbonate (Na_2CO_3) as scrubbing materials (2,3). Limestone-based FGD systems are nonregenerable processes where the reactive component in the absorbent slurry combines chemically with SO_2 to form a sludge that consists of fly ash, water, calcium sulfate, and calcium sulfite. The calcium sulfate and calcium sulfite sludges are waste by-products. Sodium-based scrubbing systems produce sludge that typically contains unspent scrubber material, sodium sulfite and sulfate, and entrained fly ash. Unlike calcium-based systems, the waters that characterize sodium-based FGD processes and their associated sludge have high concentrations of dissolved solids dominated by sodium and sulfate ions. Sodium-based FGD processes and their associated sludge pond systems may also generate hydrogen sulfide as a by-product, which could be emitted into the atmosphere.

LIMESTONE/LIME-BASED FGD SYSTEMS

In limestone-based FGD systems, ground limestone mixed with water is used for making up the scrubber slurry. The slurry water is recycled from settling ponds where solids accumulate. The SO_2 and sulfur trioxide (SO_3) are removed from the flue gas stream by reaction with the aqueous solution of limestone. The major component of limestone is $CaCO_3$. The products from the SO_2 reaction are carbonic acid (H_2CO_3) and calcium sulfite hemihydrate ($CaSO_3{\bullet}\frac{1}{2}H_2O$). The products from the SO_3 reaction are carbonic acid and calcium sulfate dihydrate ($CaSO_4{\bullet}2H_2O$). The reactions are presented here:

$$SO_2 + 1.5\ H_2O + CaCO_3 \longrightarrow H_2CO_3 + CaSO_3{\bullet}\tfrac{1}{2}\ H_2O$$
$$SO_3 + 3\ H_2O + CaCO_3 \longrightarrow H_2CO_3 + CaSO_4{\bullet}2\ H_2O$$

The pH of the slurry is maintained at 5.5 to 6.0. The optimum pH for the chemical reactions is 5.6 to 5.8. If the pH exceeds 5.8, the amount of limestone required increases, and soft scale begins to accumulate rapidly. If the pH drops below 5.6, a hard gypsum ($CaSO_4{\bullet}2H_2O$) scale builds up on scrubber surfaces. Adjusting the rate at which limestone is added to the slurry controls the pH of the slurry.

In a lime-based FGD process, lime and sulfur dioxide react to form calcium sulfite or sulfate as follows:

$$CaO_{(s)} + SO_2 + \tfrac{1}{2}H_2O \longrightarrow CaSO_3{\bullet}\tfrac{1}{2}\ H_2O$$
$$CaO_{(s)} + SO_2 + 2\ H_2O + \tfrac{1}{2}\ O_2 \longrightarrow CaSO_4{\bullet}2\ H_2O$$

In this process, first lime hydrates and dissolves in the aqueous phase. Next, sulfur dioxide dissolves in the aqueous phase where it participates in numerous ionic reactions. Finally, calcium sulfite and sulfate form precipitates that are removed from the aqueous phase.

Oxidation is important in this system. If the system oxidation is very low, all of the calcium sulfate produced will leave in the liquid phase. If the oxidation is below a critical value, generally considered to be approximately 20%, the sulfur will leave as a solid solution of calcium sulfite/sulfate. If the oxidation rate is high, the sulfate builds to supersaturation, and gypsum precipitates. If the extent of supersaturation is above 1.3 to 1.4, scaling can occur (4–6).

Under ideal conditions, a forced-oxidized limestone-based FGD system will produce wallboard grade gypsum. An important factor in the quality of the gypsum produced by such a FGD system is the amount of chlorine in the coal. The chlorine content of the fuel and the chloride concentration in the makeup water control the volume of liquid bleed needed to manage the chloride level in the FGD system. Because few chloride ions can leave the process in the washed gypsum product, almost all of the chloride that enters with the coal must be purged from the system as a blowdown. This blowdown is the FGD scrubber purge water, which will require treatment before it can be discharged to most receiving waters.

The solid wastes generated by combustion are removed from the system as slurries. The electric power industry generally uses ponds and landfills to dispose of sludge. When an oxidation step is included, the limestone-based FGD system yields a sludge that is mostly calcium sulfate (gypsum). Inhibited or nonforced oxidation systems produce sludges that are mostly calcium sulfite. The solids that settle to the bottom of the settling ponds are periodically dredged. The majority of the solid waste is disposed of in a company-owned landfill.

FGD SCRUBBER PURGE WATER CHARACTERISTICS

Table 1 presents the chemical characteristics of purge waters from forced and inhibited oxidation limestone-based FGD systems (7). These data indicate that purge water from FGD systems that are designed for forced oxidation are lower in reduced sulfur species than nonforced oxidation processes but may still contain high concentrations of thionates and sulfur–nitrogen compounds. Trithionate is the dominant thionate in nonforced oxidation systems, whereas dithionate is most prevalent in forced oxidation purge water. Thiosulfate is the dominant reduced sulfur species in nonforced oxidation FGD system purge water.

These wastewaters contain numerous alkali metals and alkaline earth metals, as indicated in Table 2; calcium,

Table 1. FGD Scrubber Purge Water Characterization[a]

Parameter	Nonforced Oxidation, mg/L	Forced Oxidation, mg/L
pH units	6.3	6.9
Total alkalinity as $CaCO_3$	130	450
Total dissolved solids	58,200	11,700
Chemical oxygen demand	1,340	1,260
Chloride	28,900	3,460
Fluoride	30	23
Ammonia as nitrogen	<5	<5
Total Kjeldahl nitrogen	9.5	7.8
Nitrate as nitrogen	<2	<2
Nitrite as nitrogen	<0.1	6.4
Sulfide	<5	<5
Sulfite	41	<6
Sulfate	815	4,730
Thiosulfate	1,010	<12
Total hydrolyzable sulfur (as sulfate)	2,570	3,600
Dithionate	54	162
Trithionate	427	<6
Tetrathionate	102	<6
Hydroxylamine disulfonate (HADS)	386	127
Selenium	0.536	0.204
Nickel	0.929	0.972
Iron	8.98	0.019
Calcium	6,770	1,190
Magnesium	4,420	1,450

[a] Reference 7.

magnesium, sodium, potassium, and barium are present at the highest concentrations (8). The high chloride content of the combusted coal is the principal reason for the elevated concentrations of calcium and magnesium in the inhibited (nonforced) oxidation limestone-based FGD system purge water. Aluminum, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, silver, nickel, and iron also are present at detectable concentrations, but only nickel exists at levels requiring treatment.

Table 2. FGD Scrubber Purge Water Metals Analysis[a]

Parameter	Nonforced Oxidation, mg/L	Forced Oxidation, mg/L
Aluminum	0.707	0.0733
Antimony	<0.00532	0.0022
Arsenic	<0.00345	<0.00345
Barium	1.02	0.245
Beryllium	<0.00198	<0.00198
Cadmium	0.00562	0.00954
Calcium	6,770	1190
Chromium	<0.00122	0.0061
Cobalt	0.0531	0.0538
Copper	<0.00166	0.00436
Lead	<0.00273	<0.00273
Magnesium	4420	1450
Manganese	1.44	40
Molybdenum	0.1	0.0663
Potassium	174	18.4
Silver	0.00164	0.00268
Sodium	1580	123

[a] Reference 8.

These purge waters also contain selenium at concentrations that require treatment to achieve an acceptable discharge quality. It is known that selenium forms complexes with both thionates and thiosulfate. Typical selenium–thionate complexes include selenopentathionate [$Se(S_2O_3)_2{}^{2-}$] and selenotrithionate; selenothiosulfate ($SeS_2O_3{}^{2-}$) is a typical complex of selenium and thiosulfate (7). These complex ions of selenium can increase the concentration of dissolved selenium in FGD sludge disposal pond waters.

ASH POND AND FGD SLUDGE POND WATER QUALITY

The ash pond and the FGD sludge pond are the major wastewater treatment facilities at electric utilities. The pond waters from FGD sludge disposal sites are usually slightly alkaline and oxidized; pH values are between 7 and 9, and oxidation–reduction potential (ORP) values are from +490 to +290 mV, respectively. Below the oxidized surface layer, the sludge and porewaters are generally highly reducing; ORP values average approximately −300 mV. In this environment, rainfall can impact the dissolution of sulfate, sulfite, and sulfide solids which in turn controls the leachate concentrations of metals (e.g., barium, calcium, cadmium, copper, iron, nickel, lead, strontium, and zinc), metalloids (e.g., antimony, boron, arsenic), and nonmetals (e.g., fluorine and selenium). Field observations have indicated that anaerobic, heterotrophic sulfate-reducing and denitrifying microbes are present in significant populations in FGD sludge and impact the geochemistry of these materials (2,3). Consequently, the low ORP measurements typically observed in FGD sludge porewater are indicative of active dissimilative metabolism that results in microbial reduction of sulfate to hydrogen sulfide.

FGD sludge porewater chemical characteristics for both calcium-based and sodium-based SO_2 scrubber systems are presented in Table 3 (2,3). These data show the range of constituent concentrations that may be found in FGD sludge porewater for a variety of coals and sulfur removal processes. Table 4 presents a comparison of constituent chemistries for FGD sludge liquors and elutriates from a variety of calcium-based and sodium-based SO_2 scrubber systems for power plants that burn either western or eastern US coals (9,10). The large variation in the water chemistry of desulfurization sludges is indicative of the complex nature of FGD sludge–water systems as well as the potential environmental impact that may result from improper disposal of these materials. Elevated concentrations of arsenic, boron, chloride, fluoride, and selenium in FGD sludge liquors and elutriates present unique problems for environmental management and control.

A high potential for H_2S odors from FGD sludges is suggested by the porewater sulfur speciation data. The substantial quantity of reduced sulfur species observed in porewaters results partly from dissimilatory sulfate reduction by *Desulfovibrio sp.* and related microorganisms (2). It is surmised that the variation in the concentrations of reduced sulfur species may result from microbial use of thiosulfate and sulfite as well as sulfate and the degree of oxygen penetration into the underlying sludge porewaters.

Table 3. FGD Sludge Porewater Chemical Characteristics

Constituent	Calcium-Based SO_2 Scrubber Systems (3), mg/L	Sodium-Based SO_2 Scrubber Systems (2), mg/L
Sulfide	<0.4–305	0.7–2,046
Thiosulfate	<0.25–345	BDL–5,200
Sulfite	<0.1–98.7	BDL–66.4
Sulfate	1,480–12,000	15,420–158,910
Aluminum	<0.05–0.28	BDL[a]
Arsenic	0.01–7.9[b]	ND[d]
Arsenic (III)	0.008–6.7[c]	ND
Arsenic (V)	<0.012–1.19[c]	ND
Barium	0.014–0.09	BDL
Boron	15.4–111	713–1,220
Calcium	607–874	7.0–682
Cadmium	<0.002–0.009	BDL
Chloride	466–4,690	13,440–86,900
Chromium	<0.003–0.3	BDL
Copper	<0.015–0.25	BDL
Fluoride	ND	249–811
Iron	<0.02–0.12	BDL
Lead	<0.028–0.23	BDL
Magnesium	<8.4–720	122–4,210
Molybdenum	<0.1–3.47	BDL
Nickel	<0.03–0.35	BDL
Potassium	ND	691–3,200
Selenium	<0.01–1.03	ND
Selenium (IV)	<0.01–0.083[c]	ND
Selenium (VI)	0.01–0.28[c]	ND
Sodium	33.6–6,290	73,200–79,000
Strontium	7.0–16.1	0.52–25
Vanadium	0.024–0.04	BDL
Zinc	<0.02–0.21	BDL

[a] BDL = Below detection limits.

[b] Mean of two samples.

[c] Mean of nine samples.

[d] ND = Not determined.

Ash pond water at a typical bituminous coal-fired power plant may contain a number of pollutants that can impact the local soil and groundwater. These include the metals aluminum, copper, mercury, lead, nickel, and thallium; the metalloids arsenic and antimony; and the nonmetal selenium. Generally, fly ash handling wastes are the largest source of pollutants to an ash pond (11,12). Other smaller sources include bottom ash handling, plant sump wastes, and cooling tower discharges. Coal pile runoff may also be an intermittent source of pollution along with fly ash sluice water, which is generally at a low pH.

Under typical conditions, ash ponds provide sufficient residence time to reduce suspended solids concentrations below discharge limits (13,14). The solid particles that remain are those that are near or below the density of water and those that are so small that they exhibit properties that create a repelling force and prevent agglomeration and settling in the residence time available to them. These particles are generally clays and fine silt soils from naturally occurring portions of the fly ash waste stream or from commingled stormwater runoff. Heavy metal contaminants such as aluminum and iron in the discharge of ash ponds are directly related to the concentration of suspended effluent solids.

Table 4. Comparison of Constituents in FGD Sludge Liquors and Elutriates[a]

Constituent	FGD Sludge Liquors Eastern Coals, ppm	FGD Sludge Liquors Western Coals, ppm
Antimony	0.46–1.6	0.09–0.22
Arsenic	<0.004–1.8	<0.004–0.2
Beryllium	<0.0005–0.05	0.0006–0.14
Boron	41	8.0
Cadmium	0.004–0.1	0.011–0.044
Calcium	470–2,600	240–45,000[d]
Chromium	0.001–0.5	0.024–0.4
Cobalt	<0.002–0.1	0.1–0.17
Copper	0.002–0.4	0.002–0.6
Iron	0.02–0.1	0.42–8.1
Lead	0.002–0.55	0.0014–0.37
Manganese	<0.01–9.0	0.007–2.5
Mercury	0.0009–0.07	<0.01–0.07
Molybdenum	5.3	0.91
Nickel	0.03–0.91	0.005–1.5
Selenium	<0.005–2.7	<0.001–2.2
Sodium	36–20,000[b]	1,650–9,000[b]
Zinc	0.01–27	0.028–0.88
Chloride	470–5,000	1,700–43,000[c]
Fluoride	1.4–70	0.7–3.0
Sulfate	720–30,000[c]	2,100–18,500[b]

[a] References 9 and 10.

[b] The high-end concentration of sodium is for dual alkali FGD sludge and reflects a single measurement on an unwashed filter cake.

[c] The high-end concentrations of chloride and sulfate are for limestone scrubbing of FGD sludge and reflect a closed-loop process using cooling tower blowdown for process makeup water.

[d] Chloride forms weak complexes with many metals, including calcium, and these may be scavenged from solution by fly ash.

Arsenic and selenium are predominately present in their dissolved state in ash pond water and are poorly removed by this treatment. The forms most commonly found in ash pond water are arsenate (Arsenic V) and selenite (Selenium IV). The speciation of these constituents affects wastewater management because each element has a different treatment requirement that results from differences in their aquatic toxicity. For example, arsenate is more toxic to aquatic life than arsenite (Arsenic III). Fortunately, arsenate is effectively removed by iron coprecipitation, which is also an effective treatment for removing selenite from ash pond water (15). However, neither arsenite nor selenate (Selenium VI) are effectively removed by ferric oxyhydroxides. The fact that soluble arsenic and selenium are not effectively removed by ash ponds suggests that coprecipitation does not occur under normal operating conditions. This indicates a lack of either a source of ferric or ferrous ions within these ponds.

The wet sluicing of fly ash to a pond will increase the apparent concentration of copper and selenium in the pond for certain coal types (8). Wet sluicing will also affect the water quality throughout the pond. The elevated selenium concentrations in ash pond water are due primarily to the increased loading of the soluble form of this constituent that results from the physical act of sluicing. Copper concentrations are also high because of the lower pH conditions that are a consequence of the wet sluicing operation. The relationship between the copper concentration and the pH is supported by solubility theory in that the apparent concentration of copper is an order of magnitude higher at pH 6 than at pH 7 in slightly acidic ash ponds. The percent sulfur in the coal and the calcium content in the dry fly ash influence the pH of the ash sluice water. The solubilities of other metals are not as impacted as is copper by pH changes in the range 5 to 7.

Similarly, the character of the ash influences the concentrations of all heavy metals in an ash pond. For example, acidic fly ash contains high levels of carbonates and sulfates that affect the solubility of certain metals (e.g., copper, nickel, zinc) in the pond water. The amount of iron hydroxide present in the water influences the removal of trace metals by precipitation. Although the range of pH changes vary in different ash pond systems, heavy metal concentrations generally increase with decreasing water pH (8).

Both arsenic and selenium have been removed from wastewater using ferric oxyhydroxide treatment at low pH (7,15). Arsenate is removed effectively by iron coprecipitation at pH values up to 9, and selenite can be treated up to pH 7. However, both constituents are removed more effectively at lower pH. Ferric oxyhydroxide treatment is also effective for removing chromium (III), cadmium, lead, nickel, zinc, and vanadium from FGD sludge pond water. However, it is less effective for removing chromate (chromium VI) and completely ineffective for removing selenate (selenium VI) and boron from FGD sludge pond water.

The metals concentrations in ash and FGD sludge ponds are different because the capture mechanisms of the electrostatic precipitator (ESP), which removes fly ash from the flue gas, and the FGD scrubber, which removes SO_2 from the flue gas, are different. The FGD system captures less ash but more of the volatile metals than the ESP system (13). This results in a higher concentration of dissolved metals in FGD sludge pond water. The two treatment systems are also different because of differences in pond pH. The pH in the FGD sludge pond is usually lower than the pH in an ash pond system because of the nature of the limestone absorption system used for acid gas control in FGD scrubbers (16).

Metals that volatilize and stay in the gaseous form are captured preferentially in the FGD scrubber. Mercury in flue gas exists either as oxidized or elemental mercury. Generally, oxidized mercury is easily captured by the FGD system (17). It is also common to detect nickel at higher concentrations in FGD sludge ponds than in ash ponds because of the effect of chloride on nickel solubility. The presence of chloride at concentrations greater than 10 mM/L in FGD process liquor results in higher nickel solubility by forming soluble nickel–chloride complexes (8). Higher nickel concentrations in FGD sludge ponds also result from the fact that this metal is added with the limestone slurry. The loading of nickel from limestone slurry accounts for approximately 75% of all nickel found in the water of FGD sludge ponds.

The water-phase concentrations of most metals (i.e., copper, mercury, nickel, and zinc) are higher in FGD sludge ponds than in ash ponds. Copper and zinc concentrations are highest at a pH below 6 but decrease as pH values increase. The concentrations of aluminum and arsenic may be higher in ash ponds than in FGD sludge ponds because the concentrations of these constituents tend to increase at the higher pH of the ash pond (8).

Selenium is generally found at higher concentrations in water from FGD sludge ponds than in typical ash ponds (7). Selenium lies just below sulfur in the periodic table, and its chemistry is similar in many respects. Selenium exhibits variable valence from −II to +VI; the most common forms are Se^{2-}, Se^{4+}, and Se^{6+}. Several compounds containing selenium in the various oxidation states are shown in Table 5 with their sulfur analogs. Selenite (selenium IV) is the predominate form of selenium found in waters from ash ponds, and selenate (selenium VI) is the predominate form of selenium found in the waters from FGD sludge ponds (8).

Selenide is the dissociated form of hydrogen selenide (H_2Se). Like its sulfur analog (H_2S), hydrogen selenide is volatile in its associated form, although its vapor pressure is slightly lower than that of hydrogen sulfide. However, hydrogen selenide has much less tendency to volatilize than hydrogen sulfide because its pK_a (3.9) is much lower than that of $H_2S(pK_a = 7.0)$. The principal forms of selenium in FGD sludge pond water are selenite and selenate, which are stable in water and act independently of each other. Generally, selenite is present at lower concentrations because it occurs mainly in acidic and moderately oxidizing waters whereas selenate is predominant in waters that are alkaline and oxidizing. The occurrence of selenium as an oxyanion in water gives it acid characteristics. Selenous acid (H_2SeO_3) is a weak acid ($pK_a = 2.8$) that dissociates in water to $HSeO_3{}^-$ and $SeO_3{}^{2-}$. The concentrations of $SeO_3{}^{2-}$ and $HSeO_3{}^-$ are pH dependent; $SeO_3{}^{2-}$ occurs predominantly at a neutral pH. The hydroxides of iron readily adsorb selenite, thus fixing it in soils as a ferric–selenite complex. However, selenic acid (H_2SeO_4) is a strong acid ($pK_a = -3.0$) that dissociates to give $SeO_4{}^{2-}$. Selenate salts are more soluble than the corresponding selenite salts and are not affected by iron hydroxides (7). Selenate behaves like the sulfate ion in natural waters. Consequently, selenium can readily enter the food chain as selenate through soils, into plants, and finally to animals. Elemental selenium exists in several crystalline and amorphous forms; the crystalline metallic form is the most stable and relatively insoluble in water.

The remaining selenium in FGD sludge pond water is probably present as selenotrithionate, a complex ion (7). It is surmised that the addition of the thiosulfate ion displaces sulfite from selenotrithionate to give

Table 5. Forms of Selenium and Sulfur in FGD Sludge Pond Water (7)

Valence	Selenium	Sulfur
−II	Selenide (Se^{2-})	Sulfide (S^{2-})
0	Elemental (Se^0)	Elemental (S^0)
+IV	Selenite ($SeO_3{}^{2-}$)	Sulfite ($SO_3{}^{2-}$)
+VI	Selenate ($SeO_4{}^{2-}$)	Sulfate ($SO_4{}^{2-}$)

Table 6. Results of TCLP Analysis of Sludges from Treatment of Oxidized FGD Scrubber Water[a]

Metal	Sludge Concentration,[b] mg/kg	TCLP Leachate Concentration,[c] mg/L	Allowable Leachate Regulatory Limit,[d] mg/L
Arsenic	0.0418	<0.0233	5.0
Barium	1.65	0.414	100
Cadmium	0.308	0.0146	1.0
Chromium	12.0	0.0047	5.0
Lead	13.8	<0.0107	5.0
Mercury	0.206	<0.0003	0.2
Nickel[e]	12.4	0.116	NA[f]
Selenium	17.3	0.341	1.0
Silver	0.0179	0.0049	5.0

[a] Reference 8.

[b] The solids resulted from selenium treatment applied to oxidized FGD scrubber water.

[c] After the leaching period, the solids were recombined with the original filtrate before the TCLP was performed. The total solution was then filtered and collected for analysis.

[d] Allowable TCLP regulatory limits in 40CFR261.24.

[e] Nickel is not a TCLP metal.

[f] NA = Not applicable.

selenopentathionate, as follows:

$$\mathrm{Se(SO_3)_2}^{2-} + 2\mathrm{S_2O_3}^{2-} \longrightarrow \mathrm{Se(S_2O_3)_2}^{2-} + 2\mathrm{SO_3}^{2-}$$

Solutions of selenopentathionate undergo slow decomposition in a FGD sludge pond to produce elemental selenium and the tetrathionate ion. This process probably accounts for the loss of selenium from nonforced-oxidized FGD sludge pond waters when these waters are retained in surface impoundments at ambient temperature for several weeks or more. Usually, the presence of selenopentathionate and selenotrithionate in FGD sludge pond water increases the concentration of dissolved selenium in pond waters. Therefore, it is surmised that inhibition of the removal of selenium from FGD sludge pond water is due to the formation of selenium–thionate complexes that are formed by the presence of thiosulfate in the pond (7).

The results of the Toxicity Characteristic Leaching Procedure (TCLP) performed on sludges from the treatment of oxidized FGD scrubber water are presented in Table 6 (8). The treatment involves contacting the FGD scrubber water with the ferrous ion and hydrated lime to remove the oxyanions of selenium and several divalent and trivalent metal cations such as chromium, lead, and nickel. These constituents appear at elevated concentrations in the resultant wastewater treatment sludge. Nevertheless, the results of the TCLP analysis on this sludge indicate that all constituents are within the allowable leachate regulatory limit.

BIBLIOGRAPHY

1. Battelle, C. (1994). *A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP/WET FGD System*. US Department of Energy, Pittsburgh Energy Technology Center, DOE/PC/93251-T2 (Volume 1).
2. Battelle, C. (1994). Pacific Northwest Laboratories. *Sodium-Based Flue Gas Desulfurization Sludge Disposal Ponds*. Electric Power Research Institute, Report TR-103915.
3. Battelle, C. (1994). Pacific Northwest Laboratories. *Calcium-Based Flue Gas Desulfurization Sludge Disposal Ponds*. Electric Power Research Institute, Report TR-103914.
4. Black & Veatch Consulting Engineers. (1982). *Full-Scale Scrubber Characterization of Conesville Unit 5*. Electric Power Research Institute, Report CS-2525.
5. Radian Corporation. (1980). *Evaluation of Chiyoda Thoroughbred 121 FGD Process and Gypsum Stacking*. Vol. I, Electric Power Research Institute, Report CS-1579.
6. Radian Corporation. (1984). *Field Investigation of FGD System Chemistry*. Electric Power Research Institute, Report CS-3796.
7. Castaldi, F.J., Behrens, G.P., and Hargrove, O.W. (2001). Removal of Selenium from FGD Scrubber Purge Water. *Proc. Water Environ. Fed. 74th Ann. Conf.* Atlanta, GA.
8. Castaldi, F.J. (2002). *Personal Data Files on Forced-Oxidation Process Limestone-Based FGD Scrubber Sludges*. Austin, TX.
9. Radian Corporation. (1979). *Review and Assessment of the Existing Data Base Regarding Flue Gas Cleaning Wastes*. Electric Power Research Institute, Report FP-671.
10. Radian Corporation. (1982). *Chemical and Physical Characterization of Western Low-Rank Coal Waste Materials*. US Department of Energy, Grand Forks Energy Technology Center, Report DOE/FC/10200-T4.
11. Radian Corporation. (1975). *Coal Fired Power Plant Trace Element Study*. For US Environmental Protection Agency, Region VIII, EPA Contract 68-01-2663.
12. Radian Corporation. (1975). *Environmental Effects of Trace Elements from Ponded Ash and Scrubber Sludge*. Electric Power Research Institute, Report 202.
13. Radian Corporation. (1994). *A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP While Demonstrating the ICCT CT-121 FGD Project*. US Department of Energy, Pittsburgh Energy Technology Center, DCN 93-643-004-03.
14. Southern Research Institute. (1994). *Characterizing Toxic Emissions from a Coal-Fired Power Plant Demonstrating the AFGD ICCT Project and a Plant Utilizing a Dry Scrubber/Baghouse System*. US Department of Energy, Pittsburgh Energy Technology Center, DOE/PC/93254-T1.
15. Benjamin, M.M., Hayes, K.F., and Leckie, J.O. (1982). Removal of toxic metals from power generation waste streams by adsorption and coprecipitation. *J. Water Pollut. Control Fed.* **54**(11): 11.
16. US EPA. (1977). *Disposal of By-Products from Nonregenerable Flue Gas Desulfurization Systems*. EPA-600/7-77-052.
17. US EPA. (1980). *Environmental Assessment of a Coal-Fired Controlled Utility Boiler*. EPA-600/7-80-086.

SLUDGE TREATMENT AND DISPOSAL

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The management of sewage sludge is a major problem in wastewater treatment. Sludge amounts to about 2% by volume of processed sewage, but handling it accounts for up to 50% of total operating costs. Furthermore, during the last few years, there has been a worldwide movement toward a common strategy for any kind of waste; the priorities are reusing waste materials and taking advantage of their energy content.

Treatment of sludge is aimed at rendering it suitable for use or disposal at minimum cost. The low solids concentration (2–3%), and the presence of pathogens, heavy metals, organic pollutants and potentially putrescible organic matter are the main problems to be faced and solved. Other factors influencing sludge processing technology are the need to extract as much energy and material as possible from the sludge itself and the introduction of stricter regulations that require higher levels of treatment before disposal.

PRODUCTION AND CHARACTERIZATION

Three principal categories of sewage sludge can be identified: primary, derived from mechanical and preliminary treatments; secondary or waste activated, from biological treatments; and tertiary, from final physicochemical treatments.

Typical sludge quantities and concentrations are reported in Table 1. They range from 0.2 to 5.0 L/cap/d and 0.7% to 10.0%, respectively; 2 L/cap/d at 4% solids concentration is the typical production of primary plus activated sludge from municipal plants.

The selection of the best processing sequence preliminarily requires knowledge of the sludge characteristics. Total, suspended, and volatile solids content, density of dry solids (1.3–2.1 g/cm^3), pH, sludge volume index (SVI), specific resistance to filtration (values of the order of 10^{12} m/kg at 49 kPa generally indicate good filterability), capillary suction time (CST, optimal values around 10 s using a 10-mm reservoir), compressibility coefficient, floc strength, caloric value (ranging from 21 to 28 × 10^3 kJ/kg volatile solids), and nutrient content are the most common parameters.

Rheological properties are also of great importance because they influence almost all treatment and utilization/disposal operations. This is particularly true for land application and storage and transportation steps because the selection of the most suitable equipment and procedure is strongly dependent on physical consistency and flow characteristics.

TREATMENT

Treatment options are numerous, but (1) thickening and dewatering to reduce sludge volume and subsequent handling costs and (2) stabilization to reduce putrescibility due to organic matter are of prevailing interest. Disinfection also plays an important role.

Thickening

Thickening, normally carried out before stabilization reduces sludge volume by two to three times. Generally, solids concentration remains below 10%, the sludge behaves as a liquid, and is still pumpable by conventional equipment.

Gravity thickening in tanks is often the most cost-effective method. A thickener may be provided with vertical pickets to facilitate the release of water and gases. Loading rates range from 1.6 to 3.3 kg/m^2/h for mixed sludges, and hydraulic retention times are lower than 24 h to avoid odor problems. As an alternative, sludges can also be thickened by various mechanical systems, such as drainage belts, rotary-drum thickeners, and centrifuges, which sometimes require adding a polyelectrolyte for sludge conditioning. Sludges can be also thickened by dissolved air flotation units.

Dewatering

By dewatering, volume reduction greater than by thickening is obtained, and the sludge becomes paste-like. To improve performance, dewatering is generally preceded by conditioning (chemical or physical).

In chemical conditioning, the particle charge is neutralized, and flocculation is promoted by organic reagents (polymeric macromolecular compounds characterized by monomer type, molecular weight, ionic charge, and degree of hydrolysis) or inorganic reagents (such as iron and aluminum salts, lime, or a combination).

The conditioner type and dosage can be assessed by general laboratory tests, for example, a jar test, specific resistance to filtration and CST, and specific tests for each type of dewatering technology. Physical methods include thermal conditioning, freezing, and the use of inorganic admixtures. Thermal conditioning involves heating sludge at 180–220 °C for 30–90 minutes; sludge sterilization also occurs. Conditioning by freezing seems to be justified only if accomplished by natural means. The use of inorganic substances (e.g., ash, diatomaceous earth) can produce a mixture that has improved filtering characteristics and is usually less compressible than the sludge alone. Dewatering can be accomplished naturally (by drying beds) or mechanically (by filtration or centrifugation).

Drying Beds

When land is available, dewatering by nature can be attractive. On the beds, sludge is placed 15–30 cm deep,

Table 1. Typical Sludge Quantities and Characteristics

Type	Quantity, L/cap/d	Solids Concentration, %	Nitrogen, %-DM	Phosphorus, %-DM	Potassium, %-DM
Raw primary	0.9–2.2	2.0–8-0	1.5–7.0	0.3–2.8	<1.0
Raw activated	1.4–7.3	0.5–1.5	3.0–10.0	1.0–7.0	0.1–0.9
Raw pr. + act.	1.8–2.8	3.0–6.0	4.0–6.0	1.0–1.2	—
Dig. pr. + act.	0.5–1.0	2.0–12.0	1.0–6.8	0.2–5.7	<4.0
Tertiary	0.2–8.0	5.0–10.0	—	—	—

Note: DM = dry matter.

and the time required to reach a liftable state ranges from a few days to several months, depending on climate and sludge characteristics. The area required ranges from 0.05 to 1.40 m^2/cap. Lagoons are similar, but sludge is placed at depths 3 to 4 times greater than in a bed. Lagoons are generally used for long-term storage and, eventually, for cold digestion.

Mechanical Equipment

Mechanical dewatering can take place by filtration, with a filter press or belt press, or by centrifugation. Schemes of these machines are shown in Fig. 1. Filtration under pressure is carried out for 1.5–6.0 h at 0.5–1.4 MPa and is the only operation that allows a cake concentration $>30\%$. Conventional plate filter press operation requires a great deal of labor to open and clean equipment, and yield is low. The automation of plate movement and cloth washing make labor reduction possible, and yield can be increased by using membrane type machines.

In belt pressing, dewatering takes place through an initial drainage step followed by compression under rollers, where sludge also undergoes shearing action due to the relative movement of the two belts. Specific flow rates of 2–3 m^3/h/m belt width are common for municipal sewage sludge, and cake concentrations of 25–30% can be expected. Special care must be taken in belt washing which requires a rinsing water flow rate of 50–200% of that of input sludge.

The type of centrifuge used mostly consists of a cylindrical–conical shell (bowl), that has an internal Archimedean screw (scroll/conveyor) that revolves at a speed slightly lower than that of the bowl. The solid–liquid separation takes place like sedimentation but at g values up to 3000. Pool depth, beach length, and bowl/conveyor differential speed are the most important variables that affect performance. The main advantages consist of indoor solid–liquid separation and limited equipment size, but cake concentrations higher than 25% are normally difficult to obtain. The main general features of filter presses, belt presses, and centrifuges are summarized in Table 2.

Innovations include the development of screw presses, continuous filter presses, high-pressure belt presses, and new generation centrifuges, such as the centripress.

Stabilization

Stabilization is employed mainly for odor control, although pathogen reduction is also achieved. Available options are biological stabilization (anaerobic digestion, aerobic stabilization, and composting), normally permanent in effect, and chemical stabilization (by lime addition), normally temporary. The addition of various oxidizing

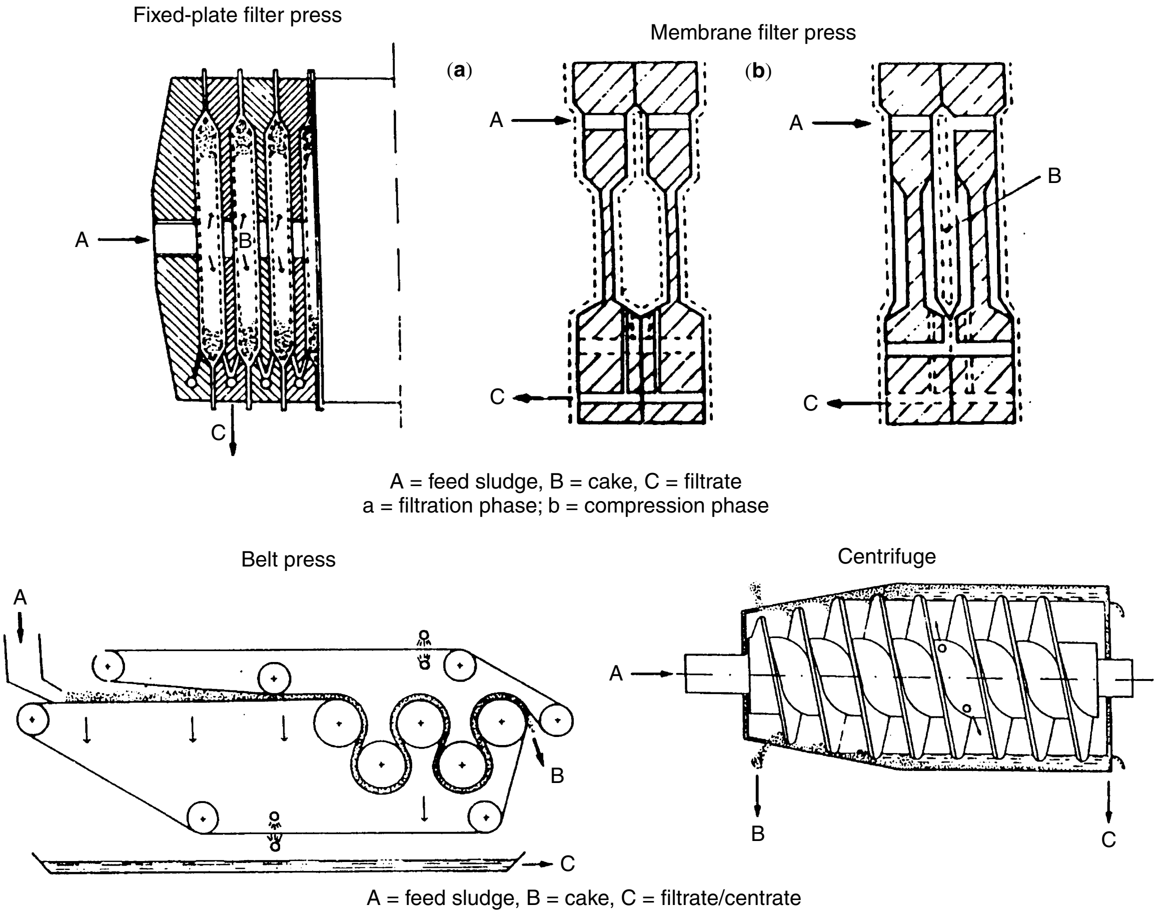


Figure 1. Schemes of dewatering machines.

Table 2. Dewatering Equipment Features

Type	Cake Concentration, %	Separation Efficiency, %	Area Requirement	Energy Demand
Filter press	>30	>95	high	low
Belt press	25–30	around 95	medium–high	medium
Centrifuge	<25	<95	low	medium–high

chemicals (ozone, hydrogen peroxide, etc.) is another possibility, but less used.

Anaerobic Digestion

Anaerobic digestion consists of biological degradation of organic substances in the absence of free oxygen. The organic matter is first liquified and converted by acid-forming bacteria to short-chain acids, then converted by strictly anaerobic methanogenic bacteria to methane, carbon dioxide, and other trace gases.

The simplest process is to store the sludge in open basins for several months, but now this has limited application, especially in cold climate, because of operational and safety problems. A heating process at 35 °C in mesophilic conditions is the norm. The advantages include methane production, no need for oxygen supply, lower net sludge production, and easier solubilization of complex organics. Among the disadvantages, operating control, maintenance problems, heat requirements, supernatant quality, and high capital costs must be mentioned.

Factors that affect the process are feeding modalities, mixing (external pumping, internal mechanical mixing, and internal gas mixing), temperature, pH, bicarbonate alkalinity, volatile acids, and toxics. Typical systems are (1) the low-rate (unheated, unmixed, and intermittently fed); (2) the one-stage high-rate (heated, mixed, and continuously fed); and (3) the two-stage high-rate, a combination of above systems (Fig. 2).

Biogas production of 0.75–1.10 m^3 per kg of volatile solids destroyed, consisting of 65–70% CH_4, 30–35% CO_2, and traces of H_2, H_2S, and volatile solids destruction as high as 60% can be expected.

The most important criterion for digester design is the volumetric loading rate. Reported values range from 0.4 to 8.0 kg volatile solids/m^3/d, depending on digester type. However, as a result of better understanding of digestion kinetics, the solids retention time parameter is now recognized as more important. Hydraulic retention times range from 7 to 30 days.

The development of low-cost spark ignition engines suitable for operation on biogas gives the possibility of

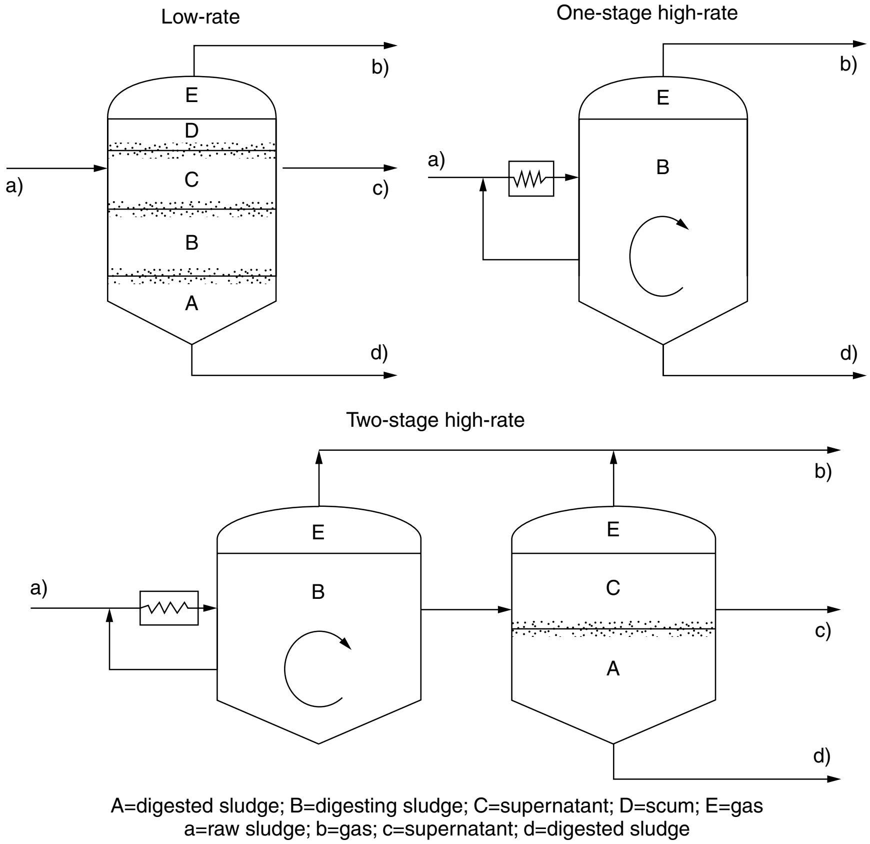


Figure 2. Anaerobic digestion systems.

generating power at small works, even rural, thus making the operation of digesters more attractive economically.

Aerobic Stabilization

Sludge can be stabilized by simply aerating it in open basins. Alternatives are cold stabilization at ambient temperature and autoheated stabilization in thermophilic conditions at high temperature. Cold stabilization involves relatively large energy use for aeration and mixing. Retention times of 10–20 days are normally necessary, but 50 days or more are not uncommon in cold climates. This process is justified at small plants, where the realistic maximum reduction of volatile solids is 40%. In an autoheated process, the heat produced by oxidation of organic matter is conserved to produce a temperature rise to 55 °C or more, thus involving stabilization in only 3–5 days and also sanitizing. The essential prerequisite of this process is effective heat insulation.

As an alternative, oxygenation can be provided by pure oxygen. The gas throughput and consequent heat losses can be minimized and the process operated in more favorable conditions. Another system is the dual-digestion process in which sludge is treated at 50–70 °C by thermophilic aerobic digestion followed by anaerobic digestion without the need for further heating.

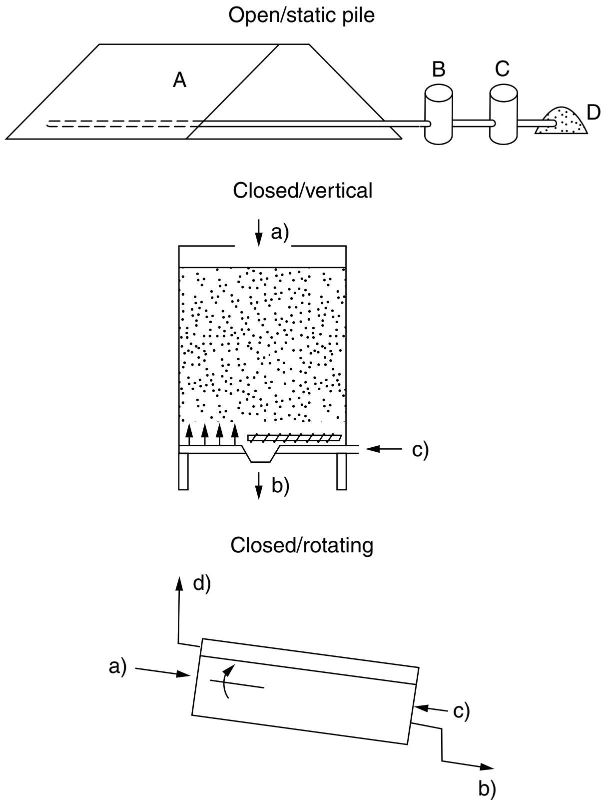
Composting

Composting is an aerobic process in the solid phase that converts biodegradable organic substances to a stable, hygienic, and humus-like material under the combined activity of a mixed population of bacteria, fungi, actinomycetes, and protozoa. Composting is considered a treatment option to sludge agricultural refuse.

The main operating variables that affect performance are (1) moisture content (optimal 50–60%) to support microbial activity; (2) carbon to nitrogen ratio (optimal 25–30) to avoid slow processing at high ratios or ammonia volatilization at low ratios; (3) aeration to permit metabolism and respiration of microorganisms and oxidation of organic molecules and avoid development of malodors; (4) temperature (optimal 55–60 °C) to obtain pathogen reduction without inhibiting microorganism growth; and (5) pH, even if quite a wide range is acceptable (5.5–8.0).

Several techniques can be adopted; they differ mainly in aeration and mixing modalities, but all of them consist of basic steps including (1) addition of bulking agents to provide a sufficiently porous and soft mixture suitable for processing; (2) aeration and attainment of a temperature of about 60 °C to destroy pathogens and reduce moisture; (3) further storage (curing) to complete stabilization; and (4) refining treatments, generally including separation and recycling of bulking agents, screening, granulation, and packaging. The general categories of composting plants are open systems, confined ones, and closed or in-vessel systems (Fig. 3).

In open systems, the material is arranged in windrows and aerated either by simply turning the mass (turned pile) or by forced ventilation (static pile). Stabilization occurs in 15–40 days, followed by a suitable period of maturation. A long, high-temperature period is to be avoided because most microorganisms do not survive temperatures above 60 °C for long time, even if this has a positive effect in reducing pathogens. Therefore, several processes include an initial phase of suction, which permits temperature to rise for a few days, followed by blowing with temperature control. Confined and in-vessel systems, both horizontal and vertical, comprise mechanical equipment that provides better control of turning, ventilation, and other operating variables. The advantages of closed systems over open ones include more effective odor control, indoor operation, insensitivity to climate, and low labor requirements.



A = compost pile; B = water removal; C = fan; D = odor removal
a = mixture to compost; b = compost; c = air; d = exit air

Figure 3. Schemes of composting systems.

Chemical

The process consists of adding lime to sludge to raise the pH above 12 and maintain it for 2 hours, at least. Capital costs are generally low, but the overall economics depend very much on the local price of lime. Calcium hydroxide (slaked lime) or calcium oxide (quick lime) can be used. Quicklime also has the ability to dewater sludge. Lime tends to eliminate odors and reduce pathogenic content, but lime-treated sludges are not chemically stable.

Disinfection

Disinfection reduces the number of pathogenic microorganisms in a raw sludge to a level where they are no longer a risk to human, animal, or plant health. Disinfection can be attained by several methods that act by different mechanisms. Only pasteurization and irradiation have disinfection as the main purpose; other processes disinfect as a secondary effect.

Pasteurization is a heat treatment process carried out at a temperature of 70 °C for 30 minutes. The process is often combined with a stabilization process; it is normally carried out before anaerobic mesophilic digestion.

Ionizing radiation for disinfection uses directly ionizing particles (electrons), produced by accelerators and indirectly ionizing electromagnetic radiation (X), obtained from radionuclides sources, such as ^{60}Co and ^{137}Cs. In general, the doses required for sludge disinfection are 500 krad for liquid sludge and 1000 krad for dewatered sludge.

In composting, the heat generated by biological oxidation is the most important lethal factor, but microbial competition also plays an important röle. A temperature of 55–60 °C for a few days seems to be the lower limit for disinfection.

When lime is added to a liquid sludge, the lethal factor for pathogens is the high pH; when calcium oxide is added to dewatered sludge, an additional factor is the temperature rise to 80 °C. In aerobic thermophilic digestion, biological oxidation results in a temperature rise through which disinfecting action may be obtained; temperatures of 60–70 °C can be reached when aerating with pure oxygen. This process should be carried out preferably as a batch process to prevent microorganisms in raw sludge from reaching the end product before they have been killed. Limited hygyenic effects can also be obtained through anaerobic and aerobic digestion. Sludge processed by thermal conditioning is sterilized and also easily dewaterable; in addition, the sterilizing effect is particularly persistent.

UTILIZATION/DISPOSAL

Land application, thermal processing, and landfilling are available and well-known practices for utilization/disposal of sludge.

Land application

Sludge can be used in agriculture by spreading it on land directly or after composting. Direct use leads to several advantages through recycling of nutrients (i.e., inorganic and organic nitrogen and phosphorus) and organic matter which positively affect soil structure by increasing porosity, stability of aggregates, water retention, and also pH and cation exchange capacity.

However, this practice raises several problems, mainly from the presence of toxic and phytotoxic pollutants, both inorganic and organic, and pathogens. Although numerous processes that can ensure disinfection have been developed, no such reliable methods exist to neutralize or eliminate heavy metals, so regulations set limits for the maximum concentrations of these metals in sludges and the soil, as well as for the maximum disposable quantities for a certain number of years.

Annual nutrient requirements depend on the crop. In most cases, sludge amounts that supply adequate nitrogen also supply phosphorus, but in excess of crop needs, at possible risk of polluting ground- and surface waters. It is also necessary to consider the actual amounts of nutrients available in the first year and those that will become available in subsequent years. Additional sources of potassium are generally required. Annual nitrogen, phosphorus, and potassium use by selected crops are listed in Table 3.

Land application is recommended for sludges from small and medium wastewater works that are close to disposal fields and serve comparatively non-industrialized areas. Direct application to land is, however, subject to great variability over time, depending on crop type and weather conditions, but sludge production is continuous. For these reasons, the agricultural use of compost is often preferred because this material can be more easily stored, transported, and used at times and on sites different from those of production. Composting also involves the production of a safer and more hygienic product.

Thermal processing

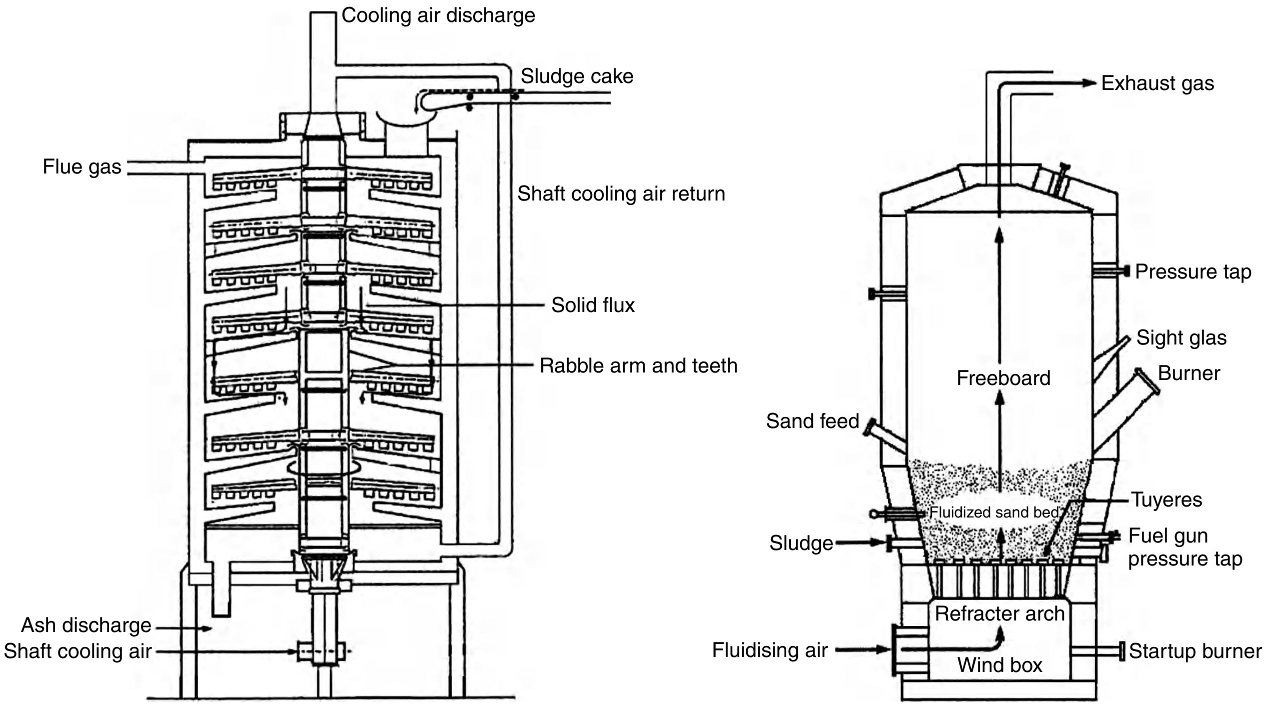
Thermal processing includes incineration, pyrolysis, and drying.

Incineration. Incineration involves complete oxidation of volatile matter and the production of an inert residue (ash). If enough water has been removed, the organic material, will sustain combustion; therefore, sludge incineration must be preceded by effective dewatering or drying. The types of sludge incinerators most commonly used are the multiple-hearth furnace (MHF) and the fluidized bed furnace (FBF). The rotary kiln furnace (RKF) is typically used for hazardous waste incineration, but it is also suitable for sewage sludge because of its great adaptability (Fig. 4).

An MHF consists of a vertical, cylindrical, refractory-lined reactor containing a number of horizontal hearths. Rabble arms, supported by a single central shaft, rake

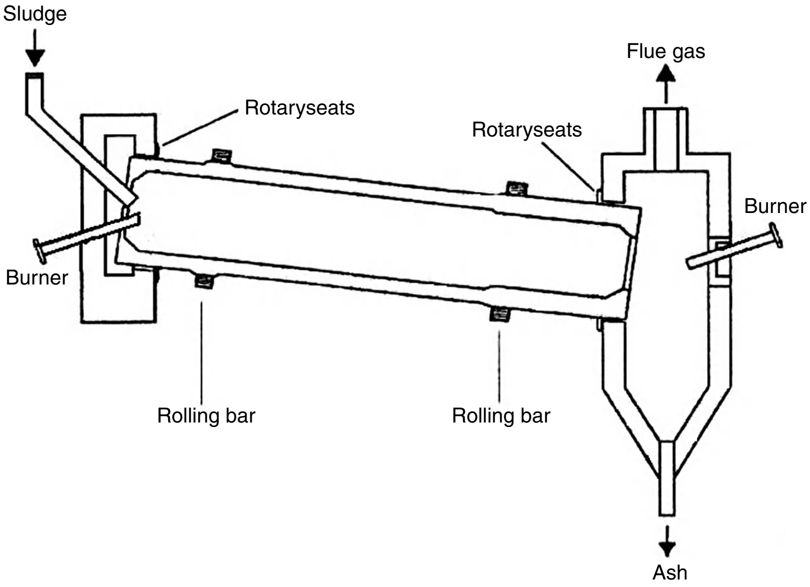
Table 3. Annual N, P, and K Use by Selected Crops

		Nutrient Requirements, kg/ha		
Crop	Yield, t/ha	N	P_2O_5	K_2O
Field				
Corn (grain)	12.3	267	111	256
Rice	7.8	122	67	189
Sugar beets	73.6	306	94	611
Wheat	7.3	194	89	157
Vegetable				
Asparagus	3.3	106	55	133
Lettuce	49.1	106	33	222
Potatoes	25.4	278	128	395
Tomatoes	73.6	278	89	534
Fruit				
Apples	36.8	111	50	200
Oranges	73.6	133	44	194
Forage				
Alfalfa	19.6	500	89	534
Timothy	9.8	167	28	278
Turf				
Bentgrass	6.1	250	89	178



Multiple-hearth

Fluidized-bed



Rotary kiln

Figure 4. Typical cross sections of furnaces.

the sludge radially across the hearths from the top to the bottom, countercurrently with air and hot gases. Three zones can be distinguished in the furnace: the drying zone in the upper part (gas temperature up to 400 °C), the burning zone in the central–low part (gas and solid phase temperatures of 850–900 °C), and the ash cooling zone in the lowest part (temperatures of ash and air generally <200 °C). The typical design values of a MHF are 2–8 m diameter, 4–14 hearths, a hearth loading rate of 30–60 kg wet sludge/m^2/h, and 100–125% excess air.

The advantages are flexibility with respect to feed quality and loading rates and low fuel consumption due to effective heat recovery inside the equipment. The disadvantages include possible odor problems and emissions of volatile substances (due to the low temperature of the exhaust gas), high need for excess air (due to low turbulence), and high maintenance costs because of many moving parts. Moreover, high fuel consumption is needed, if afterburning of exhaust gases is required to destroy volatile compounds and products of incomplete combustion.

An FBF consists of a cylindrical, refractory-lined shell containing a sand bed that is fluidized, during operation, by air through a distributor plate below the bed. The temperature of the bed is controlled at about 750 °C. FBFs fall into two categories: bubbling and circulating; the latter allows a higher fluidization velocity and very intensive mixing. Particles are carried out of the vertical combustion chamber by the flue gas and are removed in a cyclone to be returned to the FBF through a loop seal. Typical design parameters of a bubbling FBF, which is much more common than the circulating type, are 3–8 m bed diameter, a solid loading rate of 150–300 $kg/m^2/h$, 40–60% excess air, two to three times of fixed bed height (bed expansion), and 1.5–10% of sand losses in 100 h.

The advantages of FBF are low excess air (due to the high turbulence), low NO_x production (due to effective control of combustion temperature), reliability (no moving parts), flexibility for shock load, adaptability to sludges of different moisture content (dewatered, partially dried, fully dried), heat storage capacity by sand bed, and possible abatement of acidic compounds within the bed using additives such as limestone and dolomite. The disadvantages include ash and sand carryover and possible formation of a block of vitrified sand when salts of low melting points are present. This problem can be attenuated by an adding chemicals to bind the alkaline salts.

An RKF consists of a refractory-lined cylindrical shell mounted at a slight incline from the horizontal plane (2–3%) that slowly rotates (0.25–1.50 rpm). Varying the rotational speed allows control of the solid residence time and ensures adequate mixing. The excess air requirement ranges from 100–200%. The advantages include possible melting of ash (but blockage must be avoided), no need for pre-treatments, and adaptation to many feed mechanism designs.

Good performance of thermal process plants also depends on providing proper auxiliary equipment and devices, which include receiving and storage systems, pretreatment equipment, a feeding system, flue gas cleaning, heat recovery, ash handling, wastewater disposal, and process monitoring.

The main problem in incineration is the potential toxicity of gaseous emissions, but several devices are available for emission abatement at high efficiency. The particulate is generally small, and the legal standards can be easily met; a few metals, particularly Pb and Cd, are poorly retained, but the environmental hazard is slight primarily because the amounts in sludge are small. The problem of toxic substances, such as pesticides and PCBs, can be overcome by afterburning at high temperature (>1000 °C). On the other hand, flue gases represent a potential source of energy, usable to preheat the incoming furnace air, in sludge conditioning, or for external uses.

The volume reduction by incineration is more than 90% compared to the volume of dewatered sludge. The ash is free of pesticides, viruses, and pathogens, and the metals are in the less soluble oxide form.

Pyrolysis

Pyrolysis is a process in which organic material is decomposed at high temperature in an oxygen-deficient environment. This action causes irreversible chemical changes and produces gas, oil, and char (solid residue). The residence time, temperature, and pressure in the reactor are controlled to produce various combinations and compositions of these products.

True pyrolysis involves a total absence of air and applying all required heat externally to the reactor. Partial combustion, also known as starved-air combustion, involves adding a small amount of oxygen to the reactor: the oxygen sustains combustion of a portion of the reactor contents which, in turn, produces the heat required to pyrolyze the remainder of the contents. Pyrolysis has the potential advantage of reducing air pollution and producing useful by-products.

Drying

Drying is the simplest thermal process for producing a solid product. If metals and organic contaminants are low, dried sludge is an acceptable fertilizer. The main drawback is the cost to evaporate the water from the sludge cake; moreover, the end product must be sold to make the operation economical.

Landfilling

Landfilling is a convenient solution where enough space is locally available at reasonable fees. In any case, it is a necessary support to all other systems to dispose of materials that cannot be reused and for maintenance and/or emergency during shutdown periods.

Only well-dewatered sludges are suitable for landfilling. Solids concentrations of at least 20–25% are generally required, but values up to 30–35% are often necessary because the corresponding physical consistency could be too low to support the cover material. A good level of stability is also necessary to avoid possible emissions of bad odors. Co-disposal, with solid wastes or soil, is often practiced.

The basic landfill types are the (1) trench (narrow and wide), (2) area, (3) in-fill mound, (4) fill layer, and (5) dike containment modes. Sludge is spread in layers within a confined area and then daily covered with a thin, continuous layer of inert material.

The main problems are leachate and biogas control. Leachate may be controlled through natural conditions, imported soils or amendments used as liners and/or cover, membrane liners, and collection and treatment. Soil's natural permeability can be reduced by adding imported clays or synthetic materials such as high-density polyethylene (HDPE).

Biogas production typically starts a few months after deposition, reaches a maximum after 5–7 years, and continues for many years at a reducing rate. Gas control techniques can be classified as permeable and impermeable methods. Permeable methods usually entail installing a gravel-filled trench outside or wells inside the filled area to intercept and vent gas into the atmosphere or to an energy recovery system; a forced vacuum extraction system is often appropriate. Gas migration is also minimized by placing a low permeability barrier around the landfill.

PRODUCTION OF USABLE MATERIALS

Many other methods to recover usable materials from sludge are available. The recovery of nitrogen (separated by stripping or as struvite) and phosphorus (generally by chemical/physical processes) is becoming of great interest, together with that of the organic fraction as a raw material for activated carbon. Other significant alternatives include the production of (1) slag, char, and Portland cement from dewatered sludge cake and (2) slag, brick, tile, and artificial lightweight aggregate (ALWA) from incinerated ash. Use as animal feed can also be mentioned.

CODISPOSAL WITH MUNICIPAL SOLID WASTES

The combined management of sewage sludge and municipal solid wastes allows, in most cases, overcoming specific technical problems arising from handling them separately, and obtaining significant economic advantages and environmental benefits.

In composting, the different characteristics of solid wastes and sewage sludge can be integrated usefully to obtain a final product of better quality because the relatively higher solids content and carbon to nitrogen ratio of solid wastes can counterbalance the lower solids concentration and carbon to nitrogen ratio of sludge.

In co-incineration, sewage sludge drying can take place by using the excess heat recovered from solid waste combustion, but greater attention in designing and operating furnaces and exhaust gas abatement systems is required.

Co-landfilling provides faster waste stabilization, better leachate quality, and higher biogas production, but the operating procedures must be carefully planned.

WASTEWATER SLUDGE

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TYPES AND CHARACTERISTICS OF SLUDGE

Types of Sludge

The Environmental Protection Agency (EPA) has defined sewage sludge as any solid, semisolid, or liquid residue removed during the treatment of municipal wastewater or domestic sewage, including solids removed during primary, secondary, or advanced wastewater treatment, scum, septage, and sewage sludge products. Instead of using the term sludge, some specialists have used the terms residual, sediments, solids, slime-solid, or biosolids, depending on its condition or its usefulness and whether it meets the applicable criteria for that particular term.

Sludge is a suspension including solid and semisolid materials separated and generated from the liquid wastewater stream of a treatment plant during purification of municipal wastewater, industrial wastewater, or natural water in mechanical, biological, or physicochemical facilities.

Depending on the type of wastewater plants and facilities, the following sludge can be generated:

—primary raw sludge: settleable solids separated from the wastewater stream during sedimentation in clarifiers (primary settling tanks);

—activated sludge: a complex of microorganisms of the colloidal type with adsorbed and partially oxidized admixtures, precipitating in the secondary clarifiers in the biological treatment of wastewater;

—sludge generated in industrial wastewater purification. This sludge has a different chemical composition, quantity, and moisture content, depending on the type of industry and wastewater treatment processes, some levels of radionuclides may be present;

—sludge from the treatment of natural water (groundwater, surface water) that is generated during the production of potable water: the composition of this sludge depends on the composition of the natural water and the types of reagents used to purify the water.

The wastewater sludge (biosolids) products can also be classified by the type of treatment process as the following:

—aerobically digested activated sludge or a mixture of it with primary sludge;

—anaerobically mesophilic or thermophilic digested primary sludge or its mixture with thickened activated sludge;

—dewatered sludge from mechanical dewatering devices;

—dried sludge from sludge beds;

—thermally treated or dried;

—biothermally treated (compost).

The main and more useful process of municipal and industrial wastewater purification is the biological activated sludge process. The by-products of this process are two types of sludge, such as primary and waste activated sludge, containing up to 99% of contaminants removed from wastewater.

Primary Raw Sludge

Definition. Primary raw sludge is the sediment from clarifiers whereby wastewater and solids are separated to produce clarified effluent and sludge. The main raw sludge components are proteins, nitrogenous compounds, cellulose, sugar, carbohydrates, grease, fats, macronutrients (nitrogen, phosphorous, potassium), micronutrients, bacteria, and viruses. It has high moisture and poor dewatering ability. Fresh sludge is a gray or light brown colored suspension; its particles are of different sizes and composition, and it has a less intense sour odor than septic sludge. Because of the high content of organic material, it decays rapidly, the sludge condition becomes septic, its color changes to dark gray or black, and it generates an objectionable sour odor. Sludge is a hazardous waste which must be stored, disposed of, or reused, in accordance with hazardous waste regulations. Sludge regulations limit sludge disposal alternatives based on the treatment level provided, pathogen removal, and the heavy metals content. Treatment processes include conditioning, dewatering, stabilization (control of odor, pathogens, biodegradable toxins, and vectors), and disinfecting resulting in a valuable land application and soil conditioning product that has many useful properties.

Quantity and Moisture. The mean moisture content of the sludge discharged from primary clarifiers is 95% for gravity-flow removal and 93.8% for removal by plunger pumps. The quantity of raw primary sludge is approximately 0.4–0.5% of the volume of wastewater treated. The quantity of municipal wastewater primary sludge with 95% moisture can be estimated by assuming that 39.0 cu ft/1000 persons is produced daily.

Chemical Composition. The composition of sludge from primary settling tanks (clarifiers) depends on the nature of the wastewater being treated and particularly the type and quantity of industrial wastewater treated together with municipal wastewater. The dry solids of sludge consist of organic matter (60–75%) constituted of protein, fats, and carbohydrates. The ultimate composition of the dry solids of sludge includes carbon, hydrogen, sulfur, nitrogen, and oxygen. The typical composition of raw primary sludge is as follows (% of dry solids): grease and fats 6–30, protein 20–30, nitrogen 1.5–8.0, phosphorus 0.8–2.8, potassium 0.1–1.0, and cellulose 8–15. The mineral constituents include SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, and other minerals. Wastewater sludge may also contain heavy metals such as cadmium, chromium, cobalt, copper, lead, mercury, nickel, and zinc. Alkalinity and pH are the most important of the easily measured chemical parameters affecting sludge conditioning. Raw primary sludge has a pH range of 5.0–8.0, alkalinity (mg/L as $CaCO_3$) of 500–1500, and organic acid (mg/L as HAc) 200–2000.

Waste Activated Sludge

Definition. Activated sludge gets its name from the interaction between wastewater and microorganisms (bacteria, protozoa, and rotifers) in the presence of dissolved oxygen in a biological process of wastewater purification. Association of microorganisms that use organic material as food, remove suspended solids, and adsorb and mineralize wastewater contaminants are given the name activated sludge. The average sizes of activated sludge flocs are 1–4 mm; they have a light gray, yellow gray, or dark brown color. As the biological process of wastewater purification takes place, activated sludge increases. After the biological process of wastewater purification, activated sludge settles in secondary clarifiers. From the secondary clarifiers, the main part of the activated sludge is moved into aeration tanks to participate in the biological process; the other part receives treatment as waste activated sludge.

Activated sludge contains mostly bacterial cells that are viscous and difficult to dewater. The parameters of activated sludge sedimentation are sludge volume index (SVI), sludge density index (SDI = SVI/100), and sludge age determined by a settleometer test. An SVI less than 100 mL/g indicate an older, denser, fast settling sludge that has a thick, scummy, dark tan foam in aeration tanks. An SVI of more than 100 mL/g indicates a young, slow settling, light density sludge. An optimal SVI is 70–130 mL/g. An SDI of more than 1 g/cm^3 indicates old sludge; an SDI of less than 1 g/cm^3 indicates a young sludge. Sludge age refers to the number of days for which the suspended solid particles remain under aeration (5–15 days). The following microorganisms are Indicators of activated sludge age in order from young to old: amebas, flagellates, ciliates, and rotifers.

Quantity and Moisture. The moisture content of the activated sludge discharged from secondary clarifiers after aeration tanks is 99.2–99.7%. Gravity or belt gravity thickening of waste activated sludge is a very important process because of the high volume and moisture content in waste activated sludge. After gravity thickening, waste activated sludge has a moisture content of 97–98%, and volume is decreased 5–10 times. After belt gravity thickening, waste activated sludge has a moisture content of about 95%. In the process of belt gravity thickening, added polymers can reduce the moisture content. Thickened activated sludge is often treated together with primary sludge. For approximate computations, the quantity of the mixture of primary sludge and gravity thickened activated sludge at an average moisture content of 96.2% can be assumed as 0.6–1% of the volume of wastewater treated.

Chemical Composition. Activated sludge consists of microorganisms and adsorbed particles. The activated sludge dry solids consist of 70–75% organic matter. The dry solids contain carbon, hydrogen, nitrogen, sulfur, and oxygen. Activated sludge contains (% of dry solids) 6–7.5 fats, 2.4–7.5 nitrogen, 2.8–11.0 phosphorous, potassium up to 0.4%, and approximately 2.5–3 times less carbohydrates and two times more protein than primary raw sludge, the major minerals present in dry solids. Activated sludge can contain Cr, Cu, Ni, Pb, Cd, and other elements. The alkalinity of activated sludge is 580–1100 (mg/L as $CaCO_3$), organic acids 1100–1700 (mg/L as HAc), and pH 6.5–7.5.

Physical Properties

Granulometric Composition. Primary raw sludge contains 5–20% of particles larger than 7–10 mm, 9–33% 1–7 mm, and 50–88% below 1 mm in which about 45% have sizes less than 0.2 mm of the total weight of dry solids. In activated sludge, the quantity of particles less than 0.2 mm is 90%, below one mm 98%, particles of 1–3 mm 1.6%, and over 3 mm 0.4% of the weight of dry solids. The organic part of sludge decays rapidly, and an increase in the quantity of finely dispersed and colloidal particles and bound water results in a decrease in the water separation from the sludge and poor dewatering ability.

Density and Fluidity. The average density of activated sludge is 0.7–1.3 g/cm^3. The density of primary sludge is about 1 g/cm^3, and the density of the sludge dry solids is 1.2–1.4 g/cm^3. Primary raw sludge whose moisture is higher than 90% is a fluid; when moisture is 86–90%, it looks like sour cream; when moisture is 82–86%, it looks like a slush; and when moisture is less than 82%, it looks like a light thin soil. Waste activated sludge whose moisture is 88–91% looks like sour cream, and when moisture is 85–87% like thin soil. At a concentration of solids above 5% of primary sludge and above 3% of activated sludge, they are non-Newtonian which means that head losses are not proportional to velocity and viscosity. They are also thixotropic which means that they become less viscous when stirred.

Dewatering Characteristics. Dewatering is a process of natural or mechanical removal of water from sludge. The dewatering characteristics of sludge can be obtained by measuring the volume of filtrate collected from sludge and the time it takes to filter using varying doses of conditioning reagents. The most commonly used tests are the Specific Resistance Test, the Buchner Funnel Filtration Test, and the Capillary Suction Time Test (CST).

The water in sludge may be present as free water and water bound physicomechanically, physicochemically, or chemically. The more bound water present in sludge, the more energy or reagents must be used to condition sludge to remove bound water by dewatering. The separation of water from sludge depends on the size of the solid particles; the smaller the particles, the poorer the water separation from the sludge. Any process that reduces the size of the suspended solids particles has a negative effect on conditioning and dewatering. The chemical composition of sludge exerts a significant influence on its treatment. Compounds of iron, aluminum, chromium, and copper, as well as acids and alkalis, improve the processes of precipitation, thickening, and dewatering and reduce the consumption of chemical reagents for conditioning of sludge before dewatering. Oils, fats, and nitrogen compounds intensify anaerobic sludge digestion but interfere with thickening and conditioning processes.

Thermophysical Characteristics. The specific heat of a mixture of primary and thickened activated sludge is (3.5–4.7) × 10,000 Joule/(kg K). The heat of combustion of sludge dry solids equals 16.7–18.4 MJ/kg, the heat for incinerating fuel matter is 23.4–26.9 MJ/kg of sludge organic. The heat value is higher for raw sludge and lower for activated sludge. Sludge burns at a temperature of 430–500°C (800–1000°F); to eliminate odors, the temperature needs to be raised to 800–850°C (1500°F). For an increase in the moisture and ash of the sludge, there is a decrease in the heat of combustion and liberation of volatiles. In the process of thickened activated sludge aerobic digestion, 3.6 kcal are released/g volatile (organic) suspended solids oxidized (15 MJ/kg). The reduction of 1 kg of organic sludge during composting of dewatered sludge creates an average of 21 MJ/kg of heat. Raw primary sludge has a thermal content 6,800–10,000 Btu/lb.

Bacteriological Content

The activated sludge process is the most efficient biological process for removing coliforms, pathogenic bacteria, and virus particles from wastewater; they are transported to primary and activated sludge. The primary sedimentation of sewage allows reducing 30–70% of microorganisms and bacteria. After activated sludge treatment, the reduction of microorganisms and bacteria reaches 90–99%. The average level of indicator bacteria and pathogens, such as coliforms, *Streptococcus, Salmonella*, enteric viruses, and parasite ova/cysts reaches millions n/g dry weight of sludge. The diversity of microbial flora makes it difficult to enumerate the total population.

Biosolids

The Water Environment Federation (WEF) has adopted a policy of encouraging the use of the word biosolids in place of sludge to promote public acceptance of reused water projects. The term biosolids is used to connote the primary organic solid product of treatment that meets US EPA or other applicable criteria for beneficial use. The term biosolids has been used by WEF in the last few years instead of sludge. The type and level of wastewater and sludge treatment has an effect on the type, quantity, and quality of the biosolids generated. Biosolids are the solid organic matter produced as by-products of municipal wastewater treatment processes (also known as sewage sludge) that can be beneficially used, especially as a soil amendment, in accordance with standards and requirements. Sludge regulations limit biosolids disposal alternatives based on the treatment level provided.

CONCLUSION

Primary and waste activated sludge are two main types of sludge (biosolids) formed in wastewater purification. The quantity of a mixture of primary and thickened waste activated sludge whose average moisture is 96.2% reaches 1.0% of the treated wastewater. High moisture with bound water and small solid particles make sludge difficult to dewater. The dry solids of sludge consist of organic matter and minerals. The microbiological population of sludge includes millions of coliforms, pathogenic bacteria, and viruses. Sludge (biosolids) contains macronutrients, such as nitrogen, phosphorus, potassium, and micronutrients. After treatment (thickening, conditioning, stabilization, dewatering, disinfecting), biosolids meet regulatory requirements for pathogens, vector attraction reduction, and heavy metal content and become beneficial valuable products, which can be applied to land for soil conditioning, preventing soil erosion, and as fertilizer.

READING LIST

Bitton, G. (1944). *Wastewater Microbiology*. Wiley-Liss, New York.

Bruce, A.M. and Fisher, W.J. (1994). *Sewage Sludge Stabilization and Disinfecting*. Ellis Hardwood Ltd., Chichester, UK.

WEF. (1992). *Design of Municipal Wastewater Treatment Plants*. MOP 8, Vol. 2. WEF. #76.

Foess, G.M. and Siger, R.B. (1993). Pathogen/vector attraction redaction requirement of the sludge rules. *Water Eng. Manage.* **Jun.**: 25.

US EPA. (1997). *Land Application of Biosolids Process Design Manual*. US EPA.

Lue-Hing, C., Zenk, D.R., and Kuchenither, R. (1992). *Municipal Sewage Sludge Management*. Technomic, Lancaster, PA.

Siger, R.B. (1993). Practical guide to the new sludge standards. *Water Eng. Manage.* **Nov.**: 26.

Spellman, F.R. (1997). *Dewatering Biosolids*. Technomic, Lancaster, PA.

US EPA. (1990). *State Sludge Management Program Guidance Manual*. US EPA.

Tehobanoglous, G.B., Franklink, L., and Metcalf and Eddy, Inc. (1992). *Wastewater Engineering: Treatment, Disposal, and Reuse*. McGraw-Hill, New York.

Turovskiy, I.S. (2000). Biosolids or sludge? *Water Eng. Manage.* **April**: 19–21.

Turovskiy, I.S. (2001). Reduction of energy consumption in wastewater sludge treatment. *Fl. Water Resour. J.* **March**: 34–36.

US EPA. (1995). *A Guide to the Biosolids Risk Assessments for EPA Part 503 Rule*.

US EPA. (1993). *Office of Wastewater Management*. EPA 832-B-93–005.

US EPA. (1999). *Biosolids Generation, Use, and Disposal in the United States*. 530-R-99. September 10.

Vesilind, P.A. (2003). *Wastewater Treatment Plant Design*. WEF and IWA Publishing.

Ward, R.L., McFeters, G.A., and Yeger, J.G. (1984). *Pathogens in Sludge*. Sandia Report. 83–0557. TTC-0428. Sandia Natural Laboratory, Albuquerque, NM.

PROCESSING OF SLUDGE

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Wastewater sludge is a high moisture suspension in which water is bound by small solid particles. The main parts of the sludge solids are organic and contain different types of microorganisms, pathogenic bacteria, viruses, and parasites. On the other hand, sludge contains valuable organic macronutrients, such as nitrogen, phosphorus, potassium, and micronutrients, such as elements and metals. Wastewater sludge is hazardous waste which must be stored, disposed of, or be reused in accordance with standards and regulations based on the treatment level provided.

The main purpose of treatment is to prepare sludge for removal from wastewater treatment plants and to produce biosolids that can be used as a soil amendment and conditioner. To achieve this goal, treatment processes of sludge should include thickening and dewatering to decrease sludge volume and moisture and disinfection and stabilization to control odor, pathogens, and vectors.

SLUDGE TREATMENT

Thickening

Thickening is an economically effective process to increase sludge concentration and decrease sludge volume by removing some free water to the extent that the sludge remains in the fluid state. The objectives of thickening are to produce a relatively solids-free supernatant and to produce a sludge that can be pumped without difficulty. Sludge can be thickened by using gravity thickeners, gravity belt thickeners, rotary drums, separators, centrifuges, and flotators. Rotary drums and gravity belt thickeners are mechanical devices that remove free water from wastewater sludge using gravity. Centrifugation is a process in which centrifugal force (usually about 500 to 3000 times the force of gravity) is applied to a sludge slurry to accelerate the separation of the solid and liquid fractions. Flotation thickening is a solid–liquid separation caused by introducing fine air bubbles into the liquid phase. Adding polymers in waste activated sludge thickening allows removing more water.

Gravity thickening is a common method of solid–liquid separation to reduce the sludge volume handled in the dewatered/sludge disposal of a wastewater treatment facility. During the process of waste activated sludge gravity thickening, the concentration of dry solids increases, on average, from 0.2 to 2.0% and the volume of sludge is reduced 10 times. However, when the thickening process lasts 8–10 hours or more, organic putrefaction occurs, the microorganisms of the activated sludge perish without air, the amount of colloids increases, and part of the free water is transformed into a bound state of water with dry solids. Unthickened activated sludge usually has better dewatering abilities than thickened sludge. On the other hand, dewatering or digesting nonthickened activated sludge does not make sense due to the large volume and low initial concentration of dry solids. The kinetics of the process of activated sludge thickening determines the rational concentration of dry solids.

Conditioning

Conditioning is a chemical or physical process that improves the dewaterability of a sludge during its preparation for dewatering. Sludge conditioning consists of such methods as inorganic chemical conditioning, organic chemical conditioning, thermal conditioning, elutriating, and freeze–thawing. Chemical conditioning is a commonly used method. By this process, chemicals such as ferric chloride, lime, organic polymers, and others are added to sludge to coagulate or flocculate the fine particles and decrease bound water. It is a unique process vital to the successful operation of sludge thickening and dewatering systems. Thermal conditioning uses elevated temperatures and pressures to promote the separation of solids and liquid through the release of cell-bound water. By using thermal conditioning, sludge can often be mechanically dewatered without using chemicals. Freeze–thaw conditioning substantially decreases consumption of reagents required for conditioning sludge that was mechanically dewatered.

Dewatering

Dewatering is the process of natural or mechanical removal of water from sludge during which the sludge loses its fluidity, becomes damp solids, and can be transported in bulk. The dewatering processes currently in use include natural methods such as air drying on drying beds, lagoons, and mechanical methods such as belt press filtration, centrifugation, vacuum filtration, and pressure filtration. Moisture in sludge may be bound physicomechanically, physicochemically or bonded chemically and can also be present as "free water." Conditioning of sludge before dewatering allows increasing part of the free water, and more water can be removed by mechanical dewatering. Primary raw sludge has better dewatering ability than mixtures of primary raw sludge and thickened activated sludge and better than digested sludge. Dewatering often is followed by sludge aerobic or anaerobic digestion. During the dewatering process, the water is not completely removed from the sludge. The moisture remains within 70–80% limits. At that moisture level, sludge loses its fluidity and may be moved by conveyors. Sludge, generally, should be dewatered before it is thermally dried, composted, alkali stabilized, or incinerated.

Stabilization

Stabilization is one of the more frequently used methods of sludge treatment (especially if the sludge will be used as a fertilizer). All sludge requires some form of treatment, whether stabilization, thickening, or dewatering, possibly followed by drying, composting, and incineration, or a combination of one or more of these processes, before being discharged into the natural environment. Stabilization is a combination of processes of sludge treatment to meet U.S. EPA or other applicable criteria for beneficial use. The process of stabilization is necessary to eliminate the potential of putrefaction of sludge's organic part, to prevent offensive odor dissemination, and to reduce volatile and pathogen content. Two criteria typically used to measure biosolids stability include the volatile solids content and pathogen indicator organism reduction. The following methods of sludge stabilization are in use: aerobic digestion, anaerobic digestion, alkaline stabilization, composting, thermal drying, heat/wet air oxidation, acid (oxidation) disinfecting, and some others.

Aerobic Digestion. Aerobic digestion has been widely used in wastewater treatment plants (WWTP) for many years. Aerobic digestion is a process of oxidizing the organic part of the sludge by microorganisms in special tanks in the presence of oxygen (air aeration of sludge). Aerobic sludge digestion stabilizes raw sludge and produces biosolids for further treatment and disposal. The process of aerobic sludge digestion may be conducted using several technological schemas. The duration of the volatile part of solids oxidation depends on the food/microorganism ratio, temperature, intensity and quantity of the air aeration, and also on wastewater composition and technological demand. This process is more useful for digesting and stabilizing thickened activated sludge.

Anaerobic Digestion. Anaerobic digestion is a biological process that reduces volatile solids by using microorganisms in the absence of oxygen and reduces odor and pathogen content. Digesters are cylindrical reservoirs with conical bottoms; the upper section of the reservoir has a sealed cover with a device for collecting the gas. Two types of anaerobic digestion processes are in use: mesophilic and thermophilic. Mesophilic processes occur in the temperature range of 32–35 °C. The thermophilic process operates at higher temperature (50 to 55 °C) to reduce organic solids and pathogen content further. The quantity of gas obtained during digestion is approximately 1.0 m^3 for every 1.0 kg of disintegrated organic sludge. The following composition of the gas can be expected: methane—60 to 70%; carbon dioxide—16 to 34%; nitrogen, hydrogen, and oxygen—0.4 to 6%. The heat of combustion of this gas averages around 21 million Joule/m^3(MJ/m^3). Anaerobic digestion is a widely used stabilization process for primary or a mixture of primary and thickened waste activated sludge.

Alkaline Stabilization. Alkaline stabilization of sludge produces biosolids that are reduced in pathogen and vector attraction, and meet Class "A" requirements. Of the chemicals used for sludge stabilization, the most common is quicklime or hydrated lime, which is added to sludge before or after dewatering. The quantity of lime added is determined so that the pH of the sludge and lime mixture is raised to 12.0 or above for a period of 2 hours.

Composting. Various composting processes are used, such as windrow composting, aerated static piles, and in-vessel composting. This technology includes mixing dewatered sludge with an added bulking agent (sawdust, peat, wood chips, bark, etc.) and aerating the mixture. In sludge composting, a biothermal process takes place in which microorganisms reduce the sludge's organic in the presence of oxygen. This aerobic process is accompanied by a rise in temperature to about 55–65 °C and a decrease in moisture content. The quantity of organic sludge reduced during composting averages 25%. A reduction of 1.0 kg of sludge organic creates an average 21 MJ/kg of heat. Taking in to account heat losses and heating of compost material, it is necessary to spend approximately 4 MJ of heat to evaporate 1.0 kg of water. Thus, the reduction of 1.0 kg of organic sludge allows removing 5.0 kg of water from the sludge. Besides that, part of the moisture is removed from the sludge by natural evaporation. The total quantity of moisture removed from the sludge depends on climate factors, the season of the year, the dimensions of the piles, duration of composting, and intervals between shoveling over. Removal of moisture from the sludge produces compost at a moisture content of approximately 50–55%. During composting, the heat generated by the decomposition of the organic portion of the sludge stabilizes and renders the sludge harmless transforming it into usable soil conditioning biosolids.

Thermal Drying. Thermal drying is used to destroy pathogens, to eliminate odor, and to reduce most of the water content and the volume of sludge and transportation costs of the biosolids. Thermal drying of sludge is conducted in drying systems consisting of a drying device and the auxiliary equipment, which includes furnaces with a fuel supply system, feeders, cyclones, scrubbers, blowing equipment, conveyors and bins, monitoring and measurement instruments, and automatic control equipment. Depending on the consistency of the sludge, its end uses and quantity, spray dryers, drum dryers, opposed jet dryers, dryers with suspended and fluidized beds, pneumatic pipe dryers, and other different types of heat dryers can be used. Thermal drying can produce dry biosolids whose moisture content ranges from 10–40%, but it does require fuel for processing.

Incineration. Sludge is incinerated if it is impossible or economically infeasible to use, if storage is limited or unavailable, and also when it is required for sanitary and hygienic considerations. The most commonly used types of incinerators are multiple-hearth and fluidized-bed furnaces. Incineration dramatically reduces the volume of sludge and completely disinfects it. The preparation of sludge for incineration requires dewatering and/or thermal drying. When considering incineration, it is important to choose a method that yields safe exhaust gases and techniques to reduce the amount of energy required and/or provide some, if not all, of the required energy from another sludge process.

CONCLUSION

The purpose of sludge treatment is to reduce the moisture content and the volume of sludge; it renders the sludge harmless, prepares it for biosolids use, and moves biosolids from the WWTP. The most common types of sludge treatment are thickening, dewatering, and stabilization, which can be used one after the other consecutively and in various combinations. Stabilization refers to a number of processes, which reduce volatile solids, pathogen levels, vector attraction, and odor. Sludge must be stabilized before use and disposal. The variety of wastewater sludge treatment alternatives allows comparing and choosing cost-effective technology for each wastewater treatment plant.

READING LIST

Operation and Maintenance of Sludge Dewatering Systems. (1987). *Manual of Practice*. #OM-8. WPCF.

MOP. (1988). *Sludge Conditioning*. MOP ED-14.

WEF. (1996). *Standards for the Use and Disposal of Sewage Sludge—Final Rule and Phased—In Submission of Sewage Sludge Permit Application*. WEF.

WEF. (1996). *Wastewater and Sludge Treatment Processes*. WEF.

(1997). High-temperature sludge digesters and duckweed ponds reduce the cost of sludge disposal. *Chem Eng*. **February**: 81–83.

Bruce, A.M. and Fisher, W.J. (1994). *Sewage Sludge Stabilization and Disinfection*. Ellis Hardwood, Chichester, UK.

WEF. (1992). *Design of Municipal Wastewater Treatment Plants*. MOP 8, Vol. 2. WEF.

Epstein, E. (1997). *The Science of Composting*. Technomic, Lancaster, PA.

Foess, G.M. and Siger, R.B. (1993). Pathogen/vector attraction reduction requirement of the sludge rules. *Water Eng. Manage*. **June**: 25.

Ghosh, S. (1987). Improved sludge classification by two-phase anaerobic digestion. *Environ. Eng*. **June**: 1265–1284.

Lawler, D.F. and Chung, V.J. (1986). Anaerobic digestion. Effect on particle size and dewaterability. *W.P.C.F.* **December**: 1107.

Lue-Hing, C., Zenk, D.R., and Kuchenither, R. (1992). *Municipal Sewage Sludge Management*. Technomic, Lancaster, PA.

McDonald, G.J. (1995). Applying sludge to agricultural land-within the rules. *Water Eng. Manage.* **February**: 38.

Metcalf and Eddy, Inc. (1992). *Wastewater Engineering, Treatment, Disposal, and Reuse*. McGraw-Hill, New York, p. 1334.

Parkin, G.F. (1986). Fundamentals of anaerobic digestion of waste-water sludges. *Environ. Eng*. **May**: 867–920.

Spellman, F.R. (1997). *Dewatering Biosolids*. Technomic, Lancaster, PA.

Spellman, F.R. (1997). *Incinerating Biosolids*. Technomic, Lancaster, PA.

Turovskiy, I.S. (2001). Technological improvement for the aerobic digestion of sludge. *Water Eng. Manage.* **August**: 33–36.

US EPA. (1999). *Biosolids Generation, Use, and Disposal in the United States*. 530-R-99.

MUNICIPAL STORM WATER MANAGEMENT

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INTRODUCTION

Enlargement of urbanization and industrial activities around the countryside have significantly altered the natural landscape of watersheds. The hydrological changes resulting from urbanization are shown in Fig. 1 (1).

This, in turn, has adversely affected both the quantity and the quality of storm water runoff and has contributed to the chemical, physical, and biological impairment of receiving waters. Several studies have shown that heavy metals, synthetic organics, pesticides, fuels, waste oils, and pathogens commonly contaminate storm water that originates from urban and industrial areas. To help improve the quality of storm water discharges, the U.S. Congress amended the Clean Water Act in 1987, which directs the Environmental Protection Agency (EPA) to develop the National Pollutant Discharge Elimination System (hereafter termed NPDES). Under NPDES regulations, the municipalities must develop storm water management plans that include specific controls to reduce the discharge of pollutants to the maximum extent practicable. The management plans must also address the legal, administrative and financial aspects of the municipality's storm water control program.

The municipal storm water management programs all involve similar elements. These include mainly public information/participation, elimination of illegal

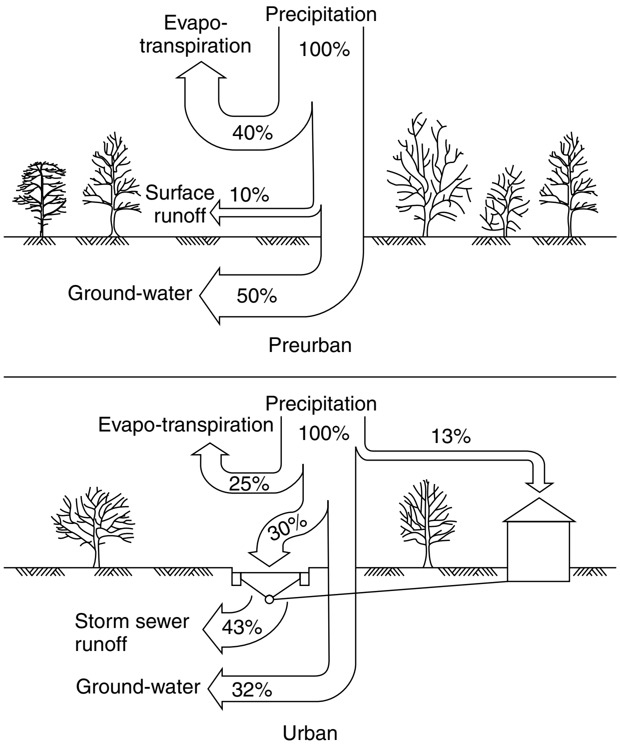

Figure 1. Comparison of water distribution before and after urbanization (1).

discharges, public agency activities, control of industrial/commercial storm water discharges, new development management, storm water treatment, program evaluation, and monitoring. The activities associated with each of these essential program components are presented briefly in the following (2):

PUBLIC INFORMATION/PARTICIPATION

This element is considered the most important early action and is the cornerstone of effective pollution prevention. Its objectives are to inform the public, commercial entries, and industries about the proper use and disposal of materials and waste and to correct the practices of storm water runoff pollution control. The public information activities include the development of general and focused information materials, as well as public service announcements. The participation activities include citizen monitoring programs, stenciling of storm drain inlets with “no dumping” signs and organized creek cleanups.

ELIMINATION OF ILLEGAL DISCHARGES

The elimination of illicit connections to the storm drain system and the prevention of illegal dumping are other essential early action elements. The objective is to ensure that only storm water or otherwise authorized discharges can enter the storm drains. The relevant activities include inspection of storm drain outfalls, surveillance of storm drain systems, and enforcement actions.

PUBLIC AGENCY ACTIVITIES

Many public agency activities may affect storm water pollution. Some activities prevent or remove storm water pollution; other activities are actually sources of pollution. The objective of this element is to ensure that routine municipal operations and maintenance activities are initiated or improved, to reduce the likelihood that pollutants are discharged to the storm drain system. The relevant activities include street sweeping; maintenance of storm drain inlets, lines, and channels and catch basins; corporation yard management; and the application of specific recycling programs. Coordination of road maintenance and flood control activities with storm water management program is also included.

CONTROL OF INDUSTRIAL/COMMERCIAL STORM WATER DISCHARGES

Industrial and commercial sources may contribute substantial pollutant loading to a municipal storm drain system. The objective of this element is to identify and effectively control the industrial and commercial sources of concern. The relevant activities include compilation of a list of industrial and commercial sources, identification of appropriate pollution prevention and control measures, and inspection of respective facilities. The focus is not only on facilities associated with industrial activity, as defined in the storm water regulations, but on any facility that conducts industrial activities, as well as commercial facilities, such as automotive operations and restaurants. This effort is expected to complement federal and state industrial storm water permitting efforts.

NEW DEVELOPMENT MANAGEMENT

New development (and redevelopment) areas offer the greatest potential for implementing the most effective pollution prevention and control measures. The objective of this element is to reduce the likelihood of pollutants entering the storm drain system from areas of new development or significant redevelopment during and after the construction period. The relevant activities include mainly the review of existing local permitting procedures and the modification of the procedures to identify and assign appropriate site design, erosion control, and permanent storm water control measures.

STORM WATER TREATMENT

The initial focus of storm water management programs is on pollution prevention and source control. The subsequent treatment of collected storm water is expected to be a rather costly alternative. There may be opportunities, however, for installation or retrofitting of structural control. The objectives of this element are to study the various treatment alternatives available, to test the feasibility of conducting the activities, and to determine the effectiveness of the treatment through pilot-scale projects. The main available treatment system alternatives are the following:

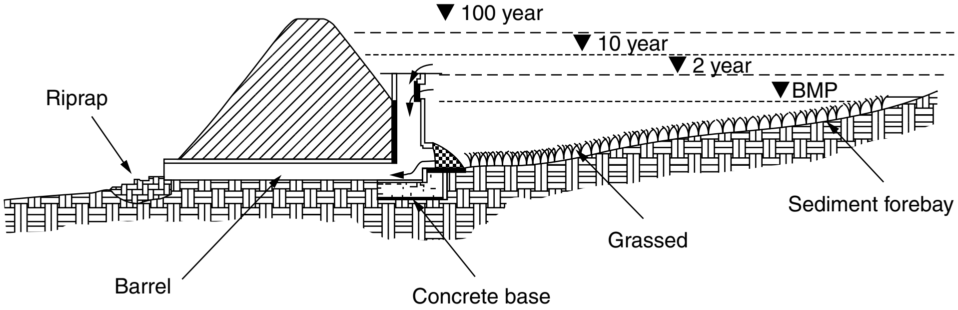

Figure 2. Detention basin (2).

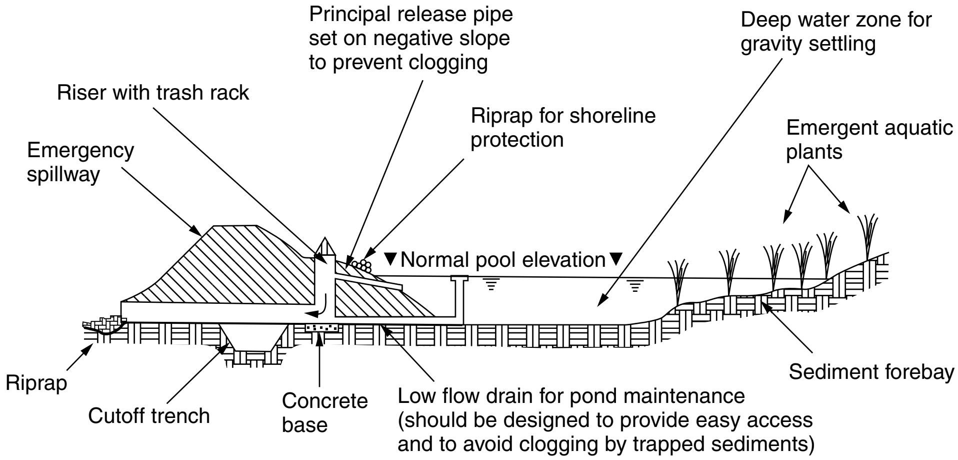

Figure 3. Retention pond (2).

1. *Infiltration systems*, which capture a volume of runoff and infiltrate it into the ground. Infiltration facilities may include infiltration basins, infiltration trenches, or porous pavement systems.
2. *Detention systems*, which capture a volume of runoff and temporarily retain that volume for subsequent release. Detention systems do not retain a significant permanent pool of water between runoff events; a common type is shown in Fig. 2.
3. *Retention systems*, which capture a volume of runoff and retain that volume until it is displaced in part or in total by the next runoff. Retention systems, therefore, maintain a significant permanent pool volume of water between runoff events. The details of a retention pond are shown in Fig. 3.
4. *Constructed wetland systems* are similar to retention and detention systems, except that a major portion of the water surface area (in pond systems) or bottom (in meadow-type systems) contains wetland vegetation. This group also includes wetland channels. A typical wetland system design is shown in Fig. 4 (3).
5. *Filtration systems* use some combination of granular filtration media, such as sand, soil, organic material, carbon or a membrane, to remove constituents found in runoff.
6. *Vegetated systems (biofilters or bioretention systems)*, such as swales and filter strips, are designed to convey and treat either shallow flow (swales) or sheet flow (filter strips) runoff. A diagram of a typical bioretention area is shown in Fig. 5.
7. The method of *minimizing directly connected impervious surfaces* describes a variety of practices that can be used to reduce the amount of surface area directly connected to the storm drainage system by minimizing or eliminating the traditional curb and gutter. This is considered to a nonstructural practice, but it has been included here because of the need to design and construct alternative conveyance and treatment options.
8. *Miscellaneous and vendor-supplied systems*, which include a variety of proprietary and miscellaneous systems that do not fit under any of the above categories. These may include catch basin inserts, hydrodynamic devices, and filtration devices.

PROGRAM EVALUATION

Storm water management programs are expected to change as they mature. Consequently, they should have built-in flexibility to allow for changes in priorities, needs, or levels of awareness. The objective of this element is to provide a comprehensive annual evaluation and report of the program's effectiveness. The measures of effectiveness include mainly quantitative monitoring to assess the effectiveness, the specific control measures, and the detailed accounting of program accomplishments and funds and staff hours expended. The annual report provides an overall evaluation of the program and sets forth plans and schedules for the coming year. The annual report is considered a program's self-audit and

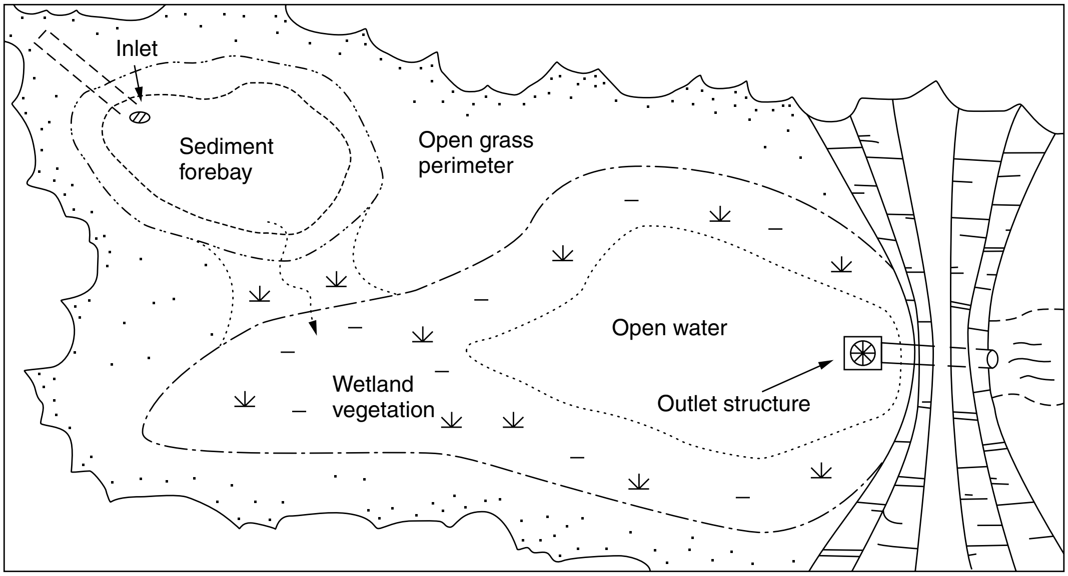

Figure 4. Constructed wetland system (3).

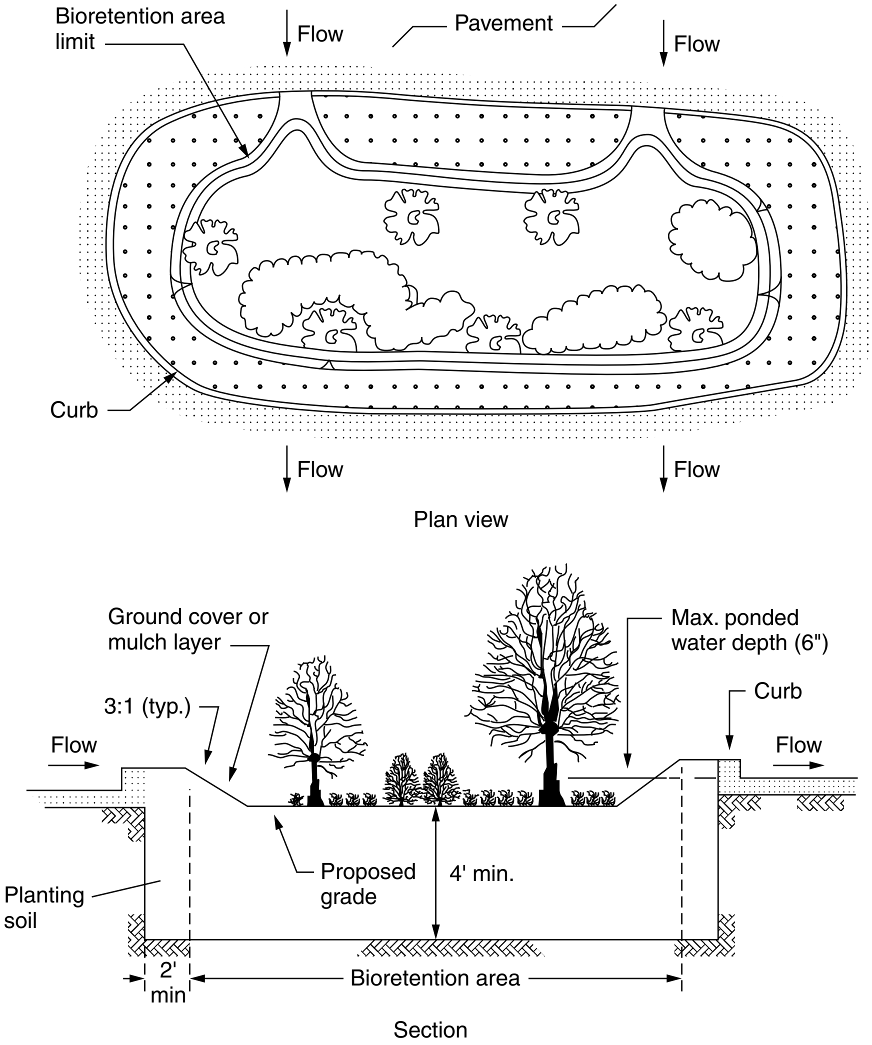

Figure 5. Bioretention system (3).

provides a mechanism to propose modifications to the storm water management plan in response to program accomplishments or failures. The annual report also serves as the key regulatory tool for providing accountability and public review in accordance with the respective NPDES permit.

MONITORING

Monitoring is an essential component of any pollution control program. The objectives are to obtain quantitative information to measure program progress and effectiveness, to identify the sources of pollutants, and to document the reduction of pollutant loads (if any). The success of the monitoring program can be measured by the ability to make more informed decisions on a program's direction and effectiveness. The monitoring activities include primarily the baseline monitoring of storm drain discharges and receiving waters and is focused on special studies to identify sources of pollutants and to evaluate the effectiveness of specific control measures. The types of monitoring may include water column measurements, sediment measurements, and nonsampling and analysis measurements, such as the number of outfalls inspected or the amount of material removed by regular maintenance actions. Toxicity identification and evaluations are also integral components of monitoring programs.

BIBLIOGRAPHY

1. Quasim, S.R. (1999). *Wastewater Treatment Plants: Planning, Design and Operation*. Technomic, Lancaster, PA.
2. U.S. EPA. (1998). *N.P.D.E.S. Storm Water Phase II Fact Sheets*, Washington, DC.
3. U.S. EPA. (1995). *National Conference on Urban Runoff Management: Enhancing Urban Watershed Management at the Local, County and State Levels*. Report EPA/625/R-95/003. Chicago, IL.

WHAT WASTEWATER UTILITIES CAN DO NOW TO GUARD AGAINST TERRORIST AND SECURITY THREATS

U.S. Environmental Protection
Agency—Office of
Wastewater Management

One consequence of the events of September 11th is a heightened concern among citizens in the United States over the security of their critical wastewater infrastructure. The nation's wastewater infrastructure consisting of approximately 16,000 publicly owned wastewater treatment plants, 100,000 major pumping stations, 600,000 miles of sanitary sewers and another 200,000 miles of storm sewers, is one of America's most valuable resources, with treatment and collection systems valued at more than $2 trillion. Taken together, the sanitary and storm sewers form an extensive network that runs near or beneath key buildings and roads, and is contiguous to many communication and transportation networks. Significant damage to the nation's wastewater facilities or collection systems would result in: lose of life, catastrophic environmental damage to rivers, lakes and wetlands, contamination of drinking water supplies, long term public health impacts, destruction of fish and shellfish production, disruption to commerce, the economy and our normal way of life. Although many wastewater utilities have already taken steps to increase security, the following recommendations provide many straightforward, commonsense actions to increasing security and reducing threats from terrorism. Many of these actions are recommended by the Association of Metropolitan Sewer Agencies, the Water Environment Federation, and other leading professional organizations. The recommendations include:

GUARDING AGAINST UNPLANNED PHYSICAL INTRUSION

- Lock all doors and set alarms at your office, pumping stations, treatment plants, and vaults, and make it a rule that doors are locked and alarms are set;
- Limit access to facilities and control access to pumping stations, chemical and fuel storage areas, giving close scrutiny to visitors and contractors;
- Post guards at treatment plants, and post "Employee Only" signs in restricted areas;
- Control access to storm sewers;
- Secure hatches, metering vaults, manholes and other access points to the sanitary collection system;
- Increase lighting in parking lots, treatment bays, and other areas with limited staffing;
- Control access to computer networks and control systems, and change the passwords frequently;
- Do not leave keys in equipment or vehicles at any time.

MAKING SECURITY A PRIORITY FOR EMPLOYEES

- Conduct background security checks on employees at hiring and periodically thereafter;
- Develop a security program with written plans and train employees frequently;
- Ensure all employees are aware of communications protocols with relevant law enforcement, public health, environmental protection, and emergency response organizations;
- Ensure that employees are fully aware of the importance of vigilance and the seriousness of breaches in security, and make note of unaccompanied strangers on the site and immediately notify designated security officers or local law enforcement agencies;
- Consider varying the timing of operational procedures if possible so if someone is watching the pattern changes.

- Upon the dismissal of an employee, change passcodes and make sure keys and access cards are returned;
- Provide Customer Service staff with training and checklists of how to handle a threat if it is called in.

COORDINATING ACTIONS FOR EFFECTIVE EMERGENCY RESPONSE

- Review existing emergency response plans, and ensure they are current and relevant;
- Make sure employees have necessary training in emergency operating procedures;
- Develop clear protocols and chains-of-command for reporting and responding to threats along with relevant emergency management, law enforcement, environmental, public health officials, consumers and the media. Practice the emergency protocols regularly;
- Ensure key utility personnel (both on and off duty) have access to crucial telephone numbers and contact information at all times. Keep the call list up to date;
- Develop close relationships with local law enforcement agencies, and make sure they know where critical assets are located. Request they add your facilities to their routine rounds;
- Work with local industries to ensure that their pretreatment facilities are secure;
- Report to county or State health officials any illness among the employees that might be associated with wastewater contamination;
- Report criminal threats, suspicious behavior, or attacks on wastewater utilities immediately to law enforcement officials and the relevant field office of the Federal Bureau of Investigation.

INVESTING IN SECURITY AND INFRASTRUCTURE IMPROVEMENTS

- Assess the vulnerability of collection system, major pumping stations, wastewater treatment plants, chemical and fuel storage areas, outfall pipes, and other key infrastructure elements;
- Assess the vulnerability of the storm water collection system. Determine where large pipes run near or beneath government buildings, banks, commercial districts, industrial facilities, or are contiguous with major communication and transportation networks;
- Move as quickly as possible with the most obvious and cost-effective physical improvements, such as perimeter fences, security lighting, tamper-proofing manhole covers and valve boxes, etc.;
- Improve computer system and remote operational security;
- Use local citizen watches;
- Seek financing for more expensive and comprehensive system improvements.

While wastewater utilities are the key to improving security of our wastewater treatment plants and collection systems, EPA, other Federal agencies, and both industry and managerial trade associations also provide help and support. EPA is working with AMSA and other groups to develop training courses and technical materials for wastewater utilities and State personnel on assessing vulnerabilities and improving security. EPA is working collaboratively with the Association of Metropolitan Water Agencies and other groups to develop an Information Sharing and Analysis Center to bolster coordinated notification and response to threats and vulnerabilities at both water and wastewater facilities. A number of technical projects are underway to help increase security of the nation's critical wastewater infrastructure.

FOR MORE INFORMATION

For more information please visit the following web sites:

EPA Counter-terrorism: http://www.epa.gov/ebtpages/ecounterterrorism.html
EPA Alert on Chemical Accident Prevention and Site Security: http://www.epa.gov/ceppo/pubs/secale.pdf
Association of Metropolitan Sewer Agencies: http://www.amsa-cleanwater.org
Association of Metropolitan Water Agencies: http://www.amwa.net/isac/amwacip.html
Water Environment: http://www.wef.org
National League of Cities: http://www.nlc.org/nlc_org/site/newsroom/terrorism_response

WASTEWATER TREATMENT TECHNIQUES—ADVANCED

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ADVANCED OXIDATION PROCESSES (AOP)

All advanced oxidation processes are characterized by a common chemical feature: production of $OH^{\bullet}$ radicals.

Table 1 and Fig. 1 show a list of AOP and their applicability.

These radicals are suitable for achieving complete abatement and mineralization of pollutants. AOP usually operate at or close to ambient temperature and pressure. The potentialities offered by AOP can be exploited to integrate biological treatments by oxidative degradation of toxic substances, entering or leaving the biological stage (1–2). The usual two AOP are the Fenton process and photocatalysis:

Fenton Process

Production of $OH^{\bullet}$ radicals by Fenton's reagent occurs when addition of H_2O_2 is added to Fe^{2+} salts (3): It has been demonstrated that Fenton's reagent can destroy toxic

Table 1. Some Advanced Oxidation Technologies

Fenton-Type reactions
$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + Fe^{3+} + OH^-$
Ozone—peroxide—UV systems
$O_3 + {}^{-}OH \rightarrow O_2{}^{-} \rightarrow {}^{\bullet}OH$
$3O_3 + UV(< 400\ nm) \rightarrow 2{}^{\bullet}OH$
$H_2O_2 + UV(< 400\ nm) \rightarrow 2{}^{\bullet}OH$
$H_2O_2 + O_3 \rightarrow 2{}^{\bullet}OH$
$H_2O_2 + O_3 + UV \rightarrow {}^{\bullet}OH$
Semiconductor oxides—UV systems
$TiO_2 + hv \rightarrow TiO_2(h^+ + e^-)$
$H^+ + OH^- \rightarrow {}^{\bullet}OH$
Radiolysis (high-energy beams)
$H_2O \rightarrow e^-{}_{aq} + H^{\bullet} + {}^{\bullet}OH + (H_2, H_2O_2, H_3O^+)$
Wet oxidation (WO) systems
$RH + O_2 \rightarrow R^{\bullet} + HO_2{}^{\bullet}$
$RH + HO_2{}^{\bullet} \rightarrow R^{\bullet} + H_2O_2$
$H_2O_2 + M \rightarrow 2\ OH^{\bullet}$
$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O$
$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$
$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
Sonolysis (ultrasound)
$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH$

Source: Reference 26.

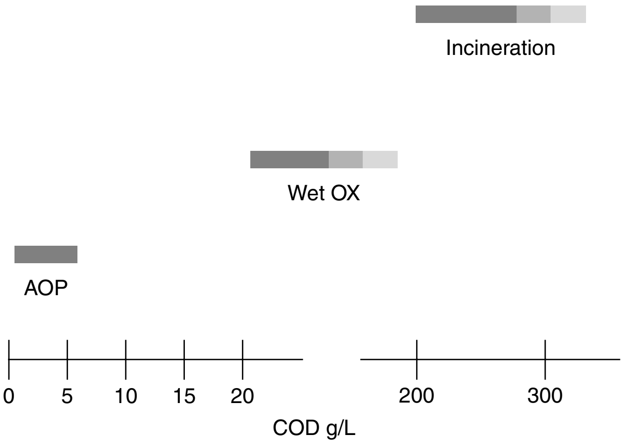

Figure 1. Suitability of water treatment technologies according to COD contents. (*Source*: Reference 1).

compounds such as phenols and herbicides in wastewaters. Irradiation by UV-vis light strongly accelerates the degradation rate of organic pollutants (4). The application of the Fenton process requires strict pH control; sludges can be formed which create disposal problems.

Photocatalysis

In this process, hydroxyl and other radicals are generated at the surface of an UV-absorbing powder (called a photocatalyst). The most widely used photocatalyst is the wide band-gap (3.2 eV) semiconductor TiO_2 in its anatase crystalline form (5–6). TiO_2 absorbs UV light at wavelengths below ~ 380 nm creating an excess of electrons in the conduction band ($e^-{}_{cb}$) and holes in the valence band ($h^+{}_{vb}$):

$$TiO_2 \longrightarrow (e^-{}_{cb} + h^+{}_{vb})$$

The carriers can diffuse to the surface where they react as follows:

$$h^+{}_{vb} + OH^- \longrightarrow OH^{\bullet}{}_{ads}$$

and

$$e^-{}_{cb} + O_2 \longrightarrow O_2{}^{\bullet -}{}_{ads}$$

where ads = adsorbed to the surface of TiO_2 particles.

Organic pollutants may adsorb on the surface of TiO_2 particles, and there they are attacked by the adsorbed $OH^{\bullet}$ radicals and holes. The $O_2{}^{\bullet -}$ radicals can further disproportionate as follows:

$$2O_2{}^{\bullet -}{}_{ads} + 2H^+ \longrightarrow H_2O_2 + O_2$$

Although the quantum yield of TiO_2 photocatalyzed reactions is rather low, the system does have the advantage that it can use UV photons in the near UV (blacklight UV fluorescent lamps or the UV portion of solar radiation) (Fig. 2). Compilations of substances which can be mineralized using photocatalysis are now available (7).

COMPLEXATION/FLOCCULATION

It has been shown that dissolved humic substances (DHS), bind (complex) organic solutes via hydrophobic interactions, forming humic–contaminant complexes in the aqueous phase. The use of DHS in flushing solutions to enhance desorption of hydrophobic contaminants from sediments was suggested by several researchers (8–10). It was further proposed to remove the humic–contaminant complexes by flocculation using alum or ferric salts, followed by press filtration and incineration or disposal of the resulting precipitate.

The treatment process follows two stages: (1) binding of Dissolved Humic Acid (DHA) by the dissolved contaminants to form complexes (complexation stage) and (2) precipitation of DHA and the associated contaminant by using a flocculant (alum or ferric chloride, flocculation stage). This process can be applied to remove various classes of hydrophobic organic pollutants such as PAHs, PCBs and chloro-organo pesticides from industrial wastewater. Additionally, this technology has the advantage that it may be coupled to the general water treatment process (Fig. 3) (11)

CONDUCTING POLYMERS

Conducting polymers have ion exchange properties induced by charging and discharging processes (12). For instance, polypyrrole (PPy) can function as an anion exchanger, whereas PPy modified with polystyrenesulfonate anions (PPy/PSS$^{\bullet}$) works as a cation exchanger (Fig. 4) (13,14). Such a modified polymer can be used as an electrochemically switchable ion exchanger for water softening (15). This ion exchanger can be regenerated without chemical additives or aqueous electrolysis.

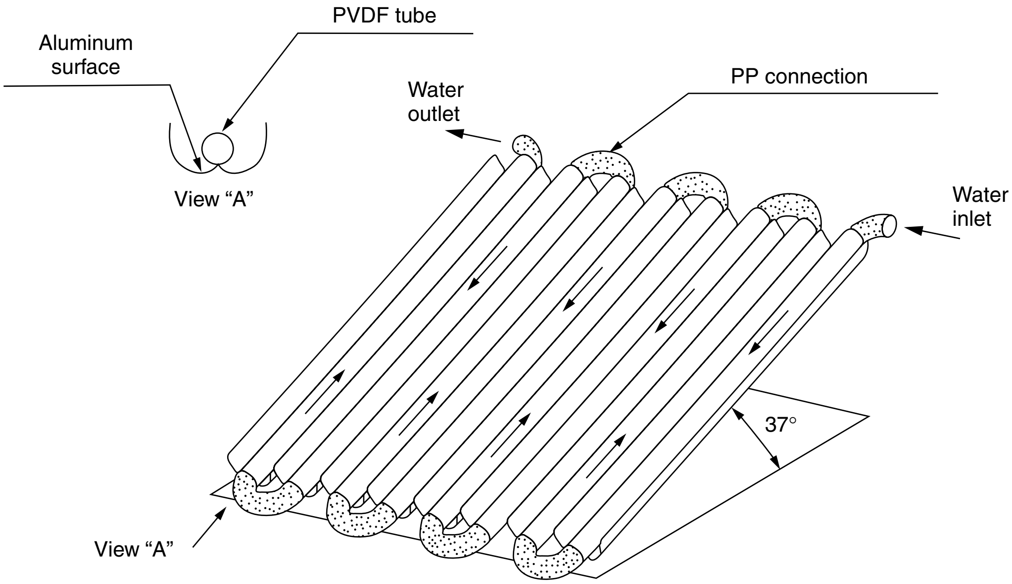

Figure 2. Scheme of one CPC module used for solar detoxification of water. (*Source*: J.M. Hermann, et al. (1998). *Appl. Catal. B: Environmental* **17**: 15).

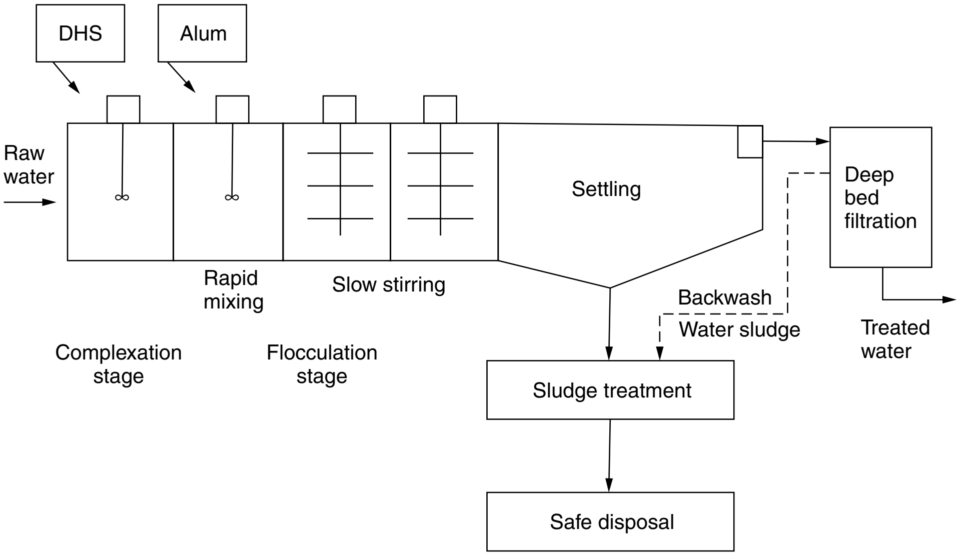

Figure 3. Flow diagram of the complexation—flocculation process coupled with a common water treatment operation. (*Source*: Reference 11).

IONIZING IRRADIATION

High energy irradiation (γ rays, X rays, and electron beams) interacts with water to generate a variety of free radicals, principally $OH^{\bullet}$, $H^{\bullet}$ and hydrated electrons. If H_2O_2 or O_3 is present in the water, the $H^{\bullet}$ and the hydrated electrons are converted efficiently to $OH^{\bullet}$ radicals. This process is based on electron accelerators. An attempt has been made to use combined electron beam and ozone for treating municipal wastewater in aerosol flow (Fig. 5) (16,17).

MEMBRANE/SONICATION/WET OXIDATION

Hybrid systems are becoming popular for treating waste streams that are otherwise difficult to handle. For instance, the powder-activated carbon–activated sludge system (PACT system by Zimpro Environmental, Inc.) is a classic example of such systems. OXYMEM is another hybrid process, where wet oxidation and nanofiltration were used together to treat bioresistant industrial wastewater containing polyethylene glycol. It has also been demonstrated that sonication followed by wet oxidation (SONIWO) is a useful hybrid process for treating refractory waste. Conventional bioprocesses may not be amenable to biodestruction of the effluent from reactive bath dye. "Membrane-sonication-wet oxidation" (MEMSONIWO) is a hybrid process applied to water conservation via recycling. The membrane unit allows concentrating the waste, and then the permeate (mostly water) can be recycled. The concentrate from the membrane unit can, then, be treated by sonication to

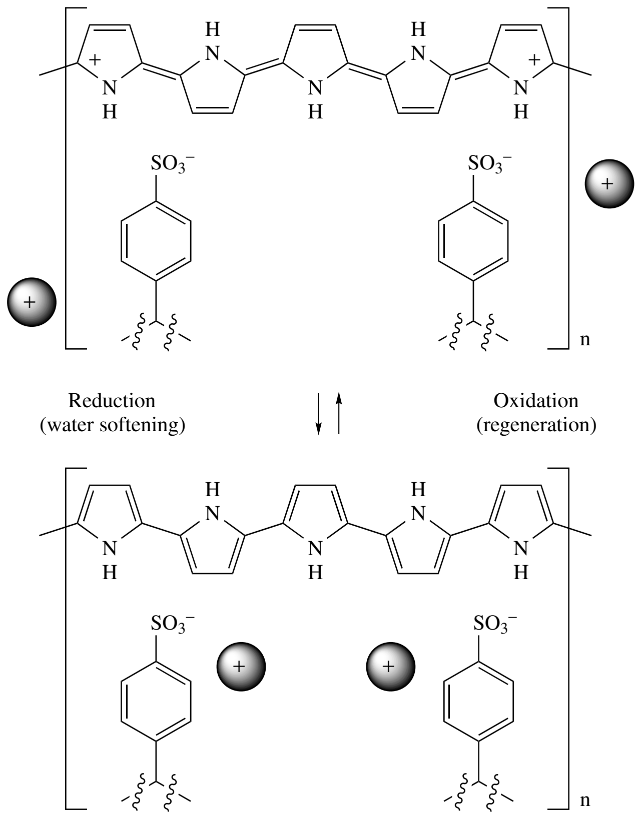

Figure 4. Polypyrrole with incorporated PSS anions working as a cation exchanger. (*Source*: Reference 15).

make it suitable for wet oxidation. After wet oxidation, the water can be discharged or recycled (18).

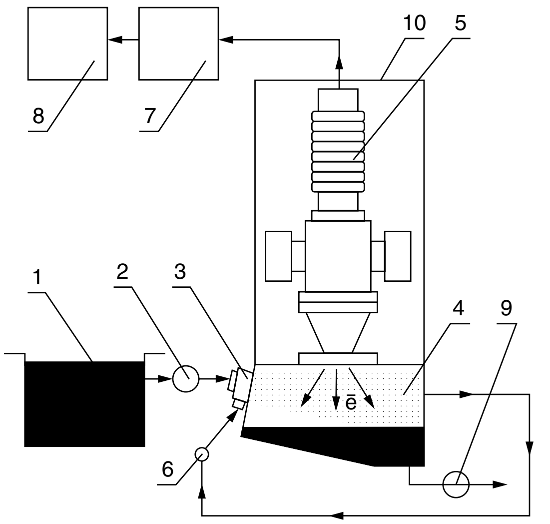

Figure 5. Scheme of pilot plant for combined electron-beam and ozone treatment of municipal wastewater in aerosol flow. (1) Reservoir of wastewater intake (2) Electric pump unit for wastewater (3) Sprayer unit (4) Irradiation chamber (5) Electron accelerator (6) Turboblower (7) Power supply (8) Control desk (9) Electric pump unit for purified water removal (10) Biological shielding (*Source*: Reference 17).

SORPTION BY ZEOLITES

It is well established that the sorption characteristics of zeolite-type materials are defined by pore size and charge properties (19). Most naturally occurring zeolites bear a relatively high framework charge arising from Al^{3+} substitution for Si^{4+} in the crystal lattice; this results in a structure of high cation-exchange capacity. Such zeolites have been used as ion exchangers to treat water and are incorporated into systems for treating radioactive waste (removal of $^{137}Cs^+$ and $^{90}Sr^{2+}$) and for removing NH_4^+ from wastewater. Zeolites that have high SiO_2/Al_2O_3 ratios have a low capacity to retain cations but are more hydrophobic and can, therefore, sorb uncharged molecules. In laboratory studies using batch sorption equilibria, high Si large-pore mordenite (MOR) and ZSM-5, it was found, have sorption properties for methyl tert-butyl ether (MTBE) and trichloroethylene (TCE) that are superior to those of activated carbon (Table 2) (20).

SUPERCRITICAL WATER OXIDATION

Supercritical water oxidation (SCWO) is considered a promising technology for treating several wastes (21–24). SCWO is a process where oxidation takes place in water above its critical point (647 K, 22.1 MPa). SCWO is an environmentally acceptable technology that produces a disposable clean liquid (pure water), clean solid (metal oxides, salts), and clean gas (CO_2, N_2). Recently, there has been increasing interest in using heterogeneous catalysts in SCWO (Fig. 6). Catalysts can increase the oxidation rates, reduce the residence times and temperatures

Table 2. Solution Concentrations and Percent Removal after Equilibration of 100 μg/L Solutions with 5 mg of Solid Phase[a]

	MTBE		$CHCl_3$		TCE	
Sorbent	μg/L	% Removal	μg/L	% Removal	μg/L	% Removal
MOR	4.0 ± 0.3a	96	62.2 ± 5.2a	38	23.2 ± 4.4a	77
ZSM-5	36.6 ± 9.4b	63	21.9 ± 1.2b	78	< 3.0b[b]	> 97
Y	94.9 ± 6.1c	5	99.6 ± 3.9c	< 1	90.9 ± 1.7c	9
AC	48.2 ± 3.9b	52	43.8 ± 2.2d	56	32.2 ± 1.6a	68

[a] Mean values within columns followed by the same letter are not significantly different from each other at $p \leq .05$.

[b] 3 μg/L was the detection limit for the method used.

Source: Reference 20.

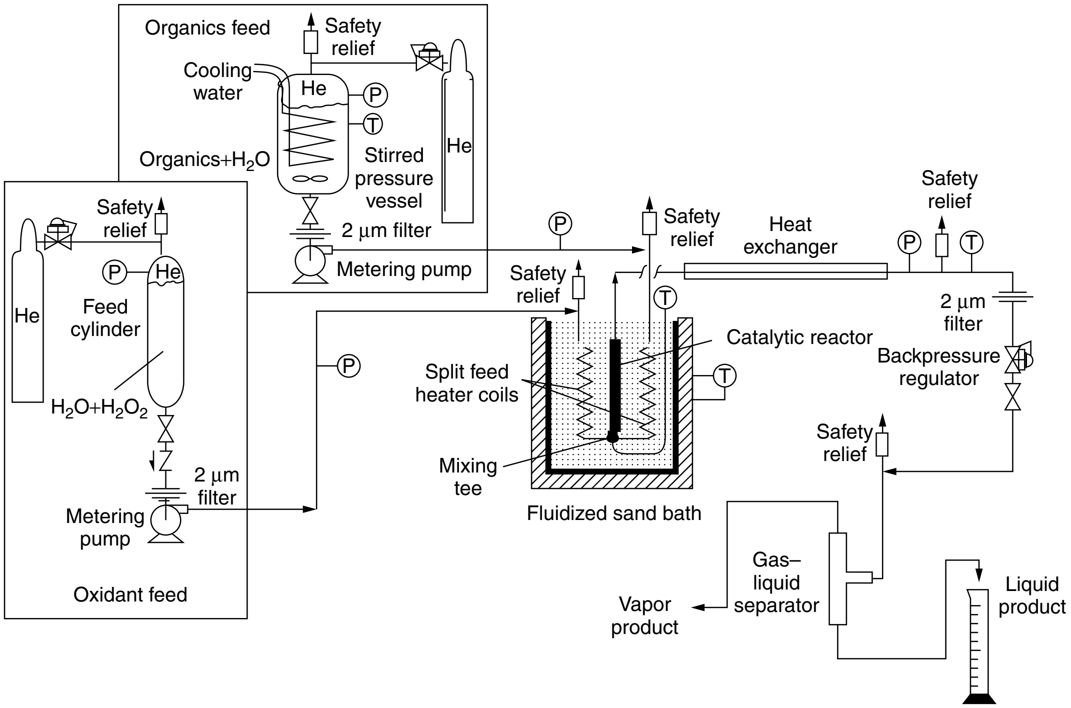

Figure 6. Experimental apparatus for catalytic SCWO. (*Source*: Reference 25).

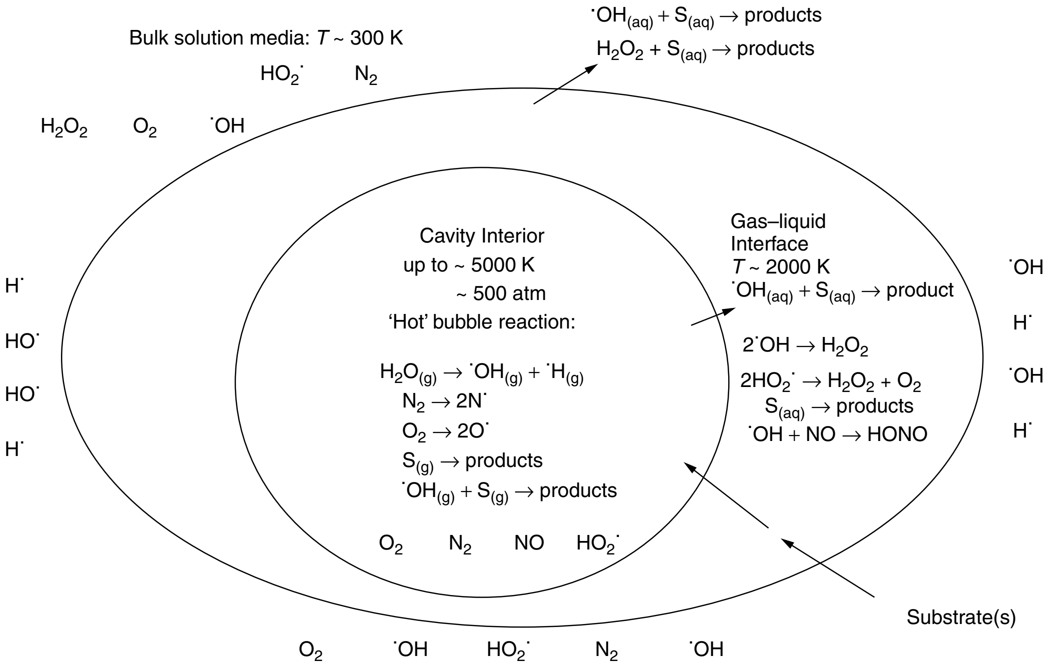

Figure 7. Three reaction zones in the cavitation process. (*Source*: Reference 26).

required for treatment, and possibly control the selectivity of the reaction pathways (25).

ULTRASONIC IRRADIATION

Sonochemical effects are due to the phenomenon of "cavitation," the nucleation and the behavior of bubbles in a liquid (26,27). In wastewater treatment, a bubble of cavitation may function as a microreactor which destroys volatile organic compounds inside (28–30). The cavity may also be thought as a $H^\bullet$, $OH^\bullet$, $OOH^\bullet$ radical source that react with pollutants in the bulk of the solution (Fig. 7). Several potential applications of ultrasonic irradiation have been reported recently.

BIBLIOGRAPHY

1. Andreozzi, R., Caprio, V., Insola, A., and Marotta, R. (1999). *Catal. Today* **53**: 51.
2. Ollis, D.F. (1993). In: *Comparative Aspects of Advanced Oxidation Processes, Emerging Technologies in Hazardous Waste Management III*. D.W. Tedder and F.G. Pohland (Eds.). Chap. 2, ACS Symposium Series 518, Washington, DC.
3. Haber, F. and Weiss, J. (1934). *Proc. R. Soc. Ser. A* **147**: 332.
4. Bauer, R. et al. (1999). *Catal. Today* **53**: 131.
5. Mills, A. and Hunte, S.L. (1997). *J. Photochem. Photobiol. A: Chem.* **108**: 1.
6. Bahnemann, D. (1999). *The Handbook of Environmental Chemistry*. Vol. 2, Part I, Environmental Photochemistry, P. Boule (Ed.). Springer-Verlag, Berlin.
7. Blake, D.M. (1999). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air*. Report NREL/TP-570-26797, National Renewable Energy Laboratory, Golden, CO.
8. Johnson, W.P. and Amy, G.L. (1995). *Environ. Sci. Technol.* **29**: 807.
9. Rebhun, M., Smedt, F.D., and Rwetabula, J. (1996). *Water Res.* **30**: 2027.
10. Liu, H. and Amy, G.L. (1993). *Environ. Sci. Technol.* **27**: 1553.
11. Rebhun, M., Meir, S., and Laor, Y. (1998). *Environ. Sci. Technol.* **32**: 981.
12. Shimidzu, T., Ohtani, A., and Honda, K. (1988). *J. Electroanal. Chem.* **88**: 323.
13. Zhong, C., Doblhofer, K., and Weinberg, G. (1989). *Faraday Discuss. Chem. Soc.* **88**: 307.
14. Ren, X. and Pickup, P.G. (1993). *J. Phys. Chem.* **97**: 5356.
15. Weidlich, C., Mangold, K-M., and Juttner, K. (2001). *Synth. Met.* **119**: 263.
16. Pikaev, A.K. et al. (1996). *Radiat. Phys. Chem.* **48**: 75.
17. Pikaev, A.K., Podzorova, E.A., and Bakhtin, O. (1997). *Radiat. Phys. Chem.* **49**: 155.
18. Dhale, A.D. and Mahajani, V.V. (1999). *Ind. Eng. Chem. Res.* **38**: 2058 and references therein.
19. Newsam, J.M. (1986). *Science* **231**: 1093.
20. Anderson, M.A. (2000). *Environ. Sci. Technol.* **34**: 725.
21. Mishra, V.S., Mahajani, V.V., and Joshi, J.B. (1995). *Ind. Eng. Chem. Res.* **34**: 2.
22. Matatov-Meytal, Y.I. and Sheintuch, M. (1998). *Ind. Eng. Chem. Res.* **37**: 309.
23. Gloyna, E.F. and Li, L. (1995). *Environ. Prog.* **14**: 182.
24. Levec, J. (1997). *Chem. Biochem. Eng. Q* **11**: 47.
25. Yu, J. and Savage, P.E. (1999). *Ind. Eng. Chem. Res.* **38**: 3793 and references therein.
26. Adewuyi, Y.G. (2001). *Ind. Eng. Chem. Res.* **40**: 4681 and references therein.
27. Thompson, L.H. and Doraiswamy, L.K. (1999). *Ind. Eng. Chem. Res.* **38**: 1215.
28. Pétrier, C. and Francony, A. (1997). *Ultrasonic Sonochemical* **4**: 295.
29. Phull, S.S. et al. (1997). *Ultrasonic Sonochemical* **4**: 157.
30. Pandit, A.B., Gogate, P.R., and Mujumdar, S. (2001). *Ultrasonic Sonochemical* **8**: 227.

TRENCHLESS REPAIR AND REHABILITATION TECHNIQUES

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Trenchless technology (TT) consists of a wide range of methods, materials, and equipment for installing new or rehabilitating existing underground pipelines and utility systems with minimal excavation of the ground. According to the North America Society of Trenchless Technology (NASTT), trenchless construction is “a family of methods, materials, and equipment capable of being used for the installation of new or replacement or rehabilitation of existing underground infrastructure with minimal disruption to surface traffic, business, and other activities.”

Open-cut trench construction has proven expensive, especially in congested urban areas, because it requires disruption of surface activities. Some problems caused by the open-cut method include traffic disruption, economic impact on local businesses, damage to existing utilities, and concerns for worker safety. The development and use of trenchless techniques has expanded rapidly over the past 10 years. The reason for this exceptional growth is the desire to install or rehabilitate underground pipeline systems with minimum impact on society and the environment. The benefits of trenchless technology are quite apparent compared with the conventional open-cut process. However, it is necessary to evaluate the suitability and appropriateness of any rehabilitation system, trenchless or otherwise, on a project-by-project basis with due consideration of all project criteria, such as size and material of pipe, level of deterioration, hydraulic capacity, etc.

According to a 2003 survey (http://www.oildompublishing.com/UC/uchome.html) of trenchless construction methods used by municipalities, the percentage of all municipal projects using trenchless construction methods has grown by 180% (new installation) and 270% (rehabilitation), respectively, over the past 5 years.

BASICS OF PIPELINE RENOVATION USING TRENCHLESS TECHNIQUES

Trenchless pipeline renewal methods offer several advantages over conventional dig-up and repair/replace methods:

- minimize disturbance to existing site, underground utilities, and environment;
- are more suitable for difficult underground conditions, such as high water table and unstable soils;
- require less exposed work area, therefore involving lesser risk to the workers and public; and
- minimize the need for spoil removal and disposal.

The primary trenchless pipeline-system renewal methods can be divided into five categories (Table 1):

Table 1. Trenchless Pipeline Renewal Methods

Method	Diameter Range, in.	Maximum Installation Lengths, ft.	Liner Material[a]	Application
		Sliplining:		
Segmental	12–150	5000	PE, PP, PVC, GRP	Gravity & pressure
Continuous	4–60	1000	PE, PP, PVC, GRP	Gravity & pressure
Spiral wound	4–100	1000	PE, PP, PVC, PVDF	Gravity
		CIPP:		
Inverted in place	4–108	3000	Thermoset resin	Gravity & pressure
Winched in place	4–54	500	Thermoset resin	Gravity & pressure
		Close-Fit:		
Swaged	4–15	700	HDPE, PVC	Gravity & pressure
Folded	3–24	1000	HDPE, MDPE	Gravity & pressure
Expanded spiral	4–36	1000	HDPE, MDPE	Gravity & pressure
		Spray-on Lining:		
Cement mortar	4–36	NA	Cement mortar	Gravity & pressure
Shotcrete	>42	NA	Cement mortar	Gravity & pressure
Epoxy	4–24	NA	Epoxy	Gravity & pressure
		Point Source Repairs:		
Robotic	8–30	NA	Epoxy & cement mortar	Gravity
Grouting	NA	NA	Chemical grouting	Any
Mechanical sleeve	4–24	NA	Mechanical sleeves	Any
Point CIPP	4–24	50	Fiberglass/polyester resin	Gravity

[a] **Definitions of Acronyms**: PE: Polyethylene; PP: Polypropylene; PVC: Polyvinyl chloride; PVDF: Polyvinylidene chloride; GRP: Glassfiber reinforced polyester; HDPE: High density polyethylene; MDPE: Medium density polyethylene.

- sliplining
- cured-in-place pipe (CIPP)
- close-fit pipe
- spray lining
- point source repair

Sliplining

Sliplining is one of the earliest forms of trenchless pipeline rehabilitation. There are three main types of sliplining: continuous, segmental, and spiral wound. A new pipe of smaller diameter is inserted by pulling, pushing, or spiral winding it into the host pipe, and the annulus between the existing pipe and the new pipe is grouted. Small liners may be pulled in manually but most require a winch (Fig. 1). The winch applies a steady, progressive pull to place the liner inside the host pipe. The liner pipe is generally butt-fused to its design length. Numerous designs of pipe pushing machines, both manual and hydraulic, are available. In most instances, an insertion pit is required for the pushing machine. The pushing machine grips the liner pipe and pushes it forward into the host pipe. The gripping mechanism is then released and returned to the starting position, and the process is repeated. Segmental liners are generally used to reduce the size of the insertion pit. Pipe joints are generally of the mechanical type with either a snap-fit or a screw-on mechanism. For spirally wound liners, strips of PVC material are passed through a winding machine and a helically wound liner pipe is manufactured *in situ*. To increase the stiffness of the liner pipe, ribbed strips are used, with “T-beams” forming on the outer surface. The winding machine is normally located down a manhole or a small excavation. The tube travels down the host pipe as more strips are fed into the machine. The whole tube is rotating during the installation, so the limiting factor is usually the friction and weight of the liner that the winding machine is capable of turning. An alternate spirally wound technique overcomes this drawback by using a winding machine that travels through the host pipe, thereby removing the need to rotate the liner itself.

This method has the merit of simplicity and is relatively inexpensive. One of the chief drawbacks of sliplining is the resulting decreased cross-sectional area. In some instances, however, despite the reduced cross section, the hydraulic capacity of the pipeline may actually increase due to the superior flow characteristics of the new pipe. The reconnection of laterals and service lines in conjunction with sliplining of gravity pipelines usually necessitates excavation. Excavation must take place and the lateral must be disconnected before grouting. Electrofusion is commonly used to connect laterals to PE liners in the same way as new installations. For glass-fiber reinforced polyester resin (GRP) pipe, laterals may be typically reconnected to the new liner pipe using “tees.”

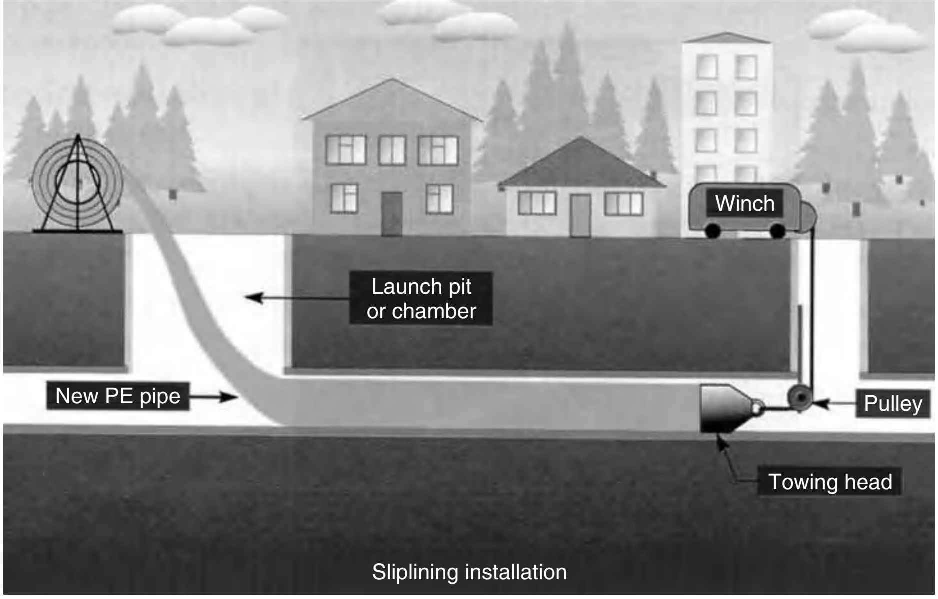


Figure 1. Continuous sliplining.

Cured-In-Place Lining (CIPP)

The main alternative to sliplining and its variants in the non-man-entry pipeline renovation market is the cured-in-place lining (CIPP), sometimes referred to as "*in situ* lining." Although several patented systems are currently available, the common feature of CIPP is the use of a polyester or epoxy resin impregnated fabric tube. The tube is inserted into the existing host pipe and inflated against the wall of the host using a hydrostatic head or air pressure (Fig. 2). The inflated liner is cured by recirculating hot water or steam. The CIPP process creates a "close-fit" pipe that has quantifiable structural strength and can be designed for specific loading conditions.

The chief advantages of CIPP is that it minimizes the reduction in cross section and the liner pipe can conform to noncircular cross sections. The laterals can be reopened remotely after lining by using a remote controlled robotic cutter. The chief disadvantage of this method is the need to take the host pipe out of service during installation and curing. Diversion or bypass pumping adds to the installation cost. CIPP is not cost-effective for large diameters.

As in all trenchless renovation systems, thorough cleaning and preparation are essential. In non-man-entry pipelines, CCTV inspection should be carried out prior to and after installation. All silt and debris should be removed completely by jetting or other means prior to installation. Intruding connections, encrustation, and other deposits should be removed by mechanical means or high-pressure jetting, followed by cleaning to remove debris. There may be short-term environmental implications with CIPP systems when using polyester resins. The solvents in the systems can give off strong odors and in high concentrations, the vapor can pose a health risk. Such levels are not typically found in CIPP installations; nonetheless, adequate ventilation of a CIPP work site is essential. This problem applies only until the resin is cured.

Close-Fit Pipe

The use of liners that are deliberately deformed prior to insertion, and then revert to their original shape once

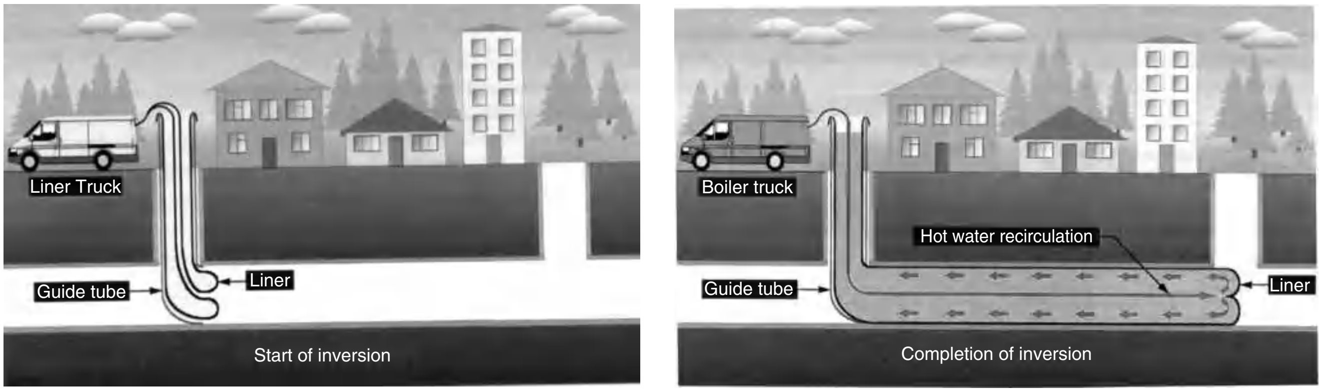
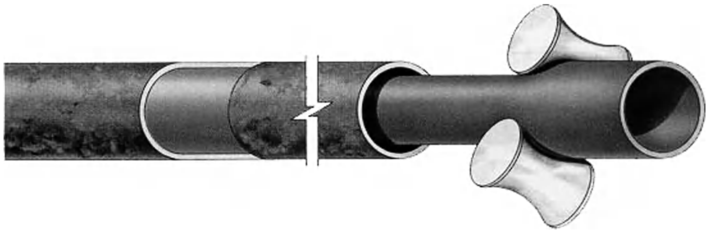


Figure 2. Cured-in-place pipe (CIPP) lining.

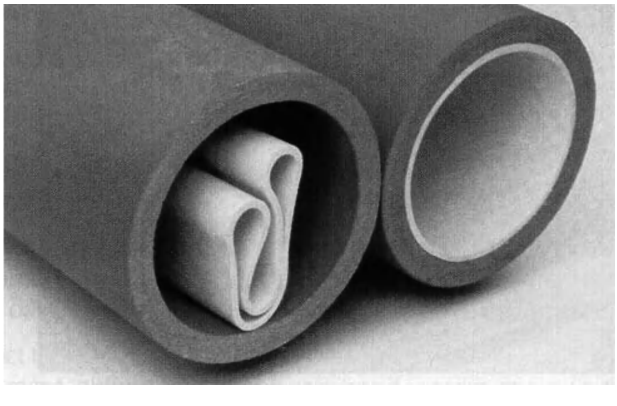


The pipe is reduced in diameter by passing it through rollers or dies, and is reverted to its original size after insertion

Figure 3. Swaged liner. Diagram courtesy of Subterra.

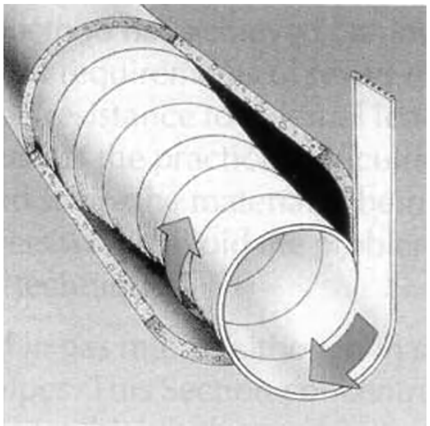
in position, so that they fit closely inside the host pipe, is called "close-fit lining." Such techniques are a logical development of basic sliplining described previously. The close-fit pipe method takes two principal forms, both of which take advantage of the built-in memory of some polymeric pipe materials. In one method, the diameter of the liner is temporarily reduced by drawing it through a set of rollers, a process referred to as "swaging," so that it can be inserted into the existing pipe (Fig. 3). Once installed in place, the liner is restored to its original size by pressurizing the line. Due to the limitations on size reduction, this technique is better suited to pressure pipes than to gravity sewers that have dimensional irregularities. The second method involves folding the liner into a "U" or "C" shape prior to insertion (Fig. 4), and then using heat and/or pressure to restore its original shape. This technique is often described as "fold-and-form." The liner diameter and wall thickness are the main limitations of this process, but it can be used for both pressure pipes and gravity sewers. Some versions of the spirally wound lining technique described previously offer the facility to expand the liner to provide a close fit with the host pipe. During installation, the joint between the adjacent turns of the helix is prevented from slipping by a locking wire. Once the liner is in position, the locking wire is pulled back progressively to allow the joint to slip and the helix to increase in diameter (Fig. 5).

Close-fit lining minimizes the need for cross-sectional reduction. Theoretically speaking, in this type of method, there is no annulus and therefore no need for annulus grouting. The curing time is reduced compared with a cured-in-place (CIPP) liner. As in CIPP, the lateral connections can be reopened remotely after lining by using a remote controlled robotic cutter. The chief disadvantage is the size limitation (for non-man-entry pipe sizes).



Folded PVC liner for sewer renovation, showing close fit after reversion

Figure 4. Fold-and-form pipe.



The spirally wound liner is expanded after insertion by allowing slippage between adjacent turns of the helix

Figure 5. Spirally wound liner being installed in a host pipe.

Spray-On Linings

Spray-On linings have a long history in potable water pipelines, where the principal objective is to remove the scale and corrosion of old pipelines, generally made of cast iron, and then apply a coating that inhibits further deterioration and seals minor leaks and cracks. The most common materials used for this purpose are *cement mortar linings* or *epoxy resin linings*. For small-to medium sized pipelines this can be achieved by a robotic spraying machine that is winched through the pipeline at a constant, predetermined rate. Development continues in achieving a cost-effective application of spray-on linings in non-man entry sewer pipeline renovation, but so far no method has commercial prominence. This may be partly due to the differing requirements for sewer renovation, where the aim is to increase the structural strength of the pipe, rather than prevent corrosion, and partly due to the practical difficulty of ensuring that the inflow into the system is completely stopped while the material is being applied and cured. For large, man-entry pipelines, the application of a mortar lining can be done manually or mechanically.

Spray-on linings are usually intended as protective coatings and rely on the bond to the host pipe for their function. Hence the preparation of the host pipe is critically important. Old water mains, particularly those made of cast iron, often have heavy internal deposits of corrosion and scale. Cleaning techniques include high-pressure water jetting, scraping, pigging, etc. There is often a balance drawn between removing all traces of corrosion and avoiding damage to the pipe wall; some of the more aggressive cleaning techniques should be used with caution.

Pipe scrapers are designed to remove hard deposits. Spring-loaded steel blades are mounted on the central shaft of a scraper. A towing eye is fitted to each end allowing the scraper to be pulled through the pipe in either direction. Wire brush pigs consist of circular wire brushes mounted on a central shaft and are used to remove the debris loosened by the scrapers or by themselves to remove loose debris from the pipe. Cleaning pigs are available in a wide range of designs and are normally driven through the pipe under water pressure. In a heavily encrusted pipe, pigging may be carried out in stages, using pig sizes of increasing diameters. Pull-through pigs, also known as "squeezes," remove fine material and fluids from pipes. They consist of rubber disks fitted to the central shaft that are towed through the pipe. Pull-throughs are often used in the final stage of pipe preparation to produce a clean, dry surface, to which the spray-on lining is applied.

The application of a *cement mortar lining* is a common and a relatively inexpensive method for water main renovation. The cement mortar serves two important functions: the alkalinity of the cement inhibits corrosion of an iron pipe, and the relative smoothness improves flow characteristics. Note that cement mortar linings are applied to many new cast iron and ductile iron pipes to inhibit corrosion. Application is generally by a spraying machine that is either fed by a hose from the surface or, for large pipes, may have its own hopper containing premixed mortar. The forward speed of the sprayer is controlled to achieve a consistent mortar thickness. Spray application may be followed by troweling. This is often carried out by rotating spatulas fitted to the spraying machine.

For renovation of large diameter brick and concrete pipelines, *shotcrete* is often used as a cost-effective means to enhance the structural integrity of a pipeline. Shotcrete is a process in which mortar or concrete is conveyed through a hose and projected at high velocity onto the surface of a pipe. Shotcrete may be applied dry or wet. The method of applying dry-mix shotcrete through a hose using compressed air is also given the trade name, *Gunite*. There are advantages and disadvantages to both methods. For instance, a wet-mix shotcrete application results in less rebound, less dust, and yields a higher compressive strength. The drawbacks of the wet-mix are limited conveying distance, increased demand on aggregate quality, and increased clean-up costs. As in other lining methods, surface preparation is critical. All deteriorated material from the pipe walls must be removed along with dirt, oil, and other bond inhibiting material. The pipe surface must be dampened in the wet method so as to be saturated surface dry (SSD) prior to application. Prepackaged mixtures of ready-to-use cementitious mortars containing various proportions of silica fume and fiber reinforcement, and admixtures for high-strength, low-shrinkage shotcrete are commercially available. For additional strength, reinforcing bars or welded wire fabrics may be used. Both wet and dry-shotcrete are shot perpendicularly to the pipeline surface to minimize rebound and to create a smooth pattern. After applying the shotcrete, it is allowed to stiffen for about 10 minutes before "bumpy" areas are troweled to give a uniform surface. Shotcrete is applied in layers (approximately 1-inch thick) until the required design thickness is reached. Before applying the next layer, the previous layer must be allowed to reach an initial set. This can take from 45 minutes to several hours depending on mix consistency and ambient temperature.

Epoxy linings are an alternative to cement mortar linings (Fig. 6). The resin bonds to the surface of the pipe, forming a coating, which inhibits water penetration and corrosion. Epoxy coatings are much thinner than cement mortar linings and therefore do not significantly reduce the pipe cross section. However, any defect in the coating may allow corrosion to start and unlike cement mortars, they do not have alkalinity to inhibit chemical deterioration. Epoxy resins are also relatively expensive compared to cementitious materials. Epoxy resins should not be used for lining water lines unless specifically approved by NSF. The resin is applied by a spraying machine with a rotating nozzle. The thickness of the coating is controlled by the flow rate and forward speed of the sprayer. In most systems, the resin base and the hardening agent are fed through separate hoses and are combined by a static mixer just behind the spray nozzle. Ideally, the cure time should be as short as possible to minimize the time during which the pipe is kept out of service. However, too rapid a cure carries the risk of causing blockage in the static mixer or the nozzle. Unlike cement mortar linings, the resin is not smoothed or troweled after spraying, and the

Figure 6. Application of epoxy resin lining.

surface quality depends on the application technique and the properties of the material.

Epoxy linings do not fulfill any structural function and are not recommended for pipes that leak significantly or for pipes with significant structural defects.

Point Source Repairs

Various localized repair systems have been developed, most aimed at sewer renovation but include some that are designed to seal joints in pressure pipes. Many techniques are adaptations of the full-length lining systems seen previously.

The economics of "spot repair" versus renovation of the entire pipe length is assessed by the Design Engineer, but as a general rule spot repair methods may prove economical where defects in the pipe are restricted to less than 25% of the length. Preinspection of the pipeline and cleaning are just as essential to localized repairs as to full-length renovation. There are four broad categories of localized repair systems: robotic, grouting, mechanical seals, and point CIPP. Sometimes point repair systems are classified into two categories, structural and nonstructural. Robotic methods, mechanical seals, and point CIPP produce increased structural strength and are hence regarded as "structural" renovation techniques; chemical grouting is often termed "nonstructural."

Point Source Repairs. Robotic techniques, used mainly in gravity pipelines, consist of a grinding robot and a sealing robot (Fig. 7). The grinding robot can be fitted with various shapes of diamond carbide cutters suitable for clayware, concrete, polymeric pipe, and even steel. The wheels are driven by an electric motor and cooled by a water jet spray. The robotic operation is monitored by a CCTV camera attached to the head. Typically, the grinding robot mills cracks to a width and depth of up to 1 inch, after which the area around the crack is cleaned. A grinding robot can also remove intruding laterals, grout deposits, and hard encrustation. Like the grinding robot, the sealing robot is self-propelled and equipped with an onboard CCTV camera. Epoxy is applied by the sealing robot to completely fill the slot milled by the grinding robot. In addition to filling slots, the sealing robot can apply epoxy around poorly made connections or leaking joints to seal connection and joints.

All robotic functions are controlled from a central console housed in a vehicle, which contains the power pack, hoist for lifting and lowering robots into manholes, and other ancillary equipment. Robotic repairs are versatile, but to be cost-effective, a consistent program of work is needed.

Grouting. Resin injection systems fall into two categories: those whose principal function is to seal the pipeline against infiltration and exfiltration and those that restore structurally damaged pipe.

A common method of sealing leaking joints in gravity pipelines is by using a special packer that combines the functions of leakage testing and grout injection. A packer with inflatable elements is positioned across a pipe joint and pressurized to isolate the joint. The joint is tested for pressure loss and if necessary a sealing gel is injected through the packer to seal the joint. The grout has little intrinsic strength but turns the ground around the leaky joint into an impermeable mass thereby enhancing the structural stability of the pipe.

In the past, the use of acrylamide grouts was commonplace. However, these grouts have been banned in the United States because the unreacted components pose a serious health risk. Today the use of polyurethane (PU) grouts is common. PU grouts react with the free water in the soil to form a viscous gel that hardens over time. Many PU grouts contain acetone to reduce viscosity. The flammability of acetone should be considered during storage and handling.

For leak sealing the entire system—main sewer, laterals, and manholes—a different approach is taken, often referred to as "fill and drain." The section of the sewer to be sealed is first isolated and then filled from manhole to manhole with an environmentally safe chemical solution (usually *sodium silicate*). After a predetermined interval to allow the chemical to permeate through leaking joints and cracks, the solution is pumped out quickly, and the section filled once again with a second chemical solution

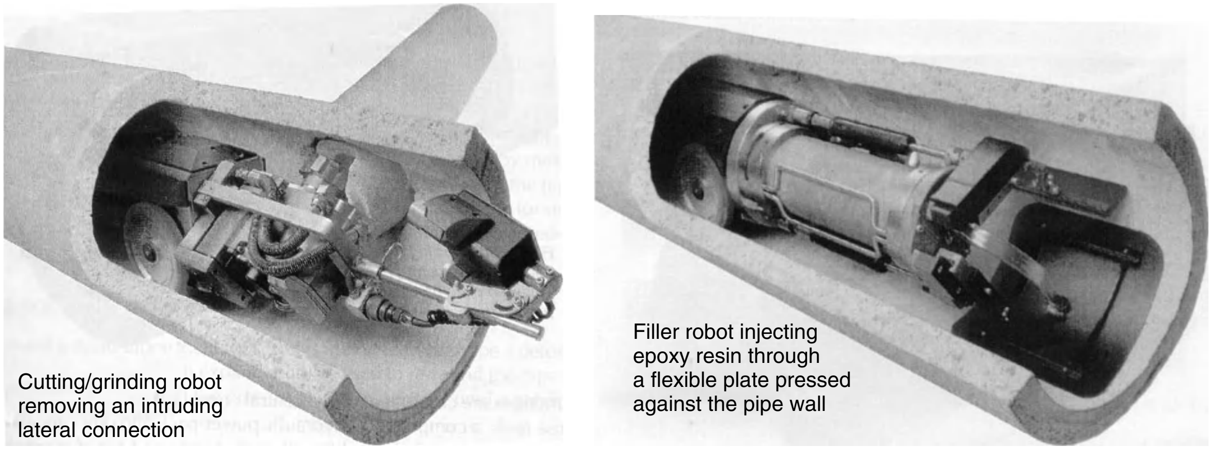


Photo courtesy of KA-TE system AG

Cutting/grinding robot removing an intruding lateral connection

Filler robot injecting epoxy resin through a flexible plate pressed against the pipe wall

Figure 7. Robotic repairs using grinding and filling remotely controlled robots.

(usually *proprietary*), which reacts with the residue of the first chemical to form a waterproof gel. The second chemical is then pumped out and the pipe cleaned before returning it to service.

An epoxy resin system is used to address structural defects in pipes. An inflatable packer isolates the defect and injects a rapid-setting epoxy resin into the crack, fracture, or hole in the pipe wall. The packer is left in position until the resin has cured, thus forming an internal collar inside the pipe.

Mechanical Seals. Mechanical seals are used primarily for sealing leaking joints. This method involves installing a metal band or clip (usually stainless steel) faced with an elastomeric material across the joint. The elastomeric material forms a seal with the inner surface of the pipe. Repair modules are installed by an inflatable packer which expands the clip and presses the elastomeric material against the pipe wall. The packer is then deflated and withdrawn. Systems of this type are available for gravity and pressure pipe. Mechanical sealing systems have the advantage of being quick and easy to install; however, the material cost is higher than in other methods. Tapered versions are available to seal between pipes of varying diameter and to seal the annulus at the ends of sliplined pipes.

Point CIPP. Most point or “patch” repairs with cured-in-place (CIPP) liner sections entail impregnating a fabric with suitable resin, pulling the patch into place within a sewer by using an inflatable packer or mandrel, and then filling the packer with water, steam, or air under pressure to press the patch against the existing sewer wall while the resin cures. After curing, the packer is deflated and removed. The repair is then inspected by CCTV, and any lateral connections present are reopened using the same techniques as for full-length CIPP liners.

Both thermal and ambient cure systems are currently available. In many respects, point repairs are a short version of cured-in-place liners, although often the fabrics and resins are specialized to achieve greater structural strengths in the patch. The fabric is commonly polyester needle-felt (unwoven), either on its own or in combination with glass fiber. Some systems use a multilayer sandwich; the glass fiber provides strength, and the felt acts as a resin carrier. Although polyester resin is used in full-length liners for economy, epoxy resins are a common alternative for local repair systems. Epoxies, unlike polyester resins, are not affected by the presence of water. This is especially relevant in techniques designed for installation without diverting the flow in the pipeline. Impregnation of the fabric is usually, but not always, carried out on site. In this case, care is needed to avoid health risks and the spillage of chemicals, some of which are toxic in the unreacted stage. During mixing and impregnation of the resin, it is important to remove all entrapped air because air can weaken the material and in severe instances results in porosity. To overcome this, some systems use vacuum impregnation.

In both ambient and thermally cured systems, it is essential to limit the rise in the temperature of the material until the patch is inflated within the host pipe. Exothermic cure begins as soon as the resin components are mixed, and the rate of temperature rise depends on the volume of resin mixed. One of the most common causes of point system failure is premature cure, where the patch has started to harden before it is in position.

BASICS OF MANHOLE RENOVATION USING TRENCHLESS TECHNIQUES

Trenchless manhole renewal methods offer several advantages over conventional dig and repair/replace methods. These advantages are similar to those in trenchless pipeline renovation, explained previously.

There are four basic methods of manhole rehabilitation:

- spot repairs (chemical grouting, plugging, and patching);
- cementitious coatings (spray and troweled);
- protective coatings (epoxy and polyurea); and
- structural repair systems (monolithic *in situ* liners)

Spot Repairs. Most injection processes use materials similar to those employed in pipe joint sealing, polyurethane or acrylic grouts. The primary purpose of pressure grouting is for I/I control and stabilization of voids around manholes.

The process generally involves drilling injection holes in a predetermined pattern, through which the grout is injected to create a flexible external membrane. Polyurethene grouts are water-reactive and can be injected without a catalyst if there is sufficient free water in the surrounding ground.

Rapid setting hydraulic cements may be used for plugging holes and cracks and are generally used prior to grout injection to prevent washout of the grout. Some hydraulic cements have a setting time of just a few seconds.

Careful inspection of the contractor’s work during the actual grouting operation is necessary to ensure adequate coating of the exterior of the manhole structure. A follow-up dye test is recommended for each manhole.

Cementitious Coatings. Cementitious coatings are typically used to inhibit I/I and are not structural. Cementitious coatings are typically made of portland cement, finely graded mineral fillers, and proprietary chemical additives. Cementitious coatings are generally brushed on in two applications, one gray and one white, to provide a visual indication of the coverage of each layer, to a total thickness of about 1/2 inch. Before applying the cementitious coatings, it is essential to prepare the interior by washing with high pressure jets and plugging and patching as required.

Protective Coatings. Protective chemical coatings, such as epoxies and polyureas, are used as barriers to bacterial corrosion on new or recently installed precast manholes. They are not used in rehabilitating badly deteriorated or structurally unsound manholes. The recommended coating thickness differs greatly among products and manufacturers, although the typical range is from 60 to 200 mils. A combination of semistructural cementitious liners with epoxy coatings has recently been introduced to provide surface restoration and protection.

Structural Repair Systems. Cementitious liners have been widely used over the past 5 years for structural enhancement of brick manholes which have lost some of their mortar joints but remain basically sound. The liners are made of high-strength, quick-setting mortars of portland or high alumina cements. Thorough preparation of the internal surface is essential, and a bonding or stabilizing agent may be necessary depending on the condition of the manhole. Structural rehabilitation generally requires a cementitious liner thickness of between 1 to 4 inches (Fig. 8).

In situ structural replacement systems fall into two categories: inserts and *in situ* lining systems. A variety of inserts made of fiberglass, polyurethane, PVC, etc., can be installed inside existing manholes and then back-grouted to create a new structure inside the host manhole. The concept is similar to sliplining in pipeline renovation. This method requires excavating the ring and the cone to allow placing the insert inside. If the manhole is tapered, it may be necessary to excavate several feet before the insert can be positioned. Careful attention is required around pipe inlets because it is difficult to make a seal when the material composition of the liner is different from that of the inlet pipe.

In situ lining systems are reconstruction techniques that require no excavation and are not disruptive. These systems use a variety of spiral-wound, cured-in-place, etc., materials to create a liners inside existing deteriorated manholes. Cured-in-place liners are generally recommended for structural rehabilitation of manholes where future corrosion is expected. A felt or a glass-reinforced "bag" is custom-made to the size of the manhole. Resin is impregnated into the bag at the job site. The bag is then lowered into the manhole, steam pressure injected for 1–2 hours to achieve curing, and holes are cut at the invert and pipe inlet locations before returning the manhole to service. Surface preparation is crucial to the success of this method. All voids and recesses need to be filled prior to undertaking cure-in-place lining. The helically wound lining technique described previously for pipeline renewal can also be used for renovating manholes. PVC strips are fed into the manhole opening and spirally wound by a winding machine into the existing manhole. Preparation involves removing ladders, step-irons, and internal backdrops before cleaning the surface by high pressure water jetting. Annulus grouting is carried out to bond the liner to the walls of the manhole.


Figure 8. Application of one-coat cementitious structural liner.

BASICS OF UNDERGROUND WATER AND SEWER PIPELINE ASSESSMENT, REPAIR, AND REHABILITATION

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In March 2001, ASCE released a Report Card for America's Infrastructure. The wastewater and drinking water infrastructure categories received a discouraging D+ overall and an estimated need for an investment of $1.3 trillion to bring conditions to acceptable levels. In September 2003, ASCE released a Progress Report (http://www.asce.org/reportcard/) that examines the current trends for addressing the nation's deteriorating infrastructure. ASCE determined that the conditions and performance had not changed significantly in 2 years.

America's industries rely on clean water to carry out activities that contribute over $300 billion to our economy each year. However, the challenge to continue providing clean water remains because our existing national wastewater infrastructure is aging, deteriorating, and in need of repair, replacement, and upgrading. In fact, EPA has reported that without improvements to the nation's wastewater treatment infrastructure, we face the very real risk of losing the environmental gains we have achieved during the last three decades since the passage of the Clean Water Act of 1972. Drinking water quality remains good, but the infrastructure of the nation's 54,000 drinking water systems is aging rapidly. Federal funding remains flat, and the infrastructure needs continue to increase. There is an annual shortfall of $11 billion needed to replace or rehabilitate facilities that are nearing the end of their useful lives and to comply with federal water regulations.

The nation's 16,000 wastewater systems face enormous needs. Some sewer systems are 100 years old and many treatment facilities are past their recommended life expectancies. For the fiscal year 2001, Congress allocated $1.35 billion for wastewater infrastructure, but currently there remains a $12 billion annual shortfall in funding for infrastructure needs. Sewer overflows and discharge of untreated or undertreated flows into streams and rivers has made more than one-third of U.S. surface waters fail to meet water quality standards.

The forecast for our nation's drinking water systems indicates a downward slope. Drinking water received a D on the 2001 Report Card, yet the situation continues to worsen as aging systems—some developed more than a century ago—continue to service our ever-growing population.

Traditionally, municipalities have constantly been a “step behind” in managing the municipal, and this is especially true of sewer systems. Municipalities have addressed the design, construction, maintenance, and rehabilitation of sewer systems by a “crisis-based” approach. Sewers are not built and/or rehabilitated until a major failure (i.e., overflow, collapse) occurs. This reactive management practice has led to inefficient use of funds and causes more frequent sewer failures, which end in difficult and costly repairs. For municipalities to be a “step ahead” in managing sewer systems, they need to have a better understanding of the existing condition of the network, which in turn will help them plan and manage maintenance to prevent major failures.

PIPELINE ASSESSMENT

A variety of ways and means exist by which existing underground pipelines may be evaluated:

- ground penetrating radar (GPR)
- sonar
- televising
- smoke testing
- dye testing
- flow monitoring
- walk-through
- pressure leak tests
- electronic leak testing

Ground Penetrating Radar

Ground penetrating radar (GPR) works by launching pulses of electromagnetic energy into the soil under investigation. These pulses propagate through the ground and are reflected by subsurface targets or at interfaces between different media. The radar measures the time taken for a pulse to travel to and from the target, which indicates its depth and location. The transit time of the pulse depends on the dielectric properties of the material. In addition, the depth and penetration obtained may vary considerably with soil conditions; for example, loam is an easy medium to penetrate, whereas clay is more difficult.

The difficulty with GPR lies in selecting the correct frequency; different types of soil respond differently to radar frequency. A large study undertaken in Canada to detect leaks in buried plastic water distribution pipes was inconclusive. However, more recent advances in GPR technology and in particular the use of multisensory systems seem to hold promise. Field trials indicate that multisensory systems are more accurate, faster, and capable of working in a variety of ground conditions. At present, however, the effectiveness of this technology in pinpointing inactive leaks in underground pipes is undocumented.

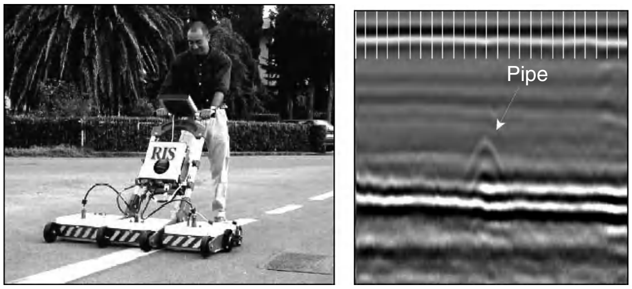

Figure 1. Multisensory ground penetration radar (GPR) used in locating underground pipe.

GPR is used today primarily to locate underground pipelines. GPR equipment is dragged across the surface in a precise fashion, and the output (radar signal) is stored and later graphed after filtering out the “noise” (Fig. 1). Computer enhancements have allowed GPR technology to become very effective in situations where an underground discontinuity (e.g., a pipeline) is known, but the plan location of a buried pipeline is unknown. However, GPR may be able to indicate that a discontinuity exists underground, but there is often an uncertainty about what the discontinuity actually is and also what is the exact depth at which this discontinuity exists.

GPR technology is an evolving field and it is expected that in the future this may very well become the most dominant method of pipeline location and assessment.

Sonar

Sonar can give a relatively accurate picture of the profile of a pipe wall and surrounding soil. The results, however, are very much open to interpretation, and a highly skilled operator is vital. Sonar techniques can, however, show flow regimes under water and are thus useful in detecting infiltration into surcharged pipes.

Televising

Pipeline televising is used to identify problems primarily in sanitary and storm sewer pipe. It is usually referred to as closed-circuit television inspection (CCTV) and consists of a remote television camera passing through a pipe that sends the live picture to a screen aboveground. The remote television camera unit is composed of a camera mounted on a skid or equipped with wheels (Fig. 2). The camera can be directed through the pipe using manholes as access points to insert cables that connect to the remote TV unit. Other cables connected to the remote TV unit carry the signal back to the screen, which is usually mounted in a truck. The screen mount in the truck incorporates a videocassette recorder slot so that data can be saved and viewed by others.

The sizes and types of pipe that can be televised are virtually unlimited, especially with newer technologies that allow smaller TV units to be pushed through small diameter pipe such as house laterals. The line televising crew usually consists of an operator stationed in the truck and one or two operators stationed near the manhole(s).

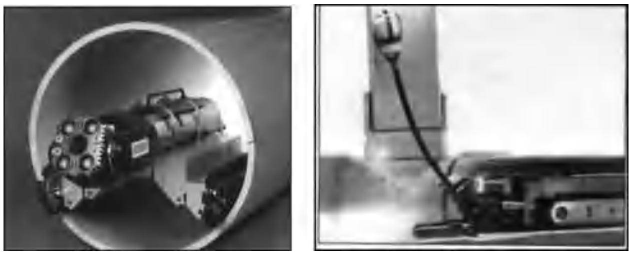

Figure 2. CCTV Systems: Mainline inspection and lateral inspection (left to right).

In most cases, the line televising crew is employed by the local utility, although private contractors perform this service as well.

Line televising is performed as part of routine operation and maintenance by most wastewater utilities. It provides a good indication of the structural integrity of the pipe and can pinpoint problems in a way that was not possible before its invention (Fig. 3).

A utility may also require postconstruction televising at the completion of a new sewer or storm pipe to determine adequacy of joint connections, service connections, or other indications of proper pipe installation. A further application might be the review of lined sewer pipe to ensure that services were properly reinstated. The applications of line televising are numerous. The information generated, in conjunction with proper consultation with the Engineer, will guide the utility toward better decisions regarding the maintenance and operation of the network.

Smoke Testing

Smoke testing is a simple test used to identify unauthorized connections to a sanitary sewer system. In systems where the sanitary and storm sewers are separate, unauthorized connections include roof leaders, downspouts, and yard drains. Smoke testing can also identify direct connections between the sanitary and storm sewer system and, to a lesser extent, locations of broken sewers or "lost" manholes. In these latter two cases, line televising is more effective.

To smoke test, a blower unit is inserted over a manhole to allow smoke to be blown into the sewer (Fig. 4). Pipe plugs are inserted into adjacent manholes to isolate a section of sewer before "smoke bombs" are inserted into the manhole where the blower is located. The smoke blown into the sewer then, in theory, has no place to escape except through unauthorized connections, direct connections from the storm sewer, plumbing vents, or defects in the sewer system. However, there is a potential that smoke can enter homes or businesses if the plumbing that connects the building to the sewer is defective or was installed improperly or if the traps are dry. For example, the absence of a vent pipe in a home may cause smoke to enter the house. For these reasons, advance warning to the residents potentially impacted is not only a good idea, but also a necessity. Further, coordination with the local Police and Fire Departments is necessary to avoid panic or alarm with the potential of smoke detected in resident's homes. Smoke testing can be a valuable tool in determining who is connected to the sanitary, or storm, sewer system.

Dye Testing

Dye testing, like smoke testing, can be used to determine connections to a sanitary, or storm, sewer system or interconnections between the two. It can also be used to determine leaking sewers that may be discharging to creeks or other bodies of water. Improper connections, such as yard drains discharging to a sanitary sewer, can be effectively identified by a dye test. It can also be used to identify positively whether a house is actually connected

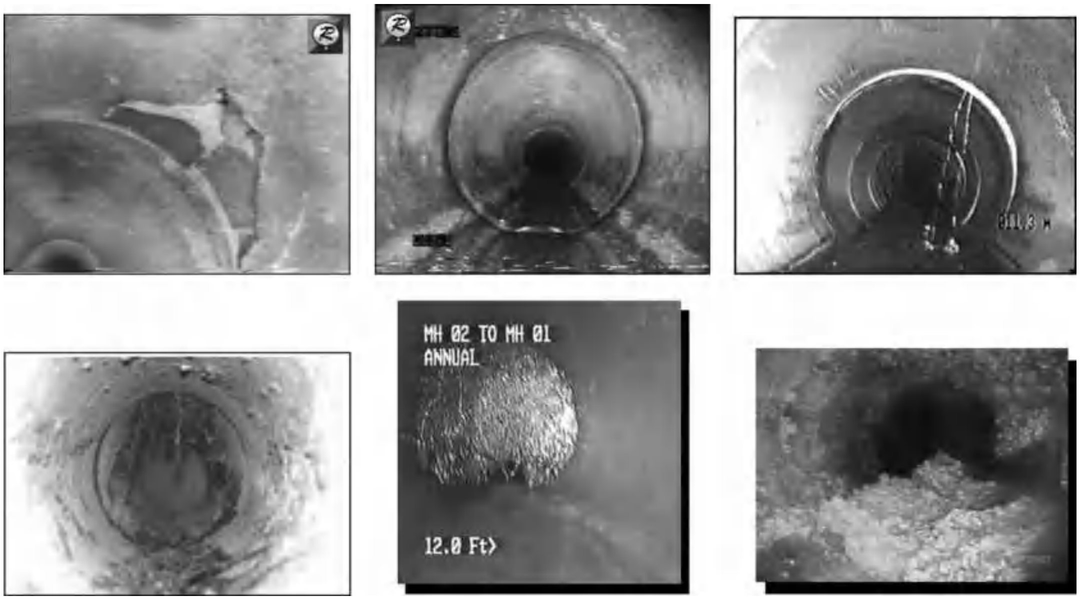

Figure 3. Pipeline Defects: Cracked pipe, offset joint, infiltration root intrusion, root blockage, and grease blockage (clockwise from top left).

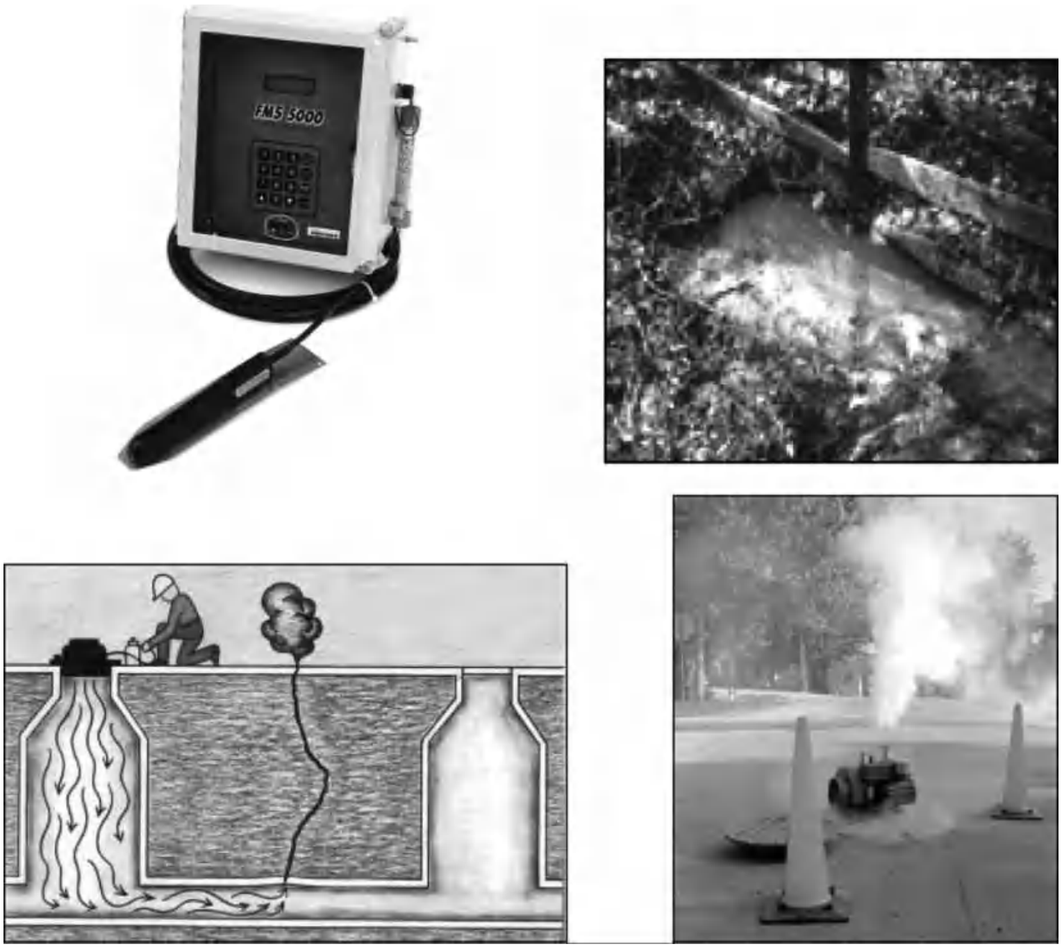

Figure 4. Flow monitoring device, dye testing, and smoke testing in sewers (clockwise from top left).

to the sanitary sewer. Rare instances where house laterals were either inadvertently not connected or wrongly connected to the storm sewer system, unfortunately, sometimes occur. A dye test is a good tool for these cases.

The dye can be in powder, tablet, or liquid form and is simply inserted into the sewer (Fig. 4). Although safe and harmless, the wastewater utility should be contacted to ensure that no regulations against the dye are in place and as a "heads-up" if appreciable quantities of the dye reach the treatment plant. Similarly, the local environmental agency should be contacted if dye testing is proposed in storm sewers. Some dyes can be mistaken for things such as "antifreeze" spills and can cause undue alarm and attention. Like smoke testing, public education is a necessity in most applications. Where access to households is necessary to test for positive connections of laterals or drains, it is probably best to work through local city or town officials.

Flow Monitoring

Flow monitors (or meters) are useful as part of a statistical modeling exercise for I&I (Fig. 4). Data on water use, and hence discharge to sewers, can be obtained through a few strategically placed flowmeters and when combined with network modeling, can present a very accurate overall picture of the system operation.

Walk-Through

The walk-through method of pipe assessment is obviously used only for large diameter pipes or large storm sewer box structures. This method can yield important information on the structural integrity of the pipe and structure, especially if trained personnel perform the inspection. The Construction Inspector must be fully aware of the safety implications of entering these pipes or structures. The decision on whether to enter a pipe or structure should be made with full regard for Occupational Safety and Health Administration (OSHA) confined space entry regulations http://www.osha.gov/.

Pressure Leak Testing

For pressure pipe, the methods of assessment for pipe in service are limited. One method used is leak testing using sound waves to pinpoint the location of the leak. The test is primarily on water mains and is usually performed by specialized firms. However, the cost of leak detection equipment has decreased to the point where most medium to large water utilities have invested in this methodology.

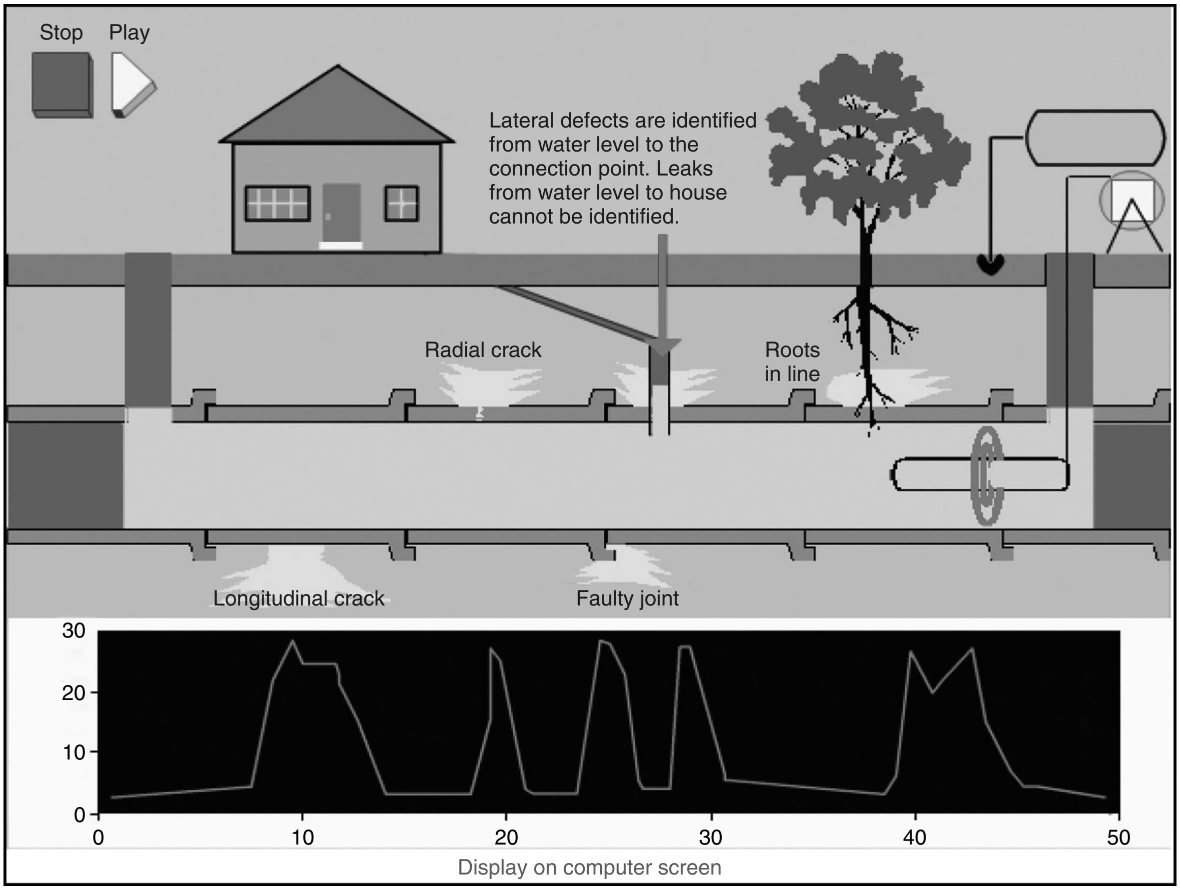

Figure 5. The FELL system.

Leak testing uses sound waves to identify the point in the pipe where a leak has occurred. The technology has evolved to a point where digital readouts can specify the exact location of the leak relative to the wire connections on water main appurtenances, usually valves. This technology could be useful when recently installed or repaired pipe cannot pass specified pressure tests.

Electronic Leak Testing

The focused electrode leak location (FELL) system measures electrical current flow between a probe that travels in a pipe and a surface electrode. Pipe defects that allow liquids to flow into or out of the pipe cause a spike in the electrical signal, thereby locating the sources of infiltration or exfiltration. The intensity of the measured current can be correlated with the magnitude of the leaks.

The FELL test system uses a specially constructed electrode called a “sonde” that generates an electric field. The sonde is 30 in. long and 3 in. in diameter. The electric field is focused into a narrow disc, 1 in. wide set normal to the longitudinal axis of the sonde. A surface electrode (usually a metal stake) is put into the ground at the surface. When the sonde is placed in a *nonconducting* pipe that contains sewage (and/or water), the electric current flow between the sonde and the surface electrode is very small. Defects in the pipe that would allow flow of fluid either *into* or *out of* the pipe provide an electrical pathway from the sonde, through the wall of the nonconducting pipe, and through the ground, to the surface electrode. When the sonde is close to such a defect, the current between the sonde and the surface electrode increases. Figure 5 illustrates the operation of the FELL system.

PIPELINE REPAIR AND RENEWAL—EXCAVATION

Sanitary and storm sewer systems and water distribution systems develop defects over time. Defects occur from a variety of causes including improper initial installation, freeze/thaw damage, and cutting by another contractor. Pressure lines typically exhibit failures rapidly; it may take years for a defect in a gravity line to be obvious. A failing pipe system can be repaired or renewed by replacing the entire pipe or manhole or by replacing only the defective portion. Construction requirements for repair and renewal are similar to original construction requirements. The following discussion highlights the different methods of repairing or renewing pipes and manholes.

PIPELINE REPAIR AND RENEWAL—WHOLE PIPE

Gravity Sewers

When the Engineer has determined that a pipe and/or manhole has deteriorated beyond trenchless rehabilitation, replacement is typically the prudent alternative. To replace a whole segment (structure to structure), the Contractor must excavate to the pipe. Paved surfaces must be saw cut prior to excavation to prevent damage beyond the construction limits. The original backfill is removed; if it is acceptable material by today's standards, it can be reused; otherwise, it must be removed. When the pipe is exposed, it is removed along with the bedding material. Lateral connections should be cut before the pipe is removed to prevent fracturing the lateral. Once enough of the pipe is removed, new segments of pipe may be installed following procedures for new pipe installation. Bedding, haunching, and backfilling are all important components of successful pipe replacement. Although it is often more difficult to prepare the bedding below the pipe because water may be flowing in the trench, proper bedding is essential for proper pipe installation. In addition, if the original pipe settled, the bedding remaining under the existing pipe will not be on grade for the installation of the new pipe. It is important to check the grade of the bedding prior to laying the new pipe.

Force Mains

If the line to be replaced is a force main, it may be designed in a new location so the existing force main can remain in service until the latest possible time. In this case, the force main installation is the same as new construction until it is time to make the final connection to the pump end of the force main. If the new force main connects to the existing force main, a pressure coupling must be used. If the new force main is connected at the discharge of the pumps, properly sized spool pieces must be on hand to complete the final connections as rapidly as possible.

Couplings to join the new force main to the old force main must be designed for the pressure the line will undergo. Pressure couplings typically have a rubber sealing sleeve surrounded by a steel or stainless steel sleeve. The sleeve is fastened to the pipe by tightening bolts provided on the clamp.

All testing of the force main must be completed prior to putting it into operation. The same tests required for new force mains must be completed on replacement force mains.

The Contractor may have to provide external pumping capacity or temporary piping to allow pumping the wastewater or storm water downstream. This can also be accomplished by a vacuum truck, with appropriate permissions to discharge into a downstream manhole.

Manhole Connections

The rubber gasket or boot used to create a watertight seal between the manhole and the pipe may need to be replaced. The importance of the gasket, whatever type is used, is to prevent groundwater from entering the pipe–manhole joint. The gasket must seal tightly to the manhole and to the pipe.

Lateral Connections

The Engineer will specify if the laterals are to be replaced to the right-of-way or easement limits or only within the trench. In either case, the lateral wye or tee must be installed in the main line approximately at the same location as the previous one. The Contractor must excavate along the lateral until sound (not broken or cracked) pipe is found and replace the lateral from that point to the main. The connection between the new pipe and old pipe is made with a special coupling. These couplings are manufactured to fit various pipe sizes and materials. They are manufactured from rubber compounds and have some type of clamp to seal the coupling to the pipe. Some of the couplings have a stainless steel sleeve to prevent misalignment of the pipe.

Testing

Testing requirements are specified in the Contract Documents. Rehabilitated pipe may be tested similarly to a new pipe installation with a low-pressure air test and a deflection test. If the main has lateral connections, the lateral connection coupling must be removed and the lateral plugged prior to the air test. To help reduce the cost of testing, the pipe can be air tested (if permitted by Contract Documents) once the pipe has been bedded and backfilled up to the elevation of the lateral couplings. Deflection testing should be completed after the required waiting time. In special circumstances, the Engineer may specify joint testing in lieu of air testing of the whole pipe. The Engineer may also specify deflection and/or television inspection of the main after the repair has been completed. Television inspection after installation is similar to the inspection described in assessment of pipes earlier in this article.

Sewage Control

The Contractor may choose (or the Engineer may require) to plug the upstream sewer line and pump the flow around the segment being replaced. This creates easier working conditions for preparing the bedding for the new pipe. As work progresses on the line segment, the Contractor may have to cope with flow from laterals. If the flow is light, the Contractor may choose to "just work in it" and let the sewage flow through the trench. This is acceptable as long as the crew is able to compact the bedding and backfill properly. If the Contractor does not bypass the wastewater, workers need to be aware of the potential for disease transmission. Rubber boots, gloves, and eye protection should be provided. Facilities must be provided for washing hands.

PIPELINE REPAIR AND RENEWAL—POINT REPAIRS FOR GRAVITY SEWERS

Gravity Sewers

If a sewer or force main has a small section that is deteriorated, it may be replaced while leaving the remaining line in service. The Contractor saw cuts pavement as necessary and excavates down to the pipe. The bad section of pipe is exposed. The pipe must be cut with a saw past the limits of the damage. It is important that the pipe is cut back to sound pipe for the repair coupling to seal against. A new section of pipe is cut to the same length as the piece removed. Repair couplings are placed on the replacement piece and the new piece is inserted into place.

Bedding

The repair piece must be bedded properly to prevent settlement or heaving of the new piece of pipe. If flexible couplings are used, this is all the more critical because the flexible couplings will deflect rapidly creating an offset in the pipe or a tear in the coupling if the offset is severe enough. If couplings with a steel sleeve are used, the offset may cause the pipe to crack if it is not bedded properly. Lean concrete or flowable fill may be used to bed the pipe.

Repair Clamps

- *Flexible Repair Coupling*: these clamps are manufactured to fit snugly on various sizes and types of pipe. Clamps can be purchased to fit VCP on one end and PVC on the other because they have different outside diameters. The proper clamp must be used to ensure a watertight connection. The rubber sleeve is tightened onto the pipe by tightening the clamps supplied with the repair coupling
- *Repair Couplings with Sleeves*: these clamps are similar to the flexible clamps described above, but they have a stainless steel (usually) sleeve that wraps around the rubber sleeve to prevent the pipes sections from being misaligned or offset.
- *PVC Repair Clamps*: these clamps can be used to repair PVC pipe with PVC pipe. The clamp is a double bell.

Testing

The most common tests for point repairs are

- *Segmental Low-Pressure Air Test*: a testing ring is inserted into the line and positioned over the repair. The positioning is observed with a television camera. The testing ring is inflated to the required test pressure.
- *Mandrel Deflection Test*: Completed in the same manner as new construction.
- *Television Inspection*: Completed in the same manner as assessment.

PIPELINE REPAIR AND RENEWAL—POINT REPAIRS FOR FORCE MAINS

Force Mains

Force mains may be point repaired by methods similar to those for gravity lines. The main difference is in the type of repair clamp and testing. If the defect in the force main is a single crack, a repair clamp of the proper pressure rating and length may be used without replacing any pipe. If the damaged section cannot be repaired by one clamp, a section of the force main may be removed by saw cutting. A new section of pipe is then secured into the line with one or two clamps (one if it is possible to use a push-on or bolt-on joint). The bedding must be moved away from the pipe to install the clamp. The pipe must be cleaned to allow the clamp to seat properly.

Bedding

The replaced section of pipe or the clamped area must be rebedded to support the pipe properly. Lean concrete or flowable fill may be used for support under the repaired area.

Repair Clamps

The surface of the existing pipe and the replacement piece must be relatively clean to allow the repair clamp to seal completely on the pipe. The clamp will leak if there is debris on the pipe.

- *Bolt-On Flanges*: for most pressure pipe, flanges can be bolted onto the existing pipe and a new flanged piece (or bolt-on flanges on the repair piece) bolted into place.
- *Pressure Couplings*: these couplings are typically made from a sheet of rubber to create the sealing surface and a stainless steel band with multiple clamps to hold and tighten the clamp onto the pipe. They are manufactured for various pressure ratings.

Testing

Typically, the repair is tested after the pipe is bedded but before backfilling is completed. The pressure is returned to the line; if no leaks are observed, backfilling is completed.

MANHOLE REPAIR AND RENEWAL

Manholes

To replace a manhole or storm structure, the Contractor must saw cut the existing pavement and excavate around the manhole. When the excavation reaches the elevation of the sewers, the excavation must follow along the pipes to allow the pipes to be saw cut. Once all lines have been freed from the manhole or structure, the manhole can be removed. The Contractor will have to provide a means of controlling wastewater flow into the excavation, as described earlier in this section.

Once the manhole has been removed, the bedding can be removed and replaced. The bedding must be compacted well, leveled, and brought up to the correct elevation. The new manhole is set similarly to new construction. Once the manhole is set, the pipes must be reconnected. New sections of pipe are inserted into the manhole, and the other end is connected to the existing pipe with a coupling as, described in the Point Repair section.

Testing

Replaced manholes are typically vacuum tested and the line connections are tested, as described in the Point Repair section.

WATER MAIN REPAIR AND RENEWAL—POINT REPAIRS FOR FORCE MAINS

Point Repairs of Water Mains

Point repairs on water mains are similar to repairs on force mains, except that water mains may be under constant pressure. Normally, a sufficient number of valves in the water distribution system can be closed to reduce or eliminate any pressure in the water main. Point repairs can be completed using a repair clamp or sleeve with the proper pressure rating and size for the pipe to be repaired. Water main pipe materials vary from ductile iron, cast iron, old sand cast iron with variable diameters and rough surfaces to asbestos cement and concrete to smooth wall PVC and polyethylene plastic. Repair clamps are normally stainless steel with rubber gaskets and seating surfaces. Repair sleeves are usually ductile iron with rubber gaskets.

If the portion of the water main to be repaired is large enough, sections of pipe may need to be removed, replaced, and connected with one or two repair clamps/sleeves. If a new bell joint can be used at one end of the repair, only one clamp/sleeve would be needed.

Pipe bedding must be removed below the clamp/sleeve for proper cleaning and preparation of the pipe to receive the repair clamp/sleeve. Once repairs have been made, the repaired section may be pressurized to check for leaks at the joints and repair clamps/sleeves.

After satisfactory testing or observation of the repair under pressure, pipe joints and repair clamps/sleeves need to be properly bedded. After bedding of the entire repair section, the trench is backfilled and compacted, as it would be for new construction. Backfill materials may be excavated soil, granular materials, and flowable fill.

Line Stops

At times, there may not be an adequate number of valves in the existing system to isolate the water main to be repaired. In these instances, it may be necessary to install line stops to complete the repair. A line stop consists of a tee installed on the water main to provide access to install a flexible rubber plug in the water main that acts as a closed valve. Line stops can be installed in a water main while the water main is still pressurized.

The tee is bolted to the water main and a specially constructed valve is installed on the branch of the tee. A cutting tool is inserted through the valve and a circular hole is cut into the existing water main. The cutting tool is retracted, the valve is closed, and the cutting tool is removed. The rubber stopper or plug is inserted through the valve and pushed into the water main, filling the entire pipe with a rubber plug. The line stop acts as a temporary closed valve. Repairs are completed to the water main using normal pipe repair methods, and once the repairs are complete, the plug and valve are removed from the line stop tee. A threaded cap is installed in the tee to close the tee. The tee is backfilled as part of the pipe but can be used again in the future if a temporary closed valve is necessary.

Insertion Valves

At times, there may not be an adequate number of valves in the existing system to isolate the water main to be repaired. In these instances, it may be desirable to insert a permanent valve to allow making the repair and to provide a way to isolate water main sections in the future. The procedures to insert a valve are similar to those for installing a line stop.

An insertion valve body consisting of at least two sections is bolted to the water main and a temporary valve is installed on top of the valve body. All work to cut the wall of the water main and to install the valve gate is done through the temporary valve. A cutting tool is inserted through the valve and a circular hole is cut in the existing water main. The cutting tool is removed and the valve gate and operator are installed in the valve body and water main. The valve body and operator are fastened together and the temporary valve is removed.

The insertion valve and joints are tested for leaks and once accepted, can be bedded and backfilled as new construction of a water main valve.

Freezing and Clamping of Service Pipes

Repair of service pipes can sometimes be completed by freezing or by clamping a service line. Wrapping dry ice around the entire circumference of the pipe usually completes freezing. For freezing to work, there must be no flow through the pipe, so one end of the service line must be plugged or crimped to stop all flow. Once the water in the service pipe is frozen, the plugged/crimped end can be cut off and repairs made.

Clamping a service line is limited to use on polyethylene plastic service pipe. Polyethylene can be completely clamped tight and once the clamp is removed, it rebounds to match its original shape closely.

Testing

As discussed before, testing usually consists of physically observing the repaired section of pipe and any valves and fittings for leaks after pressure is restored to the water main. Any leaks must be repaired to the satisfaction of the water utility or municipal personnel. It is advantageous to have the circumference of all joints exposed so any dripping on the bottom of the pipe can be observed.

Disinfection

Under normal repair conditions, the repaired water main cannot be disinfected by methods used for new construction. Repairs and water in the water main are not usually disinfected after the repair is complete because the water mains usually serve existing customers. Instead, the repair pipe, valves, fittings, line stops, etc., are cleaned and disinfected during repair procedures. Cleaning and disinfecting is done by swabbing the materials with a strong solution of chlorine prior to installation.

After the repair is complete, the water main is usually flushed with a high flow rate of water by opening one or several fire hydrants near the repair section. Many water utilities and municipalities also issue a “boil order” to have customers boil their water for 1 or 2 days following a water main repair.

Public Notification

Customers affected by reduced pressure or a water main shutdown should be notified of the repairs being made and precautions to take once water service is restored. "Boil orders" are often used to protect public health and welfare. Boil orders are issued by personal contact, door-to-door notice, daily newspaper articles, and radio/television notice. The water utility or municipality normally takes responsibility to notify its customers of repairs and precautions.

WATER HAMMER: QUANTITATIVE CAUSES AND EFFECTS

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Water hammer is a hydraulic phenomenon that has to be considered for the safe design of water-carrying pipes. It is basically a pressure fluctuation that would result in disturbing noises and, more importantly, rupture of pipes and fittings (1,2).

DEFINITION

Water hammer can be defined as a transitory increase in pressure in a water system when there is a sudden change of direction or velocity of the water. Water hammer may also be known by names like shockwave effect or hydraulic shock.

If the velocity of water flowing in a pipe is suddenly checked, the energy given up by the water will be utilized in compressing the water itself. This pressure energy is transferred to the pipe wall and this leads to the setup of shock waves in the system. These shock waves travel backward (with a speed similar to the speed of sound), until encountering a solid obstacle (the valve), and crash into the obstacle back and forth repeatedly. This repeated crashing produces an undesirable sound and may lead to rupture of valves and pipes.

The concept of water hammer is normally explained by drawing an analogy to the movement of a train. Assume a real train, instead of slowing to a stop, hits into a mountainside. The back of the train continues forward even though the front cannot go anywhere. Similarly, the hammer occurs because an entire train of water is being stopped so fast that the end of the train hits up against the front end and sends shock waves through the pipe.

EFFECTS OF WATER HAMMER

Water hammer cannot be ignored as another hydraulic effort in water conveyance, as it poses undesirable effects during water conveyance. The major effects of water hammer are the following:

1. Water hammer will cause disturbing noises that tend to be highly problematic in houses and industrial areas.
2. Water hammer may account for the malfunctioning of pipe appurtenances like pressure relief valves, mud valves, backflow preventers, or stop valves.
3. Water hammer may also lead to rupture of the pipes and connected fittings.
4. Water hammer may at times lead to minor flow losses.

CAUSES OF WATER HAMMER

The problem of water hammer can be encountered in varied places like houses, irrigation systems, domestic water supply, and industries. The causes for water hammer (i.e., causes for sudden change in flow velocity/direction) are varied, yet they can be grouped under five major cases:

- Rapid opening or closing of control valves.
- Starting and stopping of pumps.
- Recombination of water after water column separation.
- Rapid exhaustion of all air from the system.
- Power failure in water pumping system.

COMPUTATION OF WATER HAMMER

The pressure rise caused by the water hammer should be quantified to understand its impact and to sort out remedial measures. The rise in pressure due to water hammer can be attributed to pipe velocity, pipe diameter, and pressure wave travel in the pipe. The maximum pressure caused by water hammer can be obtained by the expression

$$H_{\max} = a \times V_n/g$$

where $H_{\max}$ is the maximum pressure rise due to water hammer, V_n refers to the velocity of flow in the pipe, g refers to the acceleration due to gravity, and a is the velocity of pressure wave travel, which in turn can be obtained by the expression

$$a = 1425/(1 + kd/EC)^{1/2}$$

where k is the bulk modulus of water, d is pipe diameter, C is wall thickness of the pipe in meters, and E is the modulus of elasticity of the pipe material.

The pressure exerted due to water hammer is taken into consideration for the structural design of pipelines for public water supplies. In case of unavailability of data and as a rule of thumb, Table 1 presents the extra pressures taken depending on pipe size.

Table 1. Water Hammer Pressure for Different Pipe Diameters

Diameter of pipe, mm	<250	300	400	500	600	750	>750
Water hammer pressure, kg/cm^2	8.50	7.75	7.00	6.30	5.75	5.60	4.90

Today there are a lot of computational facilities also available for the quantification of water hammer pressure.

CONTROL OF WATER HAMMER

As a hydraulic effect, water hammer is undesirable but inevitable. However, there are a lot of techniques to minimize the pressure rise due to the water hammer, which need to be exercised for proper flow profile.

1. The best and simplest technique would be to close or open the valves slowly. Even the first 80% of the valve travel may be executed conveniently, but the last 20% should be done at a snail's pace to avoid problems. The usage of flywheels for this purpose is advisable, and automatically controlled valves with slow closing are desirable.
2. The provision of check valves, surge relief valves, and similar instruments may help in reducing the water hammer. Today, specialized water hammer arrestors are commercially available for this purpose. Apart from these surge-absorbing water hammer arrestors, pressure regulation devices can also be used. An example is a pressure snubber, a device for slowing the rate of change of system flow that will protect from water hammer damage if installed (using a proper size) near the input of a pressure sensor.
3. The pumps are also a matter of concern. Pump startup problems can usually be avoided by increasing the flow slowly to collapse or flush out the voids gently. Also, an uninterrupted power supply for pumps would prevent water hammer. The above arrangements may also contribute to lower horsepower and maximum operating efficiency.
4. Great care should be taken to incorporate the pressure rise due to water hammer during the structural design of pipelines.

There has not been much study about the phenomenon of water hammer and its significance in the design and performance aspects of a water system, but the current scientific forum is coming up with better descriptions.

BIBLIOGRAPHY

1. Singh, G. (1994). *A Text Book of Water Supply Engineering*. Standard Publishers & Distributors, New Delhi, pp. 198–201.
2. Lahlou, M. (2003). Tech brief—water hammer. *On Tap Mag.*, Winter.

CONSTRUCTED WETLANDS

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The term constructed wetlands describes artificial wetlands designed to improve water quality. A constructed wetland is a complex mixture of water, substrate, plants, litter (fallen plant material), and a variety of microorganisms (most importantly, bacteria). The mechanisms for improving water quality include settling of suspended particulate matter; filtration and chemical precipitation; chemical transformation; adsorption and ion exchange on surfaces of plants, substrate, and litter; breakdown, transformation, and uptake of pollutants and nutrients by microorganisms and plants; and predation and natural die-off of pathogens.

Constructed wetlands provide the optimal treatment conditions found in natural wetlands but have the flexibility of being constructed. For optimal support of the treatment mechanisms, various types of constructed wetlands optimized for different applications are used. Free-water-surface constructed wetlands and subsurface-flow constructed wetlands are the main types of constructed wetlands. The applications include treatment of domestic, industrial, and agricultural wastewaters, storm water, and landfill leachate.

Wetland treatment systems are effective in treating organic matter, nitrogen, phosphorus, and additionally for decreasing the concentrations of heavy metals, organic chemicals, and pathogens. A good pre-treatment for suspended solids is essential for long-term operation.

MECHANISMS FOR WATER QUALITY IMPROVEMENT

Organic Matter

Treatment wetlands receive large external supplies of carbon. Degradable carbon compounds are utilized in wetland processes. At the same time, degradation processes produce biodegradable carbon compounds. Microorganisms use degradable organic matter as a substrate for respiration and growth.

In general, wetlands are efficient in reducing organic matter. Organic matter exists in particulate and dissolved form at the influent of constructed wetlands. The concentration of organic compounds is often reduced to the background level at the effluent.

In aerobic zones where dissolved oxygen is available, organic matter is decomposed by respiration of heterotrophic organisms that produce carbon dioxide (CO_2) and water. Under anoxic conditions (no dissolved molecular oxygen is available), nitrate is used as an electron acceptor and is reduced to dinitrogen (denitrification). In anaerobic zones (neither molecular nor bound oxygen is available), degradation of organic matter is a multistep process in which CO_2 and methane (CH_4) are produced. Under anaerobic conditions, organic matter can also be reduced by sulfate and iron. However, these pathways play a minor role in subsurface-flow constructed wetlands.

Particulate matter in subsurface-flow wetlands has a large impact on the porous substrate. Particles settle into the pores, and the settled matter is degraded as described before. If the decomposition rate of the particulates is less than the settling rate, the pore volume is reduced, and this causes clogging. The potential for clogging is higher near the inlet of subsurface-flow systems. To prevent clogging, only pre-treated wastewater can be used in combination with subsurface-flow constructed wetlands.

Nitrogen

Nitrogen compounds are among the most important constituents of wastewater due to their role in eutrophication, their effect on the oxygen content of receiving waters, and their toxicity to aquatic organisms and animals. The most important inorganic forms of nitrogen in wetlands are ammonia (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and dissolved elemental nitrogen or dinitrogen gas (N_2). Nitrogen is also present in many organic forms, including urea, amino acids, amines, purines, and pyrimidines. Organic nitrogen compounds are also a fraction of the dry weight of plants, microorganisms, detritus, and soils.

The various forms of nitrogen are continually involved in biochemical transformations. The major processes involved in the nitrogen cycle are ammonification, nitrification, denitrification, nitrogen fixation, nitrogen assimilation, and ammonia volatilization (Fig. 1).

Ammonification. Ammonification is the transformation of organic nitrogen to ammonia. This process occurs during the breakdown of organic matter. The rate of ammonification is directly related to the rate of degradation of organic matter.

Nitrification. Nitrification is the process of oxidizing ammonia to nitrate. The oxidation is done by autotrophic bacteria, which are entirely dependent on generating energy from nitrification. Nitrification is strictly an aerobic process (the presence of oxygen is indispensable) and takes place in two steps. *Nitrosomonas sp.* are responsible for the first step of nitrification: ammonia is oxidized, and nitrite is produced. The nitrite produced is further oxidized to nitrate by *Nitrobacter sp*. Due to the high oxygen demand of the nitrification process (4.57 g oxygen are required for 1 g of ammonia nitrogen), the elimination of ammonia nitrogen is one of the major requirements of wastewater treatment to guarantee a sufficient oxygen concentration in receivers.

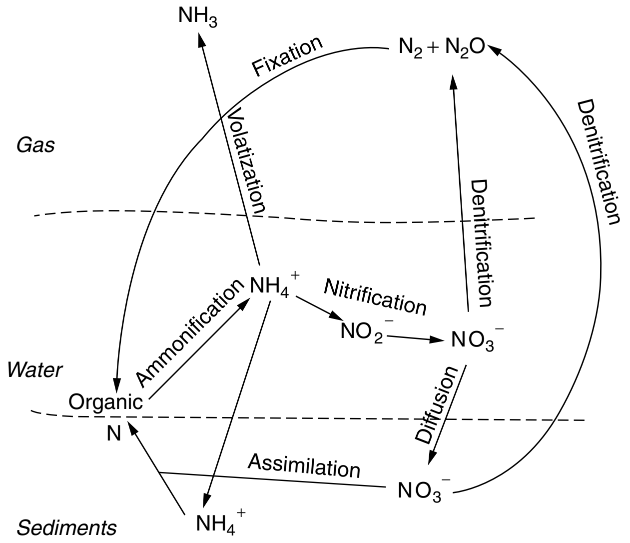

Figure 1. Simplified wetland nitrogen cycle.

Denitrification. Under anoxic conditions and if easily biodegradable organic matter is present, heterotrophic bacteria reduce nitrate to molecular dinitrogen by denitrification. Besides dinitrogen, small amounts of nitrous oxide (N_2O) and nitric oxide (NO) are produced. These dissolved gases are released to the atmosphere, and this reduces the total nitrogen content of treated water. Denitrification and nitrification occur simultaneously in soils where both aerobic and anoxic zones exist nearby. The lack of carbon in the anoxic zones where nitrate is available is the limiting factor for denitrification in wetlands.

Nitrogen Assimilation. Nitrogen assimilation refers to a variety of biological processes that convert inorganic nitrogen into organic compounds. Ammonia uptake is more favored by wetland plants and bacteria than nitrate uptake. In general, the amount of nitrogen taken up by plants and incorporated into the bacterial biomass is small compared to the nitrogen influent load of constructed wetlands for wastewater teatment.

Other Processes. Bacteria, blue-green algae, and plants can fix nitrogen. Nitrogen gas in the atmosphere diffuses into solution and is reduced to ammonia. However, this is generally not observed in constructed wetlands because fixation is more effective in nitrogen-poor environments.

Un-ionized ammonia (NH_3) is relatively volatile, so it can be removed from solution to the atmosphere via diffusion. Usually less than 1% of the total ammonia is present in un-ionized form.

Ammonium can be adsorbed onto active sites of a soil matrix. Only intermittent loading of a system will show rapid removal of ammonia by adsorption due to depletion of ammonia on the adsorption sites during resting periods.

Phosphorus

Phosphorus is typically present in wastewater as orthophosphate and organic phosphate. Phosphorus is released during the degradation of organic matter. Orthophosphate is incorporated into the biomass of organisms during growth. Phosphorus removal in wetland treatment systems occurs by adsorption, plant uptake, complexation, and precipitation.

Plant uptake is not a suitable measure of the net removal rate in a wetland because most of the stored phosphorus is returned to the water by decomposition processes. Due to the limited sorption sites in the soil matrix, phosphorus removal via adsorption is time dependent. After a phosphorus removal rate of almost 100% at the start-up of the operation of the constructed wetland, the removal rate becomes very low, once all sorption sites are filled. During times of low phosphorus influent concentration, also a release of phosphorus can be observed.

Other Substances

Besides the main constituents of wastewater, organic matter, nitrogen, and phosphorus, other pollutants such as heavy metals, specific organic compounds, and pathogens can be removed from water using constructed wetlands.

Heavy Metals. Wetlands interact strongly with heavy metals in a number of ways and thus are capable of significant metal removal. The three major mechanisms are

- binding to soil, sediments, particulates, and soluble organic matter;
- precipitation as insoluble salts, principally sulfides and oxyhydroxides; and
- uptake by plants and bacteria.

A criterion for heavy metal removal is the contact time between dissolved metals and the soil matrix. The longer the contact time, the more exchange processes occur. A particularly significant effect can be observed on the adsorbed metal concentration in the rhizosphere by using different plant species. The plant organisms can, however, become stressed at high heavy metal concentrations, so that the treatment is more appropriate to low metal influent levels. Harvesting the plants used for metal removal then provides a means to prevent metals cycling in the wetland ecosystem and a sustainable means of disposal, if the harvested plants are then appropriately dealt with. Experimental evidence has shown that heavy metal concentrations are highest in the plant roots, followed by the stems, and then the leaves, so that the whole plants must be harvested, not just the foliage.

Specific Organic Compounds. Many constructed wetlands deal with domestic wastewater where BOD and DOC are used as a sum parameter for organic matter. However, other special organic compounds can be removed by using constructed wetlands. Experience exists with waters containing surfactants, solvents, mineral oils, and pesticides. Some specific compounds that were successfully treated by constructed wetlands are, for example, MTBE, trichloroethane, BTEX, cyanide, and explosives (e.g., TNT). Major removal mechanisms are volatilization, photochemical oxidation, sedimentation, sorption, and microbial degradation by fermentation or aerobic and anaerobic respiration. Bioaugmentation of the sediment and sorption by macrophytes is particularly important. In general, there is a lack of knowledge on the detailed removal pathways for organic compounds.

Pathogens and Parasites. Human pathogens are typically present in untreated wastewater. Their populations are highly variable and depend on the health of the human population contributing to the waste. Typical pathogen populations in wastewater include viruses, bacteria, fungi, and protozoa. Parasites such as helminth worms are also common.

Natural treatment technologies can reduce populations of human pathogens by filtration, natural die-off rates, and hostile environmental conditions. Constructed wetlands reduce pathogen populations at varying but significant degrees of effectiveness. The elimination efficiency varies with macrophyte type and increases with the retention time of the wetland.

The Role of Plants

Macrophytes growing in constructed wetlands have several properties in relation to the treatment process. This makes plants an essential part of the design of constructed wetlands.

The most important effects of the macrophytes ragarding the treatment process are physical effects. The roots provide surface area for attached microorganisms, and root growth maintains the hydraulic properties of the substrate. The vegetation cover protects the surface from erosion, and shading prevents algae growth. Litter provides an insulating layer on the wetland surface (especially for operation during winter).

As far as is known, the effect of plant uptake plays a minor role in common wastewater parameters compared to the degradation by microorganisms. For other pollutants such as heavy metals and special organic compounds, the selection of different plant species can, however, play a major role in enhancing treatment efficiency. Both plant productivity and pollutant removal efficiency are relevant in finding an appropriate plant for a given application.

If the wetland is not harvested, the substances incorporated in the plant will be returned to the system during decomposition of the plants. When dead plants are degraded, the organic constituents can act as an additional carbon source for denitrification. Some plants also release organic compounds from their roots, which can also be used for denitrification.

Oxygen release from roots into the rhizosphere is well documented but *in situ* release rates, still are a matter of controversy. Compared to the amount of oxygen brought into the system from the atmosphere via convection and diffusion, the release of oxygen from plant roots can be neglected.

Plants also have other functions not directly related to the treatment process. They provide a habitat for wildlife (including birds and reptiles in large systems) and give the treatment system a more aesthetic appearance.

TYPES OF CONSTRUCTED WETLANDS

Surface-Flow Constructed Wetlands

Surface-flow (SF) or free-water-surface (FWS) wetland technology is strongly related to natural wetlands. Wetlands have been used for wastewater discharge for as long as sewage has been collected. When monitoring was initiated at some of the discharges, an awareness of the water purification potential of wetlands began to emerge. The 'technology' started in the 1970s in North America with ecological engineering of natural wetlands for wastewater treatment.

In surface-flow wetlands (Fig. 2), water flows over the soil surface from an inlet to an outlet point. Inflow water containing particulate and dissolved pollutants slows down and spreads through the area of shallow water. The main removal mechanism for particulates is settling. Particulates contain organic matter and enter the biogeochemical cycle in the water column and wetland soil surface. Dissolved pollutants are sorbed by plants, soil, and active microbial populations throughout the wetland and then also enter the overall mineral cycles of the wetland ecosystem. The amount of sorption processes is related to the area where these processes can take place. Due to

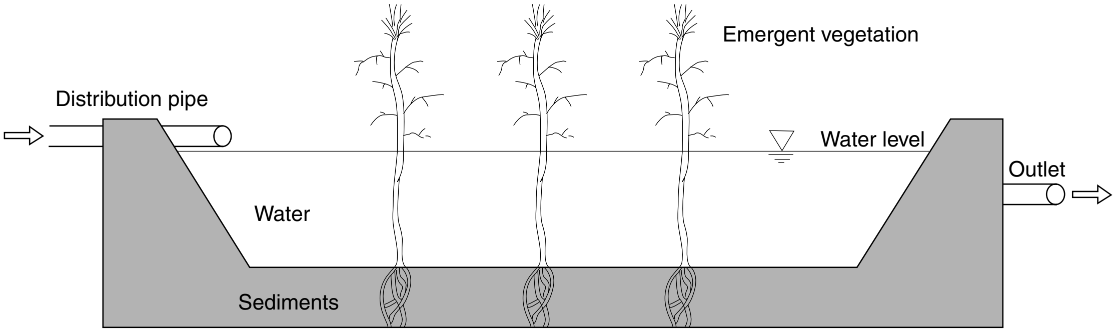

Figure 2. Surface-flow wetland containing emergent macrophytes.

the small surface area of the wetland soil, surface-flow constructed wetlands require a large area to reach good elimination rates of dissolved pollutants.

Surface-flow constructed wetlands can be classified by the plants that are used. Most treatment wetlands use emergent macrophytes (e.g., common reed—*Phragmites australis*), plants whose parts extend above the wetland waters (Fig. 2). Other types use free-floating macrophytes (e.g., water hyacinth—*Eichornia crassipes*), floating-leaved, bottom-rooted macrophytes (rooted in the soil, but their leaves float on the water surface, e.g., water lilies—*Nymphea* spp.), submersed macrophytes (plants that are buoyant and suspended in the water column), or floating mats (some emergent macrophytes can form floating mats, e.g., cattails—*Typha* spp. and common reed—*Phragmites australis*).

Summarizing, one can say that the main disadvantages of free-water-flow constructed wetlands are that they require a large area, they may freeze in temperate climates, and they provide a breeding ground for mosquitoes.

Subsurface-Flow Constructed Wetlands

Subsurface-flow (SSF) constructed wetlands can be subdivided into horizontal flow (HF) and vertical flow (VF) systems depending on the direction of water flow through the porous medium (soil or gravel). The use of subsurface-flow constructed wetlands is limited to pre-treated water, which contains only a low particulate content. Compared to surface-flow systems, the contact area of water with bacteria and substrate is much larger. This enhances the process rates of the system and therefore decreases the area requirement of the treatment system. Pathogen reductions for SSF compared with SWF for similarly sized and managed systems are higher. Subsurface-flow constructed wetlands are frequently planted with common reed (*Phragmites australis*). Therefore a common term is a reed bed treatment system. Other emergent plants like cattails (*Typha* spp.) and bulrushes (*Scirpus* spp.) are also used.

Horizontal-Flow Constructed Wetlands. In a horizontal-flow constructed wetland (Fig. 3), water is fed in at the inlet and flows slowly under the surface through the porous media until it reaches the outlet zone, where it is collected and discharged. Despite regular topography and homogenous plant growth, obtaining an ideal flow is not guaranteed, so that tracer studies are advisable to ensure good hydraulic design. During the passage through the system, water comes in contact with a network of aerobic, anoxic, and anaerobic zones in the substrate. Aerobic zones occur in the upper parts of the water table, anaerobic conditions at the bottom of the wetland.

Oxygen required for aerobic processes is supplied mainly from the atmosphere via diffusion. The oxygen transport from the roots into zones under the water table is too weak to facilitate aerobic processes. Therefore, anoxic and anaerobic processes play an important role in horizontal-flow constructed wetlands. Organic matter is decomposed aerobically and anaerobically and is, therefore, removed well. Due to the poor oxygen supply, only incomplete nitrification can take place.

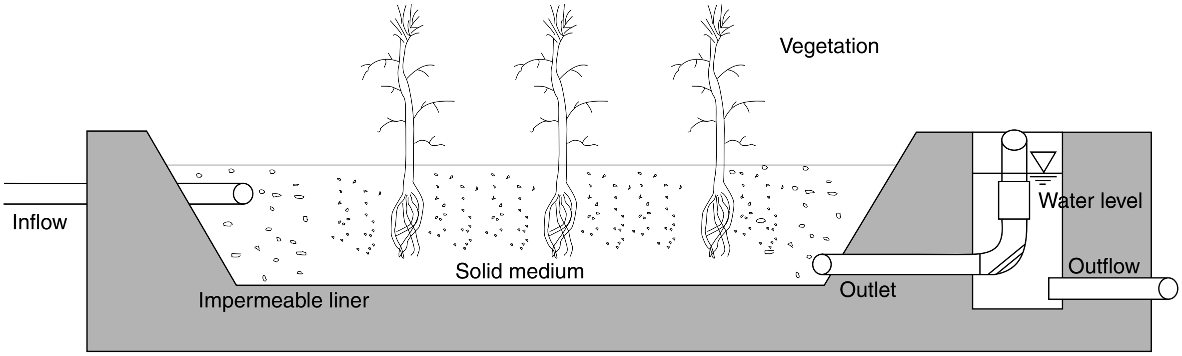

Figure 3. Longitudinal cross section of a horizontal subsurface-flow constructed wetland.

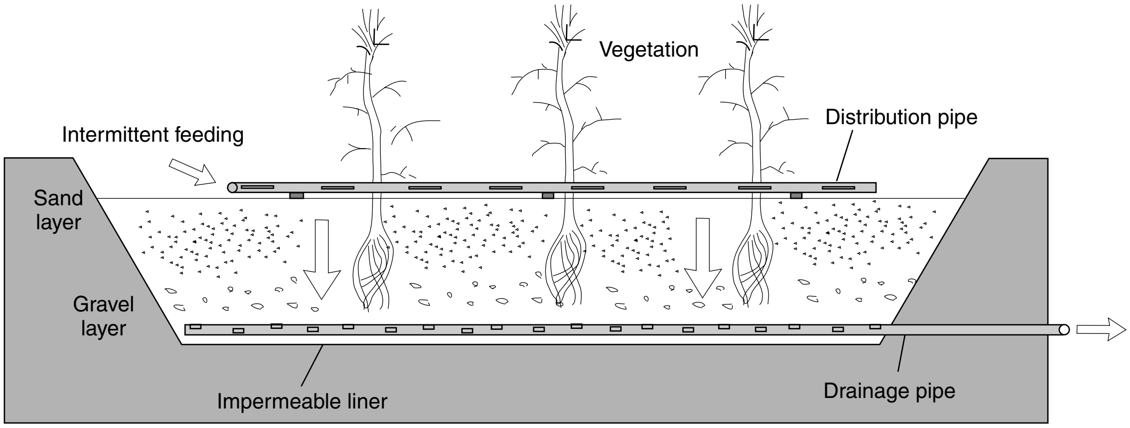

Figure 4. Typical construction of a vertical-flow constructed wetland.

Vertical-Flow Constructed Wetlands. Vertical-flow constructed wetlands look like the system shown in Fig. 4. Water is fed to the system intermittently. The large amount of water from a single feeding causes flooding of the surface. The water infiltrates into the substrate, then gradually drains down vertically, and is collected by a drainage network at the base. Until the next loading, oxygen re-enters the system, and good oxygen transfer into the system is possible. Vertical-flow constructed wetlands are, therefore, suitable when nitrification and other strictly aerobic processes are important factors in the treatment process. When high ammonia nitrogen elimination is required, only vertical-flow constructed wetlands intermittent loading can be used.

APPLICATION OF CONSTRUCTED WETLANDS

The applications of constructed wetlands for water treatment are widespread and include treatment of domestic wastewater, stormwater management in urban areas, treatment of surface water and industrial wastewater, including special wastewater (e.g., from hospitals), and sludge consolidation. Some of these of are discussed more fully here.

Domestic Wastewater. Constructed wetlands for domestic wastewater treatment are generally applied as a main or tertiary treatment stage. For use as a main treatment stage, only subsurface-flow constructed wetlands are used. For tertiary treatment, both surface and subsurface-flow constructed wetland are widely used.

As a main treatment stage, either horizontal-flow or vertical-flow constructed wetlands can be used, depending on the effluent quality desired. Good pre-treatment is necessary to reduce the loading of suspended solids. If low ammonia effluent concentrations are required, only vertical-flow constructed wetlands with intermittent loading fed can guarantee good nitrification. To improve denitrification rates, combined systems with horizontal and vertical types of SSF constructed wetlands can be used.

Sufficient oxygen supply is the main factor for good performance of vertical-flow constructed wetlands. Design recommendations can be based on calculations of oxygen demand and oxygen supply. Considerations of long-term operation of vertical-flow constructed wetlands should, in particular, consider pore size reduction from influent inorganic suspended solids.

Agricultural Wastewater and Food Wastes. Constructed wetlands were used to treat agricultural wastewater from farms with animal production. Crop runoff and pesticides such as atrazine have also been effectively treated Food processing wastes usually have high organic loads that are easily biodegradable. Constructed wetlands have been used to treat potato processing water, olive oil mill water, and dairy wastewater.

Industrial Wastewater. Constructed wetlands can be used to treat several kinds of industrial wastewater: coal and metal mining water, oil extraction, refinery effluents, oil-sand processing water, and wastewater produced by the pulp and paper industries. Many organic and heavy metal wastes have been effectively retained or removed. Constructed wetland technology was also successfully applied to treat hospital wastewater.

Landfill Leachate. Landfills generate highly pollutant leachates as they decompose anaerobically over many years. Constructed wetlands are used for leachate treatment due to their long-term sustainable treatment and low operating and maintenance costs. The retention capacity of wetlands can also be sufficient to prevent contamination of downstream water sources in a heavily contaminated area.

Stormwater and Runoff Management. Uncontrolled urban stormwater has been identified as a major contributor to the nonpoint source pollution of surface waters. Small amounts of rainwater often carry large amounts of pollutants. Three approaches are used to control urban stormwater using constructed wetlands: dry and wet detention ponds (where the ponds remain dry or wet between floods) and stormwater wetlands. Detention ponds collect stormwater and release it during dry weather. The main removal mechanism is settling.

Surface Water. Heavily polluted surface water can also be treated using constructed wetland technology. The treated water can be used, for example, for groundwater recharge and for restoring contaminated surface waters. However, it is not possible to produce an effluent quality that allows direct use as drinking water.

SUMMARY

Constructed wetlands are artificial wetlands designed to improve water quality. They provide the optimal treatment conditions found in natural wetlands but have the flexibility of being constructed. Wetland treatment systems are effective in treating organic matter, nitrogen, phosphorus, and additionally for decreasing the concentrations of heavy metals, organic chemicals, and pathogens. Various types of constructed wetlands optimized for different applications are used for optimal support of the treatment mechanisms. The main types are free-water-surface constructed wetlands and subsurface-flow constructed wetlands with horizontal or vertical flow.

In general, the use of constructed wetlands provides a relatively simple, inexpensive, and robust solution for treating water. Compared to other treatment options, constructed wetlands usually need less operation and maintenance. Additional benefits include their tolerance to fluctuations in flow, the facility of water reuse and recycling, the provision of habitat for many wetland organisms, and the more aesthetic appearance of a natural system compared with technical treatment options.

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BIBLIOGRAPHY

1. Cooper, P.F., Green, M.B., and Shutes, R.B.E. (1996). Reed beds and constructed wetlands for wastewater treatment. WRc Swindon, Swindon, UK.
2. Haberl, R., Grego, S., Langergraber, G., Kadlec, R.H., Cicalini, A.R., Martins Dias, S., Novais, J.M., Aubert, S., Gerth, A., Hartmut, A., Hartmut, T., and Hebner, A. (2003). Constructed wetlands for the treatment of organic pollutants. *JSS—J Soils & Sediments* **3**(2): 109–124.
3. Kadlec, R.H., Knight, R.L., Vymazal, J., Brix, H., Cooper, P., Haberl, R. (Eds.). (2000). *Constructed Wetlands for Pollution Control—Processes, Performance, Design and Operation*. IWA Scientific and Technical Report No. 8, IWA Publishing, London, UK.
4. Kadlec, R.H. and Knight, R.L. (1996). *Treatment Wetlands*. CRC Press, Boca Raton, FL.
5. Langergraber, G. and Haberl, R. (2001). Constructed wetlands for water treatment. *Minerva Biotechnologica* **13**(2): 123–134.
6. US EPA. (2000). *Constructed Wetlands Treatment of Municipal Wastewaters*. Report EPA/625/R-99/010. US EPA, Cincinnatti, OH.
7. Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., and Haberl, R. (Eds.). (1998). *Constructed Wetlands for Wastewater Treatment in Europe*. Backhuys Publishers, Leiden, The Netherlands.
8. Wissing, F. (1995). Abwasserreinigung mit Pflanzen. Ulmer Verlag, Stuttgart, Germany [*In German*].

USING ECOSYSTEM PROCESSES IN A CONSTRUCTED WETLAND TO TREAT MINE WASTEWATER IN IRELAND

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WASTEWATER GENERATION

The development and expansion of industrial and agricultural activities in the Western world has led to a corresponding increase in the release of potentially toxic chemicals into the environment. Although growth has had many socioeconomic benefits, it has also led to negative implications for wetland ecosystems. For instance, the intensive farming practices developed in Ireland in the 1970s led to eutrophic (overenriched) rivers and lakes as a result of inadvertent inputs of excess nitrogen and phosphorus. This resulted in algal blooms, subsequent fish mortality, and reduced biodiversity of aquatic systems. The breaching of tailings dam walls in mine storage ponds has also resulted in catastrophic impacts on neighboring watersheds, which in many circumstances has led to irreversible ecosystem damage. Therefore, a balance is sought between reducing undesirable impacts while facilitating positive economic progress. By understanding the complex processes that affect the biogeochemistry and cycling of contaminants in aquatic ecosystems, innovative treatment technologies can be applied to mitigate and treat these wastes.

During metal mining, the oxidation of ores frequently results in increased reactivity and bioavailability and possibly toxicity of heavy metals (1). Many contaminants such as heavy metals and radionuclides cannot be chemically degraded, but microbial deactivation (mainly through immobilization) is most suitable for the treatment of these types of wastes (2). Other pollutants that prove difficult to dispose of are polychlorinated biphenyls (PCBs) which were used liberally as additives in the manufacture of paints and plastics until their toxicity was realized in the mid-1960s. PCBs have very high chemical, thermal, and biological stability; these properties resulted in their bioaccumulation in sediments and biota. Excess plant nutrients such as nitrogen and phosphorus are typically easier to treat in waters because they can be easily assimilated by plants and algae.

CURRENT TREATMENT PRACTICES AND ALTERNATIVE OPTIONS

Conventional practices for treating wastewater in Ireland adopt predominantly chemical applications that require high energy demands. These traditional technologies typically include the chemical manipulation of contaminants and subsequent physical precipitation of suspended solids in the water. Other means of treating wastewater contaminated with biodegradable organic wastes have proven very successful in the past few decades as wastes are biologically converted into gaseous and solid forms. Treatment practices relying on biological processes include continuous activated sludge reactors, which operate either aerobically or anaerobically. In suspended reactor vessels, microorganisms are kept in suspension in the wastewater, whereas in attached systems, microbial masses adhere typically to an inert medium. Various modifications of the aerobic treatment processes have been developed, including stabilization ponds, aerated waste reservoirs, and rotation and filtration techniques (3). These treatment techniques rely principally on activated processes, that is, they require substantial energy inputs and risk failure without continuous energy inputs.

Nonactivated biological processes employed to degrade contaminants are a more recent practice in wastewater treatment. Worldwide, particularly in North America and Australia, emerging practices for treating wastewater include constructed wetlands. These systems operate by using natural processes and usually do not require substantial energy inputs. The biological processes are typically solar-driven and use carbon and nutrients in the substrate to drive the microbial and plant processes. Therefore, constructed wetlands can be economical and ecologically acceptable. Typically, constructed wetlands are designed specifically for the type of wastewater being treated. Nutrients can be removed in aerobic systems, and sulfates and metals can be removed from wastewater under chemically reducing conditions. Wastewater contaminated by metals has usually been treated primarily to reduce acidity, but some treatment options for this type of waste have shown that substantial metals can be removed concurrently (4).

THE TARA MINES CASE STUDY

Tara Mines Ireland, a subsidiary of the Finnish company Outokumpu-Zinc, is the largest producer of zinc in Europe and the fifth largest lead-zinc mine worldwide. They have been operating since 1977 and supply approximately 20% of the European demand for zinc (5). The local bedrock from which the ore is extracted is classified as Lower Carboniferous calcite ($CaCO_3$) and dolomite ($CaMgCO_3$), which buffers the wastewater used in the processing operations to a pH of approximately 7.8 (5). Spent water is pumped to large storage ponds for treatment at a site about 5 km from the ore extraction site. Some of this wastewater is fed to the experimental treatment wetlands described here.

Treatment wetlands were engineered on-site at Tara Mines in 1997. These wetlands, built specifically to treat sulfate and metal-enriched wastewater emanating from the mine, are the only treatment wetlands of this kind in Europe at this time. Most applications employing microbes to reduce levels of contaminants in wastewater have focused on metal removal (6); the research at Tara Mines was concerned primarily with removing sulfate from the alkaline mine water.

Construction Design at Tara Mines Wetlands

Two similar experimental treatment systems were built adjacent to large tailings ponds. Each system measured 12 m (length) × 3 m (width) × 2 m (depth) or 72 m^3 with a 4:1 (length to width) aspect ratio (7) and comprised three 12 m^2 in-series surface-flow cells: inflow, wetland, and outflow (see Fig. 1 for details). Both systems were lined with a 2000 gauge (light-insensitive) impermeable PVC sheet, and each wetland cell was planted with cattails (*Typha latifolia*), reed (*Phragmites australis*), and floating sweetgrass (*Glyceria fluitans*) in the ratio of 4:9:7 per m^2. Three wooden baffles coated with an industrial-grade waterproof varnish were also placed in each wetland cell to increase the length of the flow path of the water. Mesocosm experiments indicated that an optimal combination of plant growth and substrate permeability was achieved by using a medium containing spent mushroom substrate and fine grit in a 1:3 ratio by volume of. Each cell was filled with a similar mix of this substrate to a depth of about 50 cm (Fig. 1).

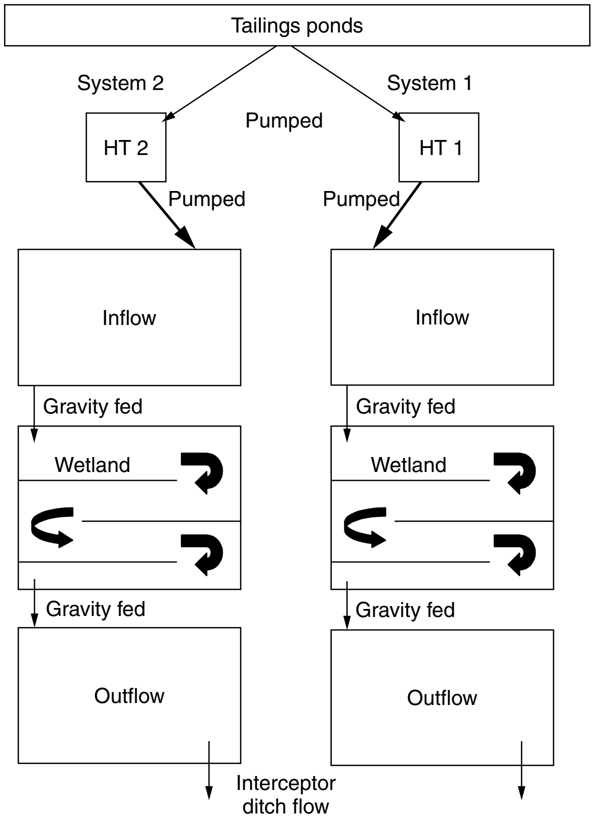

Figure 1. Schematic representation of the experimental treatment wetlands at Tara Mines, Ireland. Arrows indicate the flow path of the water, which was pumped from the storage ponds to the header tanks (HT 1 and HT 2) and subsequently to the inflow cells of each system. From there on, water traveling between cells was gravity fed (by head differences between cells) to the wetland cells and then finally to the outflow cells.

BIOGEOCHEMISTRY—THE KEY TO REMEDIATION

Wetland plants can remove pollutants from contaminated soils and water through uptake, translocation, and compartmentalization in storage tissues (2,8). However, the more significant influence of plants on metal removal from wastewater is indirect by accumulation of metals in the sediments surrounding the roots (8,9). Sufficient organic matter, provided by seasonal plant dieback, is also important in treatment systems that operate on natural biological processes. The accumulation of these contaminants is governed by microbial reactions mediated in suitable substrates and under appropriate conditions. For instance, the substrates used in the treatment wetlands at Tara Mines contained indigenous populations of sulfate-reducing bacteria, identified as the genera *Desulfovibrio, Desulfobulbus, Desulfotomaculum*, and *Desulfoccus*. The systems were permanently flooded and this provided net anaerobic substrate conditions conducive to the chemical reduction of sulfate ($SO_4{}^{2-}$) to sulfide (S^{2-}). This reaction occurred as the microorganisms assimilated sulfate in the absence of oxygen, thus reducing it to sulfide through the transfer of electrons produced by the simultaneous oxidation of the organic substrate. Sulfide anions resulting from the reaction are very unstable and readily react with free or sorbed metal cations to form metal sulfides such as zinc sulfide (ZnS), lead sulfide (PbS), and iron sulfide (FeS) (10). However, sulfide can also react with hydrogen to form hydrogen sulfide. Once the overlying water became saturated with hydrogen sulfide, it evolved to the atmosphere as a gas. Although evolution of this gas has not yet been quantified, it appears that substantial amounts were produced in the Tara Mines treatment wetlands, as evident from the frequent detection (olfactory). This may be a concern in the application of a larger scale treatment wetland and has not yet been fully addressed. Nonetheless, in the Tara Mines case study, the capacity to treat metal and sulfate contaminated wastewater using natural ecosystem processes was successfully demonstrated.

SUCCESS STORY—IN MANY WAYS

Treatment Capacity

The experimental treatment wetlands were modeled on the surface-flow design previously established in North America. Effectively, treatment occurred through bioimmobilization of the contaminants in the water as substrate, vegetation, and microbial assemblages interacted at the sediment–water interface. Although sulfate concentrations exiting the treatment systems did not comply with acceptable discharge levels (of 200 mg L^{-1}) stipulated in national legislation, up to 69% of the influent concentration (900 mg L^{-1}) was removed, and this equaled a removal rate of 29 g m^{-2} day^{-1}. Similarly, zinc and lead were removed by up to 99% and 64%, respectively, of the original concentrations supplied of 1.8 mg Zn L^{-1} and 0.2 mg Pb L^{-1}. Concentrations of these metals and of sulfides in the sediments were significantly greater than those in the original substrates, and concentrations in the soil water were also elevated compared to background water levels. Plants contained less than 1% of sulfur in their tissues, in accordance with other studies. Vegetation (including algae that voluntarily colonized the systems) sequestered metals to some extent, but plant roots had almost double the concentration of metals, compared to plant shoots. This may be explained by selective uptake and translocation mechanisms exhibited by some plants that can prevent contaminants from traveling to their shoots. The effect may also be explained by metal hydroxides that can form on plant roots (11). These hydroxides form when localized oxygenation by wetland plant roots and rhizomes induce precipitation of metals. Once metals are precipitated from solution, they become relatively immobile and thus generally less available to living organisms. The vegetation was not harvested from the treatment wetlands, so metals in these tissues were not actually removed from the systems because plant uptake and decay result in cycling of metals within such ecosystems. The most important attributes for ensuring long-term success and sustainability of constructed wetlands that treat these kinds of wastes appear to be wetland size and chemical loading rates. Therefore, these considerations must be clearly evaluated before constructing treatment wetlands.

Ecological and Societal Benefits

Wetlands are recognized for their hydrologic, economic, ecological, and aesthetic values. Natural, restored, and constructed wetlands have become the focus of many scientists in recent years for their capacity to treat wastewater in an ecologically and economically cost-effective way (12). The ecological benefits provided by the Tara Mines treatment wetlands were diverse and innumerable. Soon after they were constructed, macroinvertebrates (35 taxa), plants (6 species), algae, and microorganisms voluntarily colonized the systems. The vegetation afforded refuge to birds (e.g., moorhen) and other wildlife (foxes, rabbits, shrews, etc.), and also provided niches for microbial and invertebrate communities.

It is obvious that surface-flow wetlands offer many ancillary benefits by creating new habitats for wildlife. Initiatives to develop treatment wetlands have frequently involved local communities and educational establishments, thereby integrating educational principles into their goals. Aspects of the study at Tara Mines have been delivered to a wide spectrum of society from high-school teenagers in the local community to undergraduate and postgraduate students in universities in Ireland, Europe, and the United States. Additionally, the work has been well received by industries and local interest groups. By involving communities in the construction of wetlands, awareness of the value of such ecosystems and their capacity to recycle wastes by biological and ecologically acceptable techniques is generated.

TREATMENT SUCCESS COMPARED WITH OTHER SYSTEMS

The performance of the Tara Mines treatment wetlands for sulfate and metal removal was compared with that of other studies. Many of the other investigations quantified removal as a percentage of the influent concentration, but mass removal rates represent a more realistic estimate of the actual amount removed (4). In this instance, contaminant removal is calculated from a loading perspective; considers flow rates, concentrations, and wetland size; and expresses removal per unit time. Sulfate removal at Tara Mines was comparable with that published by Eger (13) of up to 27 g m^{-2} day^{-1}. Metal removal (from a percentage perspective) at Tara Mines was usually greater than that of other studies (e.g., Reference 14; removal of 33% Zn and 26% Pb). However, metal levels in the wastewater treated in the other studies were higher than those in the Tara Mines wastewater, and so higher mass removal rates probably occurred in these other studies.

STIMULUS FOR REVISING WASTE MANAGEMENT PRACTICES

In the past 25 years, most treatment wetland studies were concerned with removing plant nutrients from water. In the last decade, this focus has shifted toward remediating mine wastewater, principally to reduce the impact of acid mine drainage (4). However, constructed wetlands built for treating mine waste were primarily developed in North America, and the scope of similar systems in Europe has yet to be demonstrated. However, the question of long-term reliability of treatment wetlands is still not conclusively answered because most systems of this type have operated less than 15 years. Many scientists will advocate that, once they are appropriately designed and managed, they can remain self-renewing for several decades. The development of constructed wetland technology has demonstrated attractive success rates, and incurred limited financial operational costs. They can also provide ancillary ecological benefits. Increasing pressure in preparing for mine closure following ore exhaustion, coupled with societal concerns regarding environmental quality, is pressuring industries to reevaluate conventional treatment practices. Recent Irish and European Union legislation has contributed in some ways toward increasing the awareness of alternative cost-efficient treatment practices allied with sustainable development. By exploiting this newly found awareness, the possibility of implementing some innovative, ecologically sound waste technologies looks promising.

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BIBLIOGRAPHY

1. Schnoor, J. and Zehnder, A. (1996). *Environmental Modeling: Fate and Transport of Pollutants in Water, Air and Soil*. John Wiley & Sons, New York, pp. 381–451.
2. Salt, D. et al. (1995). Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology* **13**: 468–473.
3. Gray, N. (1999). *Water Technology—an Introduction for Environmental Scientists and Engineers*. John Wiley & Sons, New York, pp. 302–320.
4. Hedin, R., Nairn, R., and Kleinmann, R. (1994). *Passive Treatment of Coal Mine Drainage*. Information Circular #9389, Bureau of Mines, US Department of the Interior.
5. O'Leary, W. (1996). Wastewater recycling and environmental constraints at a base metal mine and process facilities. *Water Sci. Technol.* **33**(10–11): 371–379.
6. Song, Y., Piak, B., Shin, H., and La, S. (1998). Influence of electron donor and toxic materials on the activity of sulfate reducing bacteria for the treatment of electroplating wastewater. *Water Sci. Technol.* **38**(4–5): 187–194.
7. Crites, R. (1994). Design criteria and practice constructed wetlands. *Water Sci. Technol.* **29**(4): 1–6.
8. Otte, M., Kearns, C., and Doyle, M. (1995). Accumulation of arsenic and zinc in the rhizosphere of wetland plants. *Bull. Environ. Contam. Toxicol.* **55**: 154–161.
9. Ye, Z., Baker, A., Wong, M., and Willis, A. (1998). Zinc, lead and cadmium accumulation and tolerance in *Typha latifolia* as affected by iron plaque on the root surface. *Aquatic. Bot.* **61**: 55–67.
10. Morse, J., Millero, F., Cornwell, J., and Richard, D. (1987). The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth Sci. Rev.* **24**: 1–42.
11. Doyle, M. and Otte, M. (1997). Organism-induced accumulation of iron, zinc, and arsenic in wetland soils. *Environ. Pollut.* **96**: 1–11.
12. Mitsch, W. and Gosselink, J. (2000). *Wetlands*, 3rd Edn. Van Nostrand Reinhold, New York, pp. 688–697.
13. Eger, P. (1994). Wetland treatment for trace metal removal from mine drainage: the importance of aerobic and anaerobic processes. *Water Sci. Technol.* **29**(4): 249–256.
14. Mays, P. and Edwards, G. (2001). Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. *Ecol. Eng.* **16**: 487–500.
15. Hedin, R. (1996). Environmental engineering forum: long-term effects of wetland treatment of mine drainage. *J. Environ. Eng.* **122**: 83–85.

READING LIST

Catallo, W. (1993). Ecotoxicology and wetland ecosystems—current understanding and future needs. *Environ. Toxicol. Chem.* **12**(12): 2209–2224.

Dunbabin, J. and Bowmer, K. (1992). Potential use of constructed wetlands for treatment of industrial wastewaters containing metals. *Sci. Total Environ.* **111**: 151–168.

Foras Forbatha. (1990). *Water Resources Division in Eutrophication (1986–1990)*. Publication of the (Irish) National institute for planning and construction research.

Mora, A. (2001). *Solutions Applied to Aznalcollar Disaster*. Abstracts of the COST Action 837 (WG2) Workshop; Phytoremediation of trace elements in contaminated soils and water. C. Camara (Ed.). University of Madrid, Spain, April 5–7, p. 29.

Schuurmann, G. and Markert, B. (1998). *Ecotoxicology*. John Wiley & Sons, London.

WATER AND WASTEWATER PROPERTIES AND CHARACTERISTICS

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Water in nature is most nearly pure in its evaporative state. Because the very act of condensation usually requires a surface, or nuclei, water may acquire impurities at the very moment of condensation. Additional impurities are added as the liquid travels through the remainder of the hydrologic cycle and comes into contact with materials in the air and on or beneath the surface of the earth. Human activities contribute further impurities in the form of industrial and domestic wastes, agricultural chemicals, and other less obvious contaminants. Ultimately, these impure waters complete the hydrologic cycle and return to the atmosphere as relatively pure water molecules. However, the water quality in the intermediate stage is of greatest concern because the quality at this stage affects human use of water.

The impurities accumulated by water throughout the hydrologic cycle and from human activities may be in both suspended and dissolved form. Suspended material consists of particles larger than molecular size that are supported by buoyant and viscous forces within the water. Dissolved material consists of molecules and ions that are held by the molecular structure of water. Colloids are very small particles that technically are suspended but often exhibit many of the characteristics of dissolved substances.

Water pollution is the presence of impurities in water in such quantity and of such nature as to impair the use of the water for a stated purpose. Many parameters and characteristics have evolved that qualitatively reflect the impact that various impurities have on selected water uses. Knowledge of properties/characteristics/parameters of water and wastewater treatment processes is essential for environmental scientists and engineers.

PHYSICAL WATER QUALITY PARAMETERS

Physical parameters define those characteristics of water that respond to the senses of sight, touch, taste, or smell. Suspended solids, turbidity, color, taste and odor, and temperature fall into this category.

Suspended Solids

Solids can be dispersed in water in both suspended and dissolved forms. Solids suspended in water may consist of inorganic or organic particles or of immiscible liquids. Inorganic solids such as clay, silt, and other soil constituents are common in surface water. Organic materials such as plant fibers and biological solids (algal cells, bacteria, etc.) are also common constituents of surface waters. These materials are often natural contaminants resulting from the erosive action of water flowing over surfaces. Other suspended material may result from human use of water. Domestic wastewater usually contains large quantities of suspended solids that are mostly organic. Industrial use of water may result in a wide variety of organic or inorganic suspended impurities. Immiscible liquids such as oils and greases are often constituents of wastewater.

Suspended material in water may be objectionable for several reasons. It is aesthetically displeasing and provides adsorption sites for chemical and biological agents. Suspended organic solids may be degraded biologically, resulting in objectionable by-products. Biologically active (live) suspended solids may include disease-causing organisms as well as organisms such as toxin-producing strains of algae.

Suspended solids are likely to be organic and/or biological and are an important parameter of wastewater. The suspended solids parameter is used to measure the quality of wastewater influent, to monitor several treatment processes, and to measure the quality of the effluent. The U.S. Environmental Protection Agency (EPA) has set maximum suspended solids at 30 mg/L for most treated wastewater discharges.

Turbidity

Direct measurement of suspended solids is not usually performed on samples from natural bodies of water or on potable (drinkable) water supplies. The nature of the solids in these waters and the secondary effects they produce are more important than the actual quantity. For such waters, a test for turbidity is commonly used. Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water.

Most turbidity in surface waters results from the erosion of colloidal material such as clay, silt, rock fragments, and metal oxides from the soil. Vegetable fibers and microorganisms may also contribute to turbidity. Household and industrial wastewaters may contain a wide variety of turbidity producing material. Soaps, detergents, and emulsifying agents produce stable colloids that result in turbidity. Although turbidity measurements are not commonly run on wastewater, discharges of wastewaters may increase the turbidity of natural waterbodies.

When turbid water in a small, transparent container, such as a drinking glass, is held up to the light, an aesthetically displeasing opaqueness or “milky” coloration is apparent. The colloidal material associated with turbidity provides adsorption sites for chemicals that may be harmful or cause undesirable tastes and odors and for biological organisms that may be harmful. Disinfection of turbid waters is difficult because of the adsorptive characteristics of some colloids and because the solids may partially shield organisms from the disinfectant.

In natural waterbodies, turbidity may impart a brown or other color to water, depending on the light-absorbing properties of the solids, and may interfere with light penetration and photosynthetic reactions in streams and lakes. Accumulation of turbidity-causing particles in porous streambeds results in sediments that can adversely affect the flora and fauna of the stream.

Color

Pure water is colorless, but water in nature is often colored by foreign substances. Water whose color is partly due to suspended matter is said to have apparent color. Color contributed by dissolved solids that remain after removal of suspended solids is known as true color.

After contact with organic debris such as leaves, conifer needles, weeds, or wood, water picks up tannins, humic acid, and humates and takes on yellowish-brown hues. Iron oxides make water reddish, and manganese oxides make water brown or brackish. Industrial wastes from textile and dyeing operations, pulp and paper production, food processing, chemical production, and mining, refining, and slaughterhouse operations may add substantial coloration to water in receiving streams.

Colored water is not aesthetically acceptable to the general public. In fact, given a choice, consumers tend to choose clear, uncolored water of otherwise poorer quality over treated potable water supplies with an objectionable color. Highly colored water is unsuitable for laundering, dyeing, papermaking, beverage manufacturing, dairy production and other food processing, and textile and plastic production. Thus the color of water affects its marketability for both domestic and industrial use.

Color is not a parameter usually included in wastewater analysis. In potable water analysis, the common practice is to measure only the true color produced by organic acid resulting from decaying vegetation in the water. The resulting value can be taken as an indirect measurement of humic substances in the water.

Taste and Odor

The terms taste and odor define this parameter. Because the sensations of taste and smell are closely related and often confused, a wide variety of taste and odors may be attributed to water by consumers. Substances that produce an odor in water almost invariably impart a taste as well. The converse is not true; many mineral substances produce tastes but no odor. Many substances with which water comes into contact in nature or during human use may impart perceptible taste and odor. These include minerals, metals, and salts from the soil, end products from biological reactions, and constituents of wastewater. Inorganic substances are more likely to produce tastes unaccompanied by odor. Alkaline material imparts a bitter taste to water, and metallic salts may give a salty or bitter taste. Organic materials, on the other hand, are likely to produce both taste and odor in water; petroleum based products are prime offenders. The biological decomposition of organics may also result in taste-and odor-producing liquids and gases in water. Consumers find taste and odor aesthetically displeasing for obvious reasons. Because water is thought of as tasteless and odorless, the consumer associates taste and odor with contamination and may prefer to use a tasteless, odorless water that might actually pose more than a problem of simple aesthetics because some of those substances may be carcinogenic.

Temperature

Temperature is not used directly to evaluate either potable water or wastewater. It is, however, one of the most important parameters in natural surface water systems. The temperature of surface waters governs to a large extent the biological species present and their rates of activity. Temperature has an effect on most chemical reactions that occur in natural water systems. Temperature also has a pronounced effect on the solubilities of gases in water. The temperature of natural water systems responds to many factors, ambient temperatures are the most universal.

CHEMICAL WATER QUALITY PARAMETERS

Water has been called the universal solvent, and chemical parameters are related to the solvent capabilities of water. Total dissolved solids, alkalinity, hardness, fluorides, metals, organics, and nutrients are chemical parameters of concern in water quality management.

Total Dissolved Solids (TDS)

The material remaining in water after filtration for a suspended solids analysis is considered dissolved. Dissolved material results from the solvent action of water on solids, liquids, and gases. Like suspended material, dissolved substances may be organic or inorganic. Inorganic substances that may be dissolved in water include minerals, metals, and gases. Water may come in contact with these substances in the atmosphere, on surfaces, and within the soil. Materials from the decay products of vegetation, from organic chemicals, and from organic gases are common dissolved organic constituents of water. Many dissolved substances are undesirable in water. Some dissolved minerals, gases, and organic constituents are carcinogenic.

Because no distinction is made among the constituents, the TDS parameter is included in the analysis of water and wastewater only as a gross measurement of dissolved material. This is often sufficient for wastewaters, but it is frequently desirable to know more about the composition of the solids in water for use in potable supplies, agriculture, and some industrial processes. When this is the case, tests for several of the ionic constituents of TDS are made.

Akalinity

Alkalinity is the quantity of ions in water that will react to neutralize hydrogen ions. Alkalinity is thus a measure of the ability of water to neutralize acids. The constituents of alkalinity in natural water systems include CO_3^{2-}, HCO_3^-, and OH^-. These ions result from the dissolution of mineral substances in the soil and atmosphere. Phosphates may also originate from detergents in wastewater discharges and from fertilizers and insecticides from agricultural land. Hydrogen sulfide and ammonia may be products of the microbial decomposition of organic material. In large quantities, alkalinity imparts a bitter taste to water. The principal objection to alkaline water, however, is the reactions that can occur between alkalinity and certain cations in the water. The resultant precipitates can foul pipes and other water system appurtenances.

Hardness

Hardness is the concentration of multivalent cations in solution. At supersaturation, hardness cations react with anions in the water to form solid precipitates. The multivalent metallic ions most abundant in natural waters are calcium and magnesium, and for all practical purposes, hardness may be represented by the sum of calcium and magnesium ions.

Soap consumption by hard water represents an economic loss to the water user. Sodium soaps react with multivalent cations to form a precipitate, thereby losing their surfactant properties. Lathering does not occur until all the hardness ions are precipitated, at which point the water has been softened by the soap. Boiler scale, the result of the carbonate hardness precipitate, may cause considerable economic loss through fouling of water heaters and hot water pipes. Changes in pH in water distribution systems may also result in deposits of precipitates. Bicarbonate begins to convert to the less soluble carbonates at a pH above 9.0.

Magnesium hardness, particularly associated with the sulfate ion, has a laxative effect on persons accustomed to it. Magnesium concentrations of less than 50 mg/L are desirable in potable waters, although many public water supplies exceed this amount. Calcium hardness presents no public health problem.

Fluoride

Generally associated in nature with few types of sedimentary or igneous rocks, fluoride is seldom found in appreciable quantities in surface waters and appears in groundwater in only a few geographical regions. Fluoride is toxic to humans and other animals in large quantities, but small concentrations can be beneficial.

Metals

All metals are soluble to some extent in water. Excessive amounts of any metal may present health hazards, but only those metals that are harmful in relatively small amounts are commonly labeled toxic; other metals fall into the nontoxic group. Sources of metals in natural waters include dissolution from natural deposits and discharges of domestic, industrial, or agricultural wastewaters. Metals in water are usually measured by atomic absorption spectrometry.

Organics

Many organic materials are soluble in water. Organics in natural water systems may come from natural sources or may result from human activities. Most natural organics consist of the decay products of organic solids; synthetic organics are usually the result of wastewater discharges or agriculture practices. Dissolved organics in water are usually divided into two broad categories: biodegradable and nonbiodegradable (refractory).

Biodegradable Organics. Biodegradable material consists of organics that can be used for food by naturally occurring microorganisms within a reasonable length of time. In dissolved form, these materials usually consist of starches, fats, proteins, alcohols, acids, aldehydes, and esters. They may be the end products of the initial microbial decomposition of plant or animal tissue, or they may result from domestic or industrial wastewater discharges. Although some of these materials may cause color, taste, and odor problems, the principal problems from biodegradable organics are the secondary effects from the action of microorganisms on these substances.

Nonbiodegradable Organics. Some organic materials are resistant to biological degradation. Tannic and lignic acids, cellulose, and phenols are often found in natural water systems. These constituents of woody plants biodegrade so slowly that they are usually considered refractory. Molecules that have exceptionally strong bonds (some of the polysaccharides) and ringed structures (benzene) are nonbiodegradable.

Nutrients

Nutrients are elements essential to the growth and reproduction of plants and animals. Aquatic species depend on the surrounding water to provide their nutrients. Although a wide variety of minerals and trace elements can be classified as nutrients, those required in most abundance by aquatic species are carbon, nitrogen, and phosphorus. Carbon is readily available from many sources. Carbon dioxide from the atmosphere, alkalinity, and decay products of organic matter all supply carbon to the aquatic system. In most cases, nitrogen and phosphorus are the nutrients that limit aquatic plant growth.

BIOLOGICAL WATER-QUALITY PARAMETERS

Water may serve as a medium in which literally thousands of biological species spend part, if not all, of their life cycles. Aquatic organisms range in size and complexity from the smallest single-cell microorganism to the largest fish. All members of the biological community are to some extent, water quality parameters, because their presence or absence may indicate in general terms the characteristics of a given body of water. As an example, the general quality of water in a trout stream would be expected to exceed that of a stream in which the predominant species of fish is carp. Similarly, abundant algal populations are associated with a water rich in nutrients.

Biologists often use a species-diversity index (related to the number of species and the relative abundance of organisms in each species) as a qualitative parameter for streams and lakes. A body of water that hosts a large number of species with well-balanced numbers of individuals is considered a healthy system. Based on their known tolerance for a given pollutant, certain organisms can be used as indicators of the presence of pollutants.

Pathogens

From the perspective of human use and consumption, the most important biological organisms in water are pathogens, organisms that infect or transmit diseases to humans. These organisms are not native to aquatic systems and usually require an animal host for growth and reproduction. They can, however, be transported by natural water systems, thus becoming temporary members of an aquatic community. Many species of pathogens can survive in water and maintain their infectious capabilities for significant periods of time. These waterborne pathogens include species of bacteria, viruses, protozoa, and helminths (parasitic worms).

Bacteria. Bacteria are single-cell microorganisms, usually colorless, and are the lowest form of life that can synthesize protoplasm from the surrounding environment. Gastrointestinal disorders are common symptoms of most diseases transmitted by waterborne bacteria. Among the most violent waterborne bacterial diseases, cholera causes vomiting and diarrhea that, without treatment, result in dehydration and death.

Viruses. Viruses are the smallest biological structures known to contain all the genetic information necessary for their own reproduction. So small that they can only be “seen” with the aid of an electron microscope, viruses are obligate parasites that require a host in which to live. Symptoms of waterborne viral infections usually involve disorders of the nervous systems rather than of the gastrointestinal tract. Waterborne viral pathogens cause poliomyelitis and infectious hepatitis.

Protozoa. The lowest form of animal life, protozoa are unicellular organisms more complex in their functional activity than bacteria or viruses. They are complete, self-contained organisms that can be free-living or parasitic, pathogenic or nonpathogenic, microscopic or macroscopic. Highly adaptable, protozoa are widely distributed in natural waters, although only a few aquatic protozoa are pathogenic. Protozoal infections are usually characterized by gastrointestinal disorders of a milder order than those from bacterial infections.

Helminths. The life cycles of helminths, or parasitic worms, often involve two or more animal hosts, one of which can be human or animal waste that contains helminths. Contamination may also be via aquatic species of other hosts, such as snails or insects. Aquatic systems can be the vehicle for transmitting helminthal pathogens, but modern water treatment methods are very effective in destroying these organisms. Thus, helminths pose hazards primarily to those persons who came into direct contact with untreated water.

READING LIST

Metcalf & Eddy, Inc. (2003). *Wastewater Engineering: Treatment, Disposal, Reuse*, 4th Edn. McGraw-Hill, New York, pp. 27–139.

Peavy, H.S, Rowe, D.R., and Tchbanoglous, G. (1985). *Environmental Engineering*, International Edn. McGraw-Hill, New York, pp. 11–57.

ANAEROBIC WASTEWATER TREATMENT

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Anaerobic digestion is a natural process in which different microorganisms of the biological kingdoms of Bacteria and Archaea work together to convert organic compounds through a variety of intermediates into biogas, a mixture of methane and carbon dioxide and small amounts of hydrogen sulfide and hydrogen. This ancient process, brought about by living species long before the presence of oxygen in the atmosphere, is presently gaining an increased interest because of its potential in the treatment of solid organic waste, sludge, and wastewater.

HISTORY OF THE APPLICATION OF ANAEROBIC PROCESSES

Volta is considered to be the first to realize that there was a relationship between decaying vegetation and the occurrence of inflammable gas. In 1776 he showed that “combustible air” was formed from sediments in lakes, ponds, and streams (1). The initial use of anaerobic fermentation for pollution prevention has been for the treatment of domestic wastewater using anaerobic filters and hybrid systems, the latter consisting of a combination of an anaerobic tank and an anaerobic filter. The first recorded anaerobic treatment process was an air-tight chamber called the Mouras Automatic Scavenger, which was developed in the 1860s in France (2). Based on this concept Cameron developed a kind of septic tank in England to treat the wastewater of the city of Exeter in 1895, and Talbot developed a similar tank with baffles in Illinois in the United States in 1894.

In the first half of the twentieth century, anaerobic processes were especially applied for the digestion of sewage sludge. During the 1920s and 1930s, interest in the utilization of methane generated in sludge digesters grew, especially in Germany. Gas was used for heating of digesters, and in 1927 the Ruhrverband in Germany started to use sludge gas to generate power for a biological treatment plant. The generated (waste) heat was used for heating the digester. This is now common practice throughout the world.

The development of anaerobic treatment of industrial wastewater started in the second half of the twentieth century, also thanks to extensive studies in the first half of the century by Buswell. To reduce the size of the treatment systems, in the 1950s in South Africa, Stander (3) developed the clarigester, a modified Imhoff tank with an internal settler on top. In the same period, Schroepfer (4) used a reactor with recirculation of sludge from the settling tank, similar to aerobic treatment. This process was called the anaerobic contact process.

The development of anaerobic industrial wastewater treatment got a big boost after the energy crisis in the early 1970s, as anaerobic treatment is more energy efficient than aerobic treatment. A major factor in the development was also the recognition of the importance of sludge retention. New reactor concepts resulted in a further reduction of reactor volumes that could accommodate much higher loading rates than conventional aerobic treatment processes. The most prominent of these new systems is the UASB-process developed by Lettinga in The Netherlands (5).

In the last two decades a renewed interest has emerged in the application of anaerobic pretreatment for domestic wastewater in countries with a warm climate. The anaerobic treatment step is usually followed by an aerobic post-treatment.

THE ANAEROBIC PROCESS

The most important polluting compounds in wastewater are usually organic polymers such as fats, proteins, and carbohydrates. For the degradation of these polymers four main steps can be distinguished in anaerobic fermentation: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (see Fig. 1).

In the hydrolysis step, extracellular complex organic polymers (proteins, carbohydrates, and lipids) are hydrolyzed by exoenzymes into smaller molecules (mono- and oligomers: amino acids, sugars, and long-chain fatty acids), which can pass through bacterial cell membranes for further decomposition. For complex wastewaters, containing a large fraction of polymers, hydrolysis is the rate-limiting factor. During acidogenesis, the mono- and oligomers are acidified, which means that they are converted into simple organic acids, hydrogen, and carbon dioxide. In the third step, called acetogenesis, acetate is formed out of the simple (volatile) acids other than acetate. Under standard conditions, acetogenic conversions are endothermic and cannot take place. Only by immediate consumption of the products of this conversion step (hydrogen and acetate) by the methanogenic Archaea, can this conversion become thermodynamically favorable (exothermic). Finally, in the last step (methanogenesis) biogas is formed, either out of hydrogen and carbon dioxide or out of acetate. Roughly 70% of the biogas is produced via the acetate route. Due to the low growth rates of acetotrophic methanogens (the growth rate $\mu_{\max}$ of *Methanosaeta soehngenii*, which is usually the most predominant methanogen in the anaerobic sludge, is around $0.1\ d^{-1}$), acetotrophic methanogenesis is a crucial conversion in the total anaerobic digestion process.

If sulfate is present in the wastewater, part of the organic compounds will be degraded by sulfate-reducing bacteria. Sulfate mediates the degradation of organic compounds and will thereby be reduced to hydrogen sulfide, which will partly end up in the biogas.

BIOGAS PRODUCTION

For more concentrated types of wastewater, biogas production forms a welcome source of renewable energy. Theoretically, about $0.5\ m^3$ biogas can be produced per kilogram of converted COD. The basic principle of anaerobic fermentation is that part of the carbon is completely oxidized to CO_2, whereas the other part is completely reduced to CH_4 with the result that the average oxidation state of the carbon stays the same. N and O will stay completely reduced. Buswell derived an equation to determine the theoretical biogas production for any given organic compound. Assuming that of an organic molecule with the general formula of $C_nH_aO_bN_d$ a fraction x of C goes to CH_4 (oxidation state $C = -4$) and a fraction $(1 - x)$ of C goes to CO_2 (oxidation state $C = +4$) and taking into account that that does not change, it can be derived that the average oxidation state of the organic molecule $(2b + 3d - a)/n$ equals $-4x + 4(1 - x)$. From this the Buswell equation is obtained:

$$\begin{aligned} C_nH_aO_bN_d &+ (n - a/4 - b/2 + 3d/4)H_2O \\ &\rightarrow (n/2 + a/8 - b/4 - 3d/8)CH_4 \\ &\quad + (n/2 - a/8 + b/4 + 3d/8)CO_2 \\ &\quad + dNH_3 \end{aligned}$$

The real amount depends on various factors such as temperature, atmospheric pressure, pH, heat production, biodegradability of the pollutants in the wastewater, amount of COD used for cell maintenance and growth, and sulfate concentration in the wastewater. The CO_2 content is strongly related to the pH: the higher the pH, the lower the partial pressure of CO_2 in the biogas. Sulfate will reduce the CH_4 content of the biogas. Theoretically, sulfate-reducing bacteria will reduce 2 g of COD per gram of sulfate, with the effect that the generated electrons are used for formation of H_2S rather than CH_4. This results in a biogas with lower methane content.

Biogas can be used as a replacement for natural gas in different ways. It can be used directly in burners, in boilers, or in gas engines or fuel cells for electricity generation.

ANAEROBIC TREATMENT TECHNOLOGY

Anaerobic treatment has some clear advantages over conventional aerobic treatment. It has to be noted though that anaerobic treatment still needs further aerobic treatment of the remaining BOD. Most importantly, the aerobic activated sludge process needs energy for aeration (about 100 kWh per 100 kg COD), whereas in anaerobic

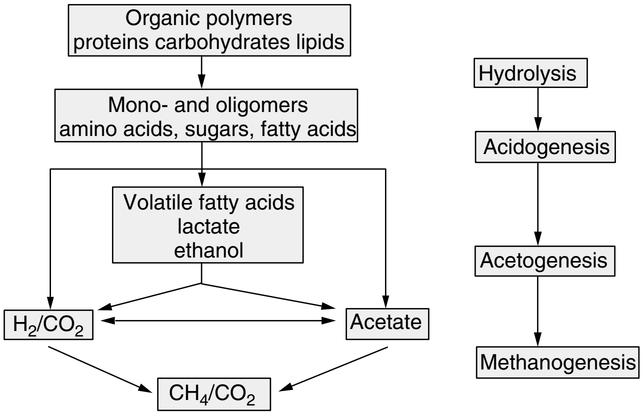


Figure 1. Schematic representation of the anaerobic fermentation of complex organic polymers into biogas.

Table 1. Comparison of Various Characteristics of Aerobic and Anaerobic Degradation of Glucose

Characteristic	Aerobic	Anaerobic
Reaction	$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$
Energy release	$\Delta G^0 = -2840$ kJ/mol	$\Delta G^0 = -393$ kJ/mol
Carbon balance	50% → CO_2 50% → biomass	95% → $CH_4 + CO_2$ (biogas) 5% → biomass
Energy balance	60% → biomass 40% → heat	90% retained in CH_4 5% → biomass 5% → heat
Biomass production	Yield > 0.5 kg VSS/kg COD	Yield = 0.05—0.15 kg VSS/kg COD
Energy input for aeration	1 kWh/kg COD	None

treatment energy is produced in the form of biogas. Over 285 kWh of electrical power can be produced per 100 kg COD.

In aerobic treatment much more sludge is produced than in anaerobic treatment. This is caused by the big difference in sludge yield factors (= grams of biomass formed per gram of degraded COD). For aerobic sludge this factor usually is around 0.5, whereas for anaerobic sludge it is generally below 0.15. As sludge management is a major cost factor in wastewater treatment, a strongly reduced sludge production is a big advantage. Contrary, comparing the effluent qualities of aerobic and anaerobic treatment shows that aerobic treatment is superior to anaerobic treatment in COD removal efficiency. Usually anaerobic treatment needs further post-treatment to meet common effluent discharge standards. However, an anaerobic system with appropriate post-treatment, in which the bulk of the organic pollutants is treated in the anaerobic step, is more cost effective than conventional aerobic treatment. The above mentioned difference between aerobic and anaerobic degradation is further illustrated for glucose as a model pollutant in Table 1.

ANAEROBIC REACTOR SYSTEMS

Key to the worldwide interest in anaerobic treatment is that it allows for an extreme uncoupling of the solid retention time from the hydraulic retention time. This uncoupling can be achieved by various means of sludge retention, such as sedimentation, immobilization on a fixed matrix or moving carrier material, and granulation. Granulation is a form of autoimmobilization typical for anaerobic biomass. Under appropriate conditions, dispersed sludge gradually transforms into a granular type of sludge. Granules are usually 0.5–3 mm in diameter and have high specific methanogenic activities and high settleabilities (up to 60 m/h). They are far more resistant to external shear forces than flocs. In practice, uncoupling of the hydraulic retention time from the solids retention time means that small reactor systems can be applied at high volumetric loading rates.

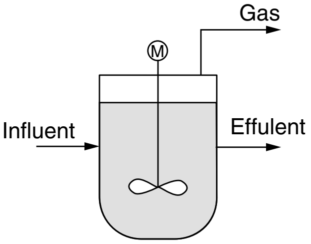
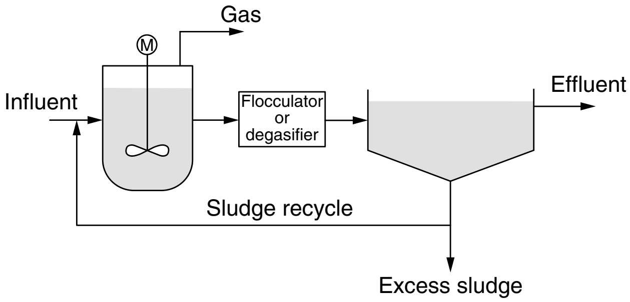
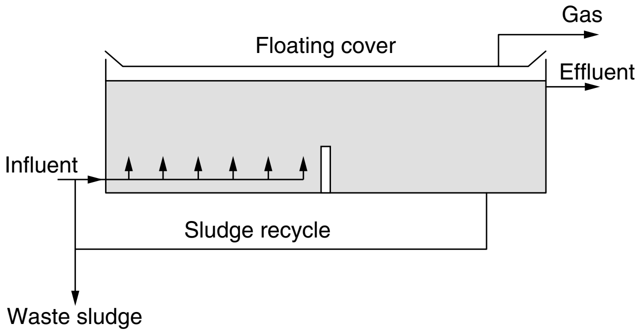
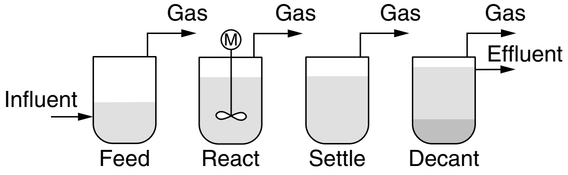
Tables 2, 3, and 4 give an overview of the most common low rate, high rate, and super high rate processes that are presently applied on full scale.

The anaerobic filter (AF) was used in early applications for domestic sewage treatment. It was further developed in the United States (6,7) for the treatment of industrial wastewater treatment. The reactor is filled with a packing material for bacterial attachment. Sludge retention is also achieved by accumulation of anaerobic biomass in the crevices of the packing. This reactor type can be operated both in an upflow and downflow mode.

In the Upflow Anaerobic Sludge Bed (UASB) reactor (5,8) sludge retention is achieved by sedimentation of granular or thick flocculent sludge in an internal settler located in the upper part of the reactor. This internal settler is also called a gas–liquid–solids (GLS) or three-phase separator. In this separator biogas is captured in a gas hood, creating a quiet zone above this hood, allowing solids to settle and return to the lower reactor compartment where the anaerobic conversion takes place. The water leaves the reactor on top of the reactor as effluent. About 60% of all full-scale anaerobic reactors that have been built worldwide are of the UASB type. Alternative sludge bed processes are the Anaerobic Baffled Reactor (ABR) (9,10) and the Anaerobic Migrating Blanket Reactor (AMBR) (11). UASB and AF reactors are used for the treatment of both industrial and domestic wastewater.

Common super high rate processes are the Expanded Granular Sludge Bed (EGSB) reactor (12) and the Internal Circulation (IC) reactor (13) presented in Table 4. These reactor systems can treat at volumetric loading rates up to 30 kg COD/$m^3 \cdot$ d. The EGSB is operated with anaerobic granular sludge. EGSB reactors are more widely applied than fluidized bed (FB) reactors. The upflow velocity in EGSB reactors is up to 10 m/h. Like the UASB reactor, the EGSB system has an internal settler on top of the reactor. IC reactors are also operated with anaerobic granular sludge. In this reactor an internal liquid recycling is created by a so-called gas lift of the water by the generated biogas. This internal recycling results in optimal mixing and an intense contact between wastewater and sludge. Contrary to external recirculation, the internal recirculation does not lead to higher average upflow velocities in the system. EGSB and IC reactors are tall and slim and therefore have a small footprint.

Table 2. Most Common Low Rate Anaerobic Treatment Systems (Volumetric Loading Rate <5 kg COD/m^3·d)

Reactor Type	Characteristics
Completely Stirred Tank Reactor (CSTR)	
	• Suitable for sludge and manure digestion • No sludge retention • Long hydraulic retention times (15–30 days)
Anaerobic Contact Process	
	• Suitable for wastewaters rich in suspended solids • Sludge retention by external sedimentation and sludge recycling
Covered Anaerobic Lagoon	
	• Suitable for wastewaters rich in suspended solids • Sludge retention by sedimentation • Large reactor with large footprint • Long hydraulic retention times
Anaerobic Sequencing Batch Reactor (ASBR)	
	• Suitable for wastewaters rich in suspended solids • Sludge retention by sedimentation

BASIC DESIGN PRINCIPLES

There are three important factors that determine the design of anaerobic reactors:

1. The biological conversion capacity.
2. The maximum allowable hydraulic loading rate.
3. The maximum allowable gas loading rate.

For the design of a system treating concentrated wastewaters the biological conversion capacity is the determining factor. The conversion capacity is determined by the amount of biomass that can be retained in the reactor and the specific methanogenic activity of this biomass. This activity is influenced by various factors such as pH, temperature, intensity of the contact between wastewater and the biomass, COD composition, presence of inhibiting or toxic compounds, and presence of sufficient macro- and micronutrients.

For diluted wastewaters the limiting factor is the hydraulic capacity of the reactor. If the hydraulic load

Table 3. Most Common High Rate Anaerobic Treatment Systems (Volumetric Loading Rate 3–20 kg COD/m^3·d)

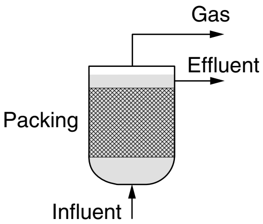
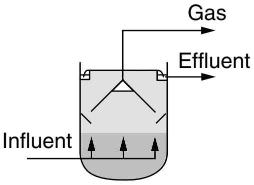
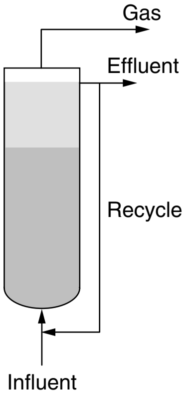
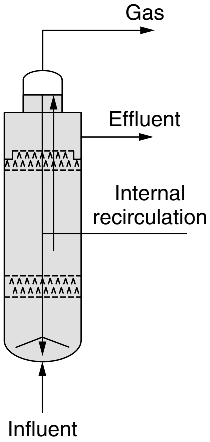
Reactor Type	Characteristics
Anaerobic Filter (AF)	
	• Sludge retention by attachment on filter material and entrapment in voids in the filter • Can be operated upward and downward
Upflow Anaerobic Sludge Bed (UASB) Reactor	
	• Sludge retention by granulation and settling • Internal three-phase separator to separate gas, sludge, and water • Optimal contact of water with biomass by gas mixing

Table 4. Most Common Super High Rate Anaerobic Treatment Systems (Volumetric Loading Rates 10–30 kg COD/m^3·d)

Reactor Type	Characteristics
Expanded Granular Sludge Bed (EGSB) Reactor	
	• Suitable for medium to low strength wastewater and low temperatures (<25 °C) • Comparable to fluidized bed reactor • External recirculation • Upflow flow rate in the reactor is up to 10 m/h
Internal Circulation (IC) Reactor	
	• Requires anaerobic granular sludge • Two internal three-phase separators • Internal circulation of water by gas lift principle

exceeds the hydraulic capacity of the system, the sludge washout from the reactor can become higher than the sludge yield by bacterial growth. This will result in a gradual drop in the quantity of active biomass in the reactor and ultimately in reactor failure.

PHYSICAL SEPARATION OF ACIDOGENESIS FROM METHANOGENESIS

Fairly common in anaerobic treatment is the physical separation of hydrolysis and acidification in an acidifying reactor and acetogenesis and methanogenesis in a second reactor. This phase separation was supported by a school of researchers (14–17), who claimed that such a separation would lead to better control of the overall digestion process. Under optimal mesophilic conditions a slight preacidification of the wastewater is certainly beneficial, but generally this is already accomplished during the transport of the wastewater in the sewer system. For soluble and not or partially acidified carbohydrate-containing wastewaters, phase separation is therefore not required. For the formation of granular sludge it is even better to have no phase separation. However, for treatment of hardly acidified carbohydrates under psychrophilic conditions, the use of a preacidification step is required: the in-growing voluminous acidifying organisms do not decay sufficiently fast, and therefore they will accumulate in the retained methanogenic sludge, creating a bulking type of sludge. As a result, the sludge characteristics will deteriorate (18).

Staging of anaerobic treatment systems can be considered beneficial for the treatment of various types of complex wastewaters, such as domestic sewage or wastewaters containing slowly biodegradable or inhibitory compounds (19). In such staged reactors in principle all phases of the anaerobic degradation process are allowed to proceed to some extent simultaneously in each reactor module. A staged reactor system will provide a higher treatment efficiency, because more difficult compounds like intermediates such as propionate, or possibly even xenobiotic compounds (when present in the wastewater), will find a more optimal environment for degradation due to the development of appropriate microbial communities in each stage. The process stability of a staged system is also substantially higher than in the present commonly practiced one-step systems.

APPLICATION OF ANAEROBIC WASTEWATER TREATMENT

Anaerobic treatment has been applied primarily for medium to high strength wastewaters of (agro-) industrial origin with COD concentrations over 1000 mg/L. Common industries generating wastewater that can be well treated by anaerobic processes are starch factories, breweries, pulp and paper mills, and distilleries. More recently, other industries with wastewater containing organic pollutants have started using anaerobic treatment, such as chemical and pharmaceutical industries.

Since 1985 interest has grown in anaerobic treatment of domestic sewage in countries with tropical or subtropical climates (20). The full-scale plants mostly use UASB reactors for the anaerobic step and they are constructed all over South America and Asia, especially in Brazil and India. As indicated in Fig. 2 the advantage of anaerobic sewage treatment over aerobic treatment is that four components of the latter (primary clarifier, activated

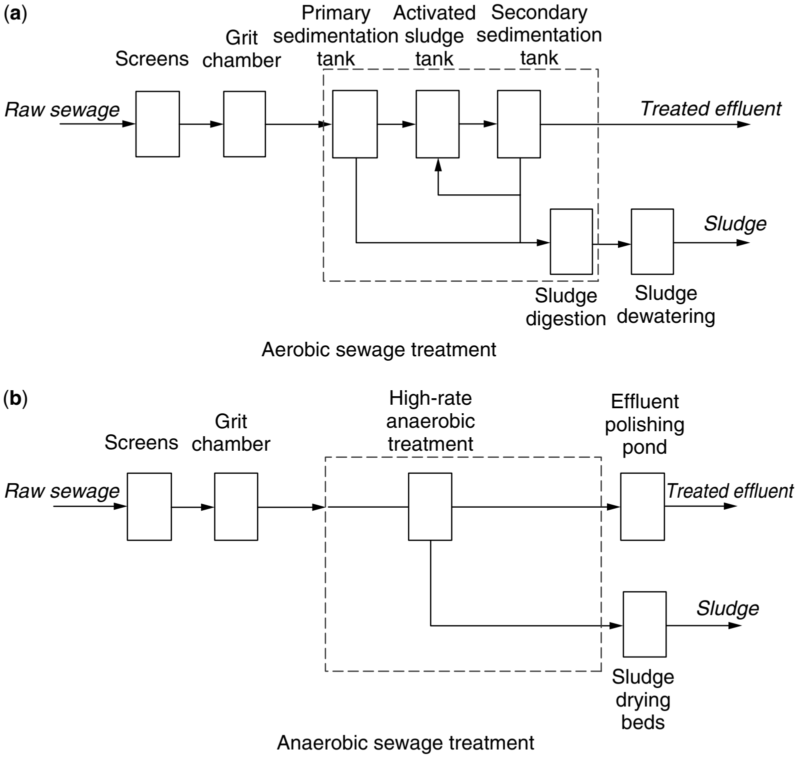


Figure 2. Flowsheets of aerobic sewage treatment (**a**) using the activated sludge process and anaerobic sewage treatment (**b**) with post-treatment in a polishing pond.

sludge tank, secondary clarifier, and sludge digester) can be combined in one single reactor. In this reactor removal of COD and sludge stabilization takes place simultaneously.

Anaerobic treatment has traditionally been applied under optimal mesophilic temperature conditions (around 30 °C). Anaerobic digestion however, is, feasible under a wide range of conditions, such as temperatures ranging from 4 to 70 °C, high salinity, the presence of recalcitrant or toxic compounds, and for wastewater with very low COD/sulfate ratios.

CONCLUSION

Anaerobic digestion is implemented for the treatment of industrial and domestic wastewater, sludge, and solid waste for the removal of biodegradable compounds from the waste. Anaerobic processes require only a small energy input and a renewable energy source is generated in the form of biogas. Anaerobic treatment is a standard technology for wastewater of agroindustrial origin in the industrialized world. In developing countries, interest in and application of anaerobic treatment of domestic sewage are emerging.

The applicability of anaerobic processes is further extended to hot and cold wastewater as well as wastewater from the (petro-) chemical, pharmaceutical, textile, and mining industries.

BIBLIOGRAPHY

1. Barker, H.A. (1956). Biological formation of methane. In: *Bacterial Fermentations*. Wiley, Hoboken, NJ, p. 1.
2. McCarty, P.L. (2001). The development of anaerobic treatment and its future. In: *Anaerobic Digestion for Sustainable Development, Proceedings of the farewell seminar of Prof. Gatze Lettinga*. March 29–30, Wageningen, The Netherlands.
3. Stander, G.J. (1966). Water pollution research—a key to wastewater management. *J. Water Pollut. Control Fed.* **38**: 774.
4. Schroepfer, G.J., Fullen, W.J., Johnson, A.S., Ziemke, N.R., and Anderson, J.J. (1955). The anaerobic contact process as applied to packinghouse wastes. *Sewage Ind. Wastes.* **2**: 117–142.
5. Lettinga, G. et al. (1980). Use of the Upflow Sludge Blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. *Biotechnol. Bioeng.* **22**: 699–734.
6. Young, J.C. and McCarty, P.L. (1969). The anaerobic filter for waste treatment. *J. Water Pollut. Control Fed.* **41**: R160.
7. Young, J.C. and Dahab, M.F. (1983). Effect of media design on the performance of fixed bed anaerobic reactors. *Water Sci. Technol.* **15**: 369–383.
8. Lettinga, G. and Hulshoff Pol, L.W. (1991). UASB process design for various types of wastewaters. *Water Sci. Technol.* **24**: 87–107.
9. Bachmann, A., Beard, V.L., and McCarty, P.L. (1985). Performance characteristics of the Anaerobic Baffled Reactor. *Water Res.* **19**(1): 99–106.
10. Barber, W.P. and Stuckey, D.C. (1999). The use of the Anaerobic Baffled Reactor (ABR) for wastewater treatment: a review. *Water Res.* **33**: 1559–1578.
11. Angenent, L.T., Banik, G.C., and Sung, S. (2000). Psychrophilic anaerobic pretreatment of low-strength wastewater using the Anaerobic Migrating Blanket Reactor. In: *Proceedings of the 73rd Annual Water Environment Conference*, New Orleans, LA.
12. Zoutberg, X. and de Been, X. (1997).
13. Yspeert, P., Vereijken, T., Vellinga, S., and de Vegt, A. (1993). The IC reactor for anaerobic treatment of industrial wastewater. In: *Proceedings of the 1993 Food Industry Environmental Conference*, Atalanta, GA, pp. 487–497.
14. Breure, X. (1986).
15. Breure, X. et al. (1985).
16. Cohen, X. et al. (1985)
17. Pohland, X. and Ghosh, X. (1971).
18. Rebac, X. (1999).
19. van Lier, J.B. et al. (2001). Advances in high-rate treatment: staging of reactor systems. *Water Sci. Technol.* **44**(8): 15–25.
20. van Haandel, A.C. and Lettinga, G. (1994). *Anaerobic Sewage Treatment. A Practical Guide for Regions with a Hot Climate*. John Wiley, Chichester, UK.

SEWERAGE ODORS—HOW TO CONTROL

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WHAT ARE ODORS?

Odors result from the perception of chemicals by the olfactory system. The chemicals are detected in the mouth and nasal passages. Sensations are conveyed to the brain where they may be negatively perceived. The olfactory nerve (first cranial nerve) conveys the perception of chemical odorants to the brain. The trigeminal nerve (fifth cranial nerve) relates the pungency or irritability due to chemical exposure to the brain. Many of the chemicals that cause a negative reaction, bad odors, are related to bacterial emissions that may indicate the presence of pathogenic organisms. The human olfactory system can detect many of these pathogenic indicator chemicals at concentrations of only a few parts per billion (ppb). The chemicals that cause the olfactory response are called odorants. The human olfactory system is capable of detecting a wide variety of odorants.

The human response to odorants present in the air depends on the odor concentration, intensity, persistence, and character. Odor concentration can be measured as a dilution ratio and results may be reported as a detection threshold, recognition threshold, or dilution-to-threshold ratio. Odorants can be measured analytically in the field or laboratory and their concentrations are typically reported in parts per million (ppm) or parts per billion (ppb) by volume. Odor intensity is often related to the equivalent intensity produced by exposing an odor panel to the sample of interest and correlating the odor panel response to a butanol-based standard scale. Odor persistence is interpreted as the duration of exposure and is reported as a dose–response function. The odor character is a descriptive scale, which describes what the odor smells like based on categorical descriptive terms. These terms provide scientists and engineers with the measurement and descriptive techniques relating odorants to odors and hold the key to understanding odor control strategies. Prior to describing control techniques, it is helpful to understand what causes odors and how they are generated in the sewers.

WHAT CAUSES ODORS?

Wastewater or sewage water is a complex mixture of organic and inorganic wastes. The organic wastes consist of a mixture of human wastes, food wastes, and industrial wastes. Simple organic compounds such as sugars and carbohydrates are broken down aerobically into carbon dioxide and water, and anaerobically into methane. More complex organic molecules, such as proteins and amino acids, are also broken down into carbon dioxide, water, and methane; however, the remaining sulfur and nitrogen present in these compounds may result in the production of hydrogen sulfide, ammonia, and other strong odorants as illustrated in Fig. 1.

Aerobic wastewaters commonly contain many odorants, including indole, skatole, organic acids, esters, alcohols, and aldehydes. However, microbial activity in the sewers depletes the oxygen, creating anaerobic conditions. When anaerobic conditions develop, the types and concentrations of odorants in the sewer rapidly increase. Most sewage odor problems are related to the odorants formed under anaerobic conditions, including hydrogen sulfide, mercaptans, ammonia, amines, and volatile fatty acids.

Hydrogen sulfide is typically the odorant of greatest concern in sewers due to its low detection threshold, high concentration, and acidic nature. Hydrogen sulfide is generated from the anaerobic biological reduction of sulfate ($SO_4{}^{2-}$) or thiosulfate. One common mechanism is described by

$$SO_4{}^{2-} + 2C + 2H_2O \xrightarrow{\text{anaerobes}} 2HCO_3{}^{-} + H_2S$$

Hydrogen sulfide is generated in the slime layers and sludge deposits in sewer collection systems as illustrated in Fig. 2. Key parameters that control sulfide generation include the concentration of organic materials and nutrients in the sewage, sulfate concentrations, temperature, dissolved oxygen, pH, and residence time of the sewage and sludge deposits in the sewer system.

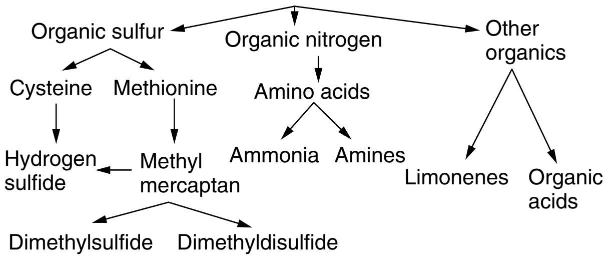

Figure 1. Odorants generation mechanisms from organic wastes.

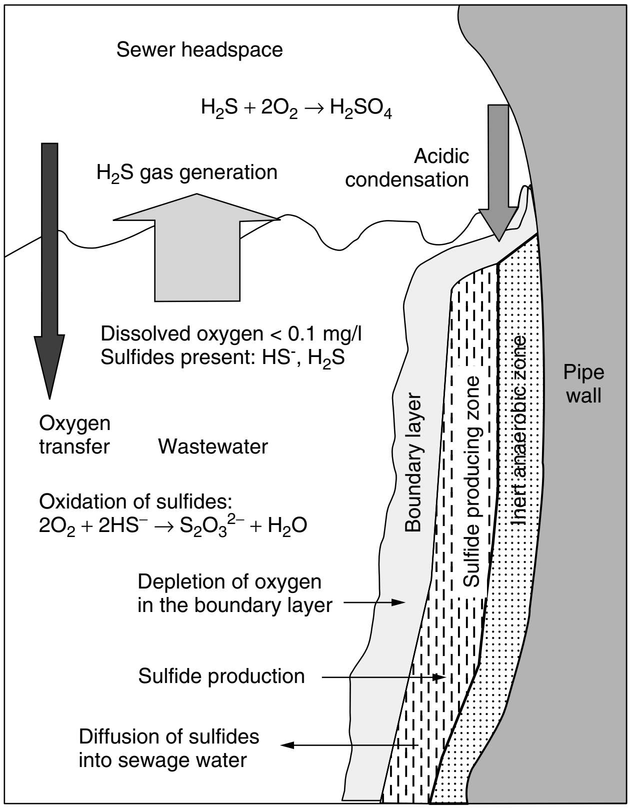

Figure 2. Sulfide generation in sewers (adapted from Ref. 1).

Pomeroy and Parkhurst (1) developed a predictive model for estimating sulfide generation in wastewater collections systems:

For pipes flowing full:

$$S_2 = S_1 + (M)(t)[\mathrm{EBOD}(4/d + 1.57)]$$

For less than full pipes:

$$S_2 = S_{\lim} - \frac{(S_{\lim} - S_1)}{\log^{-1}\left[\dfrac{m(su)^{3/8}t}{2.31d_m}\right]}$$

where S_2 = predicted sulfide concentration at time t_2 (mg/L)
S_1 = sulfide concentration at time t_1 (mg/L)
$S_{\lim}$ = limiting sulfide concentration, $S_{\lim} = (M'/m)\ \mathrm{EBOD}(su)^{-3/8}(\mathrm{P/b})$ (mg/L)
M = sulfide flux coefficient, typically 0.5×10^{-3} to 1.0×10^{-3} (m/h)
M' = effective sulfide flux coefficient in gravity sewers, typically 0.32×10^{-3} (m/h)
m = empirical coefficient for sulfide loss, typically 0.96
t = detention time in the sewer reach with constant diameter and flow (h)

EBOD = effective biochemical oxygen demand, $\mathrm{EBOD} = \mathrm{BOD} \times 1.07^{(T-20)}$ (mg/L)
d = pipe diameter (m)
T = wastewater temperature (°C)
s = slope (m/m)
u = stream velocity (m/s)
d_m = mean hydraulic depth, equal to area of flow divided by surface width (m)
P = wetted perimeter (m)
b = width of wastewater stream at the surface (m)

Odor emission of other compounds present in the sewage, like hydrogen sulfide, increase with increased turbulence of flow. The solubility of the odorant, concentration, temperature, pH, and mass transfer coefficient are all factors that affect the emission rate of odorant in the sewer. Weirs, junction chambers, and holding tanks may represent significant sources of odor.

Odor emissions are dependent on the chemical nature of the odorant of concern and the composition of the wastewater. Emissions are also dependent on the mechanical operating parameters of the sewer. Odor emissions are of greatest concern when odorants are in close proximity to receptor populations. Nuisance odors are often reported because pressurization of the sewer atmosphere results in odorant emissions from manholes, house vents, and other structures. Pressurized conditions can result from inverted siphons, drop structures, discharges of forces mains, reductions in pipe diameter, and sags in the sewer that restrict air movement.

Odor control measures are designed to prevent the formation of hydrogen sulfide or remove hydrogen sulfide from sewer exhaust. Prevention of hydrogen sulfide formation is usually accomplished by either improving oxygen transfer or the addition of chemical or microbial additives to the sewer.

ODOR PREVENTION

Improving Oxygen Transfer

Ventilation of the sewer system can be improved through proper maintenance or the addition of appurtenances to increase the rate of oxygen transfer. Sewer system ventilation is a dynamic parameter that varies with change in barometric pressure along the sewer, wind velocities past vents, sewage drag, sewage flow rates, and the relative density of sewer and outside air. Partial blockages of flow and buildup of the slime layer within the sewers significantly affect ventilation and increase hydrogen sulfide emissions. These conditions can be mitigated through a regular program of inspections and cleaning. Regular cleaning has been shown to temporarily reduce the rate of sulfide buildup, particularly when sewage deposit buildups are problematic (2).

Oxygen can be transferred mechanically into the sewer to increase the dissolved oxygen concentration in the wastewater and reduce hydrogen sulfide generation. Air or oxygen may be directly injected into the sewer. The rate of air flow required for odor reduction with direct air injection depends on the oxygen uptake rate, detention time in the downstream sewer, temperature and pressure, and degree of odor control required. Direct air injection rates utilized in practice in the United States are highly variable, but typical ranges are 0.75–2.25 $\mathrm{m^3}$ air/$\mathrm{m^3}$ wastewater or 0.7–1.3 $\mathrm{m^3}$/h/cm-pipe-diameter. Other appurtenances used to increase oxygen transfer into the wastewater include venture aspirators, air lift pumps, U-tube injection lines, and pressurized air tanks, which are described in more detail in the referenced literature (1–8). The costs associated with air injection are illustrated in Table 1.

Additives

A variety of chemical additives have been employed to reduce odors from sewers and wastewater treatment facilities. The additives reduce hydrogen sulfide emissions by chemical oxidation, microbial inhibition of sulfate reduction, precipitation, and pH control. The most effective chemical additives for control of sewage odors have been chlorine agents, peroxides, and metal salts.

Chlorine has been used effectively to control hydrogen sulfide emissions from wastewater. Chlorine may be added to wastewater as hypochlorite or as chlorine gas. Hypochlorite solutions may be used for small chlorine dosages, but chlorine gas is more cost effective when 2.3 kg/d of chlorine or more is required. Chlorination systems are designed based on the level of sulfide control required, the characteristics of the wastewater, and the degree of process control required. Sulfide is oxidized to

Table 1. Typical Costs for Increasing Oxygen Transfer in 2003 Dollars[a]

Condition	Small Air Injection System	Large Air Injection System	Small Oxygen Injection System	Large Oxygen Injection System
Flow, $\mathrm{m^3/d}$	3,785	37,850	3,785	37,850
Pipe diameter, cm	25.4	61.0	36	76
Pipe length, m	1,600	1,600	1,600	1,600
Air pressure, kPa	158	158	NA	NA
Air flow, $\mathrm{m^3/min}$	2.5	15.3	NA	NA
Oxygen required, kg/d	NA	NA	93	310
Capital cost, $	37,000	96,000	35,000	89,000
Oxygen cost, $/yr	NA	NA	16,000	35,000

[a] Update by the Consumer Price Index from 1984 dollars (1).

sulfate in wastewater when excess chlorine is present:

$$HS^- + 4Cl_2 + 4H_2O \longrightarrow SO_4{}^- + 9H^+ + 8Cl^-$$

At least 8.87 parts by weight of chlorine are required to oxidize sulfide according to the above equation. However, higher dosages are required in full-scale applications due in part to limitation on the amount of mixing. Field application rates typically required 10–15 kg Cl_2/kg H_2S. Full-scale studies should be performed for a period of several weeks to ensure adequate odor control is achieved based on the control system and chlorine dose. Chlorine feed rates may be optimized through monitoring residual chlorine, sulfide, and wastewater flow rate. Table 2 illustrates the typical costs associated with chlorine injection systems.

Hydrogen peroxide has been utilized to oxidize hydrogen sulfide and reduce odorous emissions from sewage. The hydrogen peroxide oxidation occurs rapidly and excess peroxide results in a higher dissolved oxygen concentration. Hydrogen peroxide is also an attractive reagent because it can be used for gravity and pressurized sewers, feed systems are relatively simple, and peroxide provides effective sulfide control for up to 4 h.

The chemical mechanism of sulfide oxidation is dependent on the pH of the wastewater:

$$\text{For pH} < 8.5: H_2O_2 + H_2S \longrightarrow S + 2H_2O$$
$$\text{For pH} > 8.5: 4H_2O_2 + S^- \longrightarrow SO_4{}^- + 2H_2O$$

The stoichiometric peroxide dose required is 1 g H_2O_2/g H_2S. Dosage varies with the BOD, pH, and temperature of the wastewater and the hydraulic characteristics of the sewer. Typical peroxide dosages in practice range from 0.9 to over 3.0 g H_2O_2/g H_2S. The peroxide dose can be optimized by monitoring wastewater flow rates, sulfide concentrations, and chemical feed rates. The costs associated with peroxide addition systems are shown in Table 2.

Many metal ions react with dissolved sulfides to form insoluble salts that precipitate from the solution. Iron and zinc salts have been added for control of sulfur emission. The proposed mechanism of sulfur removal with iron salts is represented by

$$Fe^{2+} + 2Fe^{3+} + 4HS^- \longrightarrow Fe_3S_4 + 4H^+$$

The overall removal mechanism can be expressed as

$$FeSO_4 + H_2S \longrightarrow FeS + H_2SO_4$$

Stoichiometric removal of sulfur requires 1.6 g Fe/g H_2S removed. Actual dosages require field testing to optimize the iron dose required for the desired odor reduction. The costs associated with iron injection for hydrogen sulfide control are shown in Table 2.

Nitrates, alkalis, ozone, and potassium permanganate have been utilized for short-term odor control measures. These additives have been shown to help control short-term odor problems and spikes in odor at specific locations that require only small doses of the additives. However, these chemicals have not been cost effective for long-term sulfide control in large sewers.

Biological additives have been marketed to help control odor emissions from sewage. These products may alter the metabolism of existing microorganisms or be "designer" microorganisms that out-compete odor-producing microorganisms and thus reduce emissions. Metabolic modification with anthraquinone products has been effective in treating small diameter pipes and force mains where there is a large slime layer or septic sediments are problematic. The product is cost effective when used as a preventative measure for small lines with high sulfide concentrations and slow moving gravity lines. Recommended dosages are based on the surface area of the slime layer and are approximately 0.24 kg of the product per 1000 m^2 of surface area. Nitrate and metabolic modifiers may be a cost-effective combination for minimizing odors.

ODOR REMOVAL

If odor prevention is not cost effective or sufficient to control nuisance odors, various odor control technologies are capable of removing odorous compounds exhausted from confined sources. The most common technologies for

Table 2. Typical Costs for Chemical Additives in 2003 Dollars[a]

Condition	Chlorine Injection System	Hydrogen Peroxide Injection System	Iron ($FeSO_4$) Injection System
Flow, m^3/d	3,785	3,785	3,785
[H_2S], mg/L	5	5	5
Dose, mg/L	30	10	23
Capital cost, $	32,000	44,000	18,000
Chemical cost, $/yr	25,000	37,000	23,000
Flow, m^3/d	37,850	37,850	37,850
[H_2S], mg/L	5	5	5
Dose, mg/L	30	10	23
Capital cost, $	71,000	89,000	23,000
Chemical cost, $/yr	243,000	335,000	230,000

[a] Update by the Consumer Price Index from 1984 dollars (1).

treating sewer-related odors are carbon adsorption, biofiltration, absorption, ozonation, and thermal oxidation.

Four major factors need to be considered to select and design a cost-effective system to remove odorants from exhaust air. The concentration and composition of the odorants in the air stream must be determined from sampling and laboratory analysis. The flow rate of the exhaust air stream must be minimized. The cost associated with the control technologies, both capital and operational costs, must be considered. Selection and design of control technologies should include pilot scale testing to ensure odors are adequately removed. Experience and judgment are inherent and necessary parts of designing an effective odor control system.

Adsorption Systems

Carbon adsorption systems utilize the attractive van der Waals forces on porous granulated activated carbon (GAC) surfaces to capture and contain organic pollutants. GAC systems are commonly applied to a wide variety of odor control situations due the simplicity of design, low capital costs, and minimal maintenance requirements. Carbon adsorption systems are ideal for small applications dictated by space and low capital investment.

The activated carbon acts as a capture and control device. The odorants adhere to the surface of the GAC and eventually consume all available surface sites. The mass-transfer zone (MTZ), where odorants are being removed, gradually moves from the inlet side of the carbon bed to the outlet side. As time passes and more odorants are adsorbed, the amount of spent carbon increases. Breakthrough occurs when the zone of mass transfer reaches the exit of the carbon bed and there is no longer an excess of active carbon sites available. When the carbon adsorption bed efficiency decreases, as the bed nears saturation, the carbon must be replaced or regenerated. The vendor of the material typically regenerates the GAC off-site.

Monitoring of the carbon adsorption system is critical to prevent and detect breakthrough of the odorants as the bed nears the end of its useful life span. Regular monitoring of the system allows accurate measurement of cycle times and service contracts should be created to minimize episodes of poor efficiency. The capital costs, illustrated for two different air flow rates in Table 3, and the operational costs may be considerable.

Biological Control Systems

Biofilters have been used for many years in the United States for odor control and have a reputable history for odor control in many European countries. Odorants are degraded by microorganisms in the biofilter. Odorant removal occurs in a thin liquid film or biofilm. The end products of the degradation are carbon dioxide, water, biomass, and (when removing high concentrations of hydrogen sulfide) sulfuric acid. Because biotrickling filters have the ability to "store" the contaminants as a food source, they are often applied to situations that have variable influent loading rates.

Biofilters represent a low cost alternative for treating low concentration, high volume exhaust streams as shown in Table 3. The capital and operational costs for biofiltration systems are relatively low. In addition, biofilters produce no secondary waste if properly operated, except for periodic media replacement. Historically, biofilters were limited in their application due to variable removal efficiencies caused in part by their intolerance to fluctuation in air flow rates, concentrations, and temperatures. In addition, biofilters typically require a very large area footprint compared to other types of organic control technologies.

Absorption Systems

Absorption systems or scrubbers involve the selective transfer of the odorants from the gas phase to a contacting liquid. The odorants must have preferential solubility in the liquid. The soluble odorants diffuse from the gas through a gas–liquid interface and the odorants are dispersed in the liquid.

Absorption systems are ideal for controlling water-soluble odorants, such as hydrogen sulfide, ammonia, and organic acids. The soluble pollutants must be continually destroyed or treated to maintain operational efficiencies. For both ammonia and hydrogen sulfide removal, the pH of the system must be continuously monitored and controlled. Absorption systems are sometimes combined with chemical additives to increase aqueous phase reaction rates. Absorption systems are often used to remove large quantities of hydrogen sulfide prior to a second stage scrubber or carbon bed used to remove less concentrated odorants such as mercaptans and volatile acids, which without treatment would result in nuisance odors.

Ozone Contactors

Ozone is utilized for odor control in the exhaust air as well as preventing odors from forming in the wastewater. Sufficient time and ozone concentrations are required in the contacting chamber to ensure adequate ozone removal. Detailed ozone reaction mechanisms are complex and

Table 3. Typical Costs for Odor Removal from Confined Space Exhaust Air in 2003 Dollars[a]

Air Flow Rate, m^3/min	Adsorption		Biofiltration		Absorption		Ozone Contactor	Thermal Oxidizer
	Capital	Annual	Capital	Annual	Capital	Annual	Capital	Capital
28	53,000	11,000	17,000	500	69,000	4,000	54,000	56,000
280	227,000	85,000	158,000	5,000	136,000	35,000	120,000	91,000

[a] Update by the Consumer Price Index from 1984 dollars (1).

highly dependent on the chemical composition of the treated wastewater or air stream. Examples of overall reactions of ozone with hydrogen sulfide, amines, and mercaptans are illustrated by

$$H_2S + O_3 \xrightarrow{\text{major pathway}} S + H_2O + O_2$$

$$H_2S + O_3 \xrightarrow{\text{minor pathway}} SO_2 + H_2O$$

$$R_3N + O_3 \longrightarrow \underset{\text{(amine oxide)}}{R_3NO} + O_2$$

$$\underset{\substack{\text{Methyl}\\ \text{mercaptan}}}{CH_3SH} + O_3 \longrightarrow CH_3S - SCH_3$$

$$+O_3 \longrightarrow \underset{\substack{\text{methyl sulfonic}\\ \text{acid}}}{CH_3SO_3H} + O_2$$

Ozone is an unstable gas that must be produced on-site. Ozone is typically generated by corona discharge, which requires significant electrical consumption and excess heat. Three to four ppm of ozone are required in the exhaust air to sufficiently control odors. Reaction times, typically in the range of 10–60 s, vary widely depending on the degree of control required, odorant concentration, humidity, and ozone concentration. The ozone dosage must be controlled to minimize the discharge of unreacted ozone or excess ozone can be discharged into the wastewater. Occupational and environmental health and safety aspects must be considered due to the potential exposure to ozone and electrical currents. Typical costs for ozone contactors are provided in Table 3.

Thermal Oxidation Systems

Thermal oxidation systems reliably maintain nearly complete destruction of odor-causing compounds. Thermal oxidizers are designed based on operating temperature, residence time, and turbulence or mixing in the reactor. Temperature requirements for destruction range from typical design temperatures of 480 to 870 °C. Thermal oxidation systems can maintain high destruction efficiencies even with wide fluctuations in concentration. However, thermal oxidation systems do not tolerate wide flow rate fluctuations well. Thermal oxidation systems also consume large quantities of fossil fuels and as a result they are sources of nitrogen oxides, carbon dioxide, and possibly acid gases for sulfur-containing waste streams. Furthermore, thermal oxidation systems are typically run 24 h/d due to the long start-up and shut-down times required for operation.

The volumetric flow rates of the fuel and air streams along with the size of the reaction chamber are important to ensure adequate retention time and destruction efficiency. For low concentration air streams, additional make-up air is not necessary if there is sufficient oxygen in the polluted air stream to maintain combustion. A mass balance and enthalpy balance should be performed to estimate the required fuel flow rate to maintain the desired operational temperature.

Fuel costs make up the majority of operational costs and must be considered in order to select the most cost-effective treatment systems. Adequate design and operation of thermal oxidation systems is dependent on the temperature, the residence time of the gas, and turbulence or mixing within the reaction chamber. These variables are dependent on one another. The kinetic rate constants increase exponentially with temperature. Reaction times on the order of 0.1–0.5 s are usually sufficient to allow the reactants to reach the desired degree of chemical destruction. Turbulence within the reaction chamber ensures sufficient mixing. Therefore, a higher reaction temperature results in a shorter residence time, a smaller combustion chamber, and lower capital costs. A higher residence time lowers the operating temperature, results in less fuel usage, and in higher capital costs. The operational costs versus capital investment should be considered during selection and design of thermal oxidation systems. Factors that should be considered when determining the capital costs illustrated in Table 3 include the materials of construction, instrumentation, costs of heat exchangers, engineering fees, and construction fees.

CONCLUSION

Odor control requires a comprehensive maintenance program, preventive measures to reduce odor control costs, and possible implementation of control systems where sewage odor is a nuisance. Research, experience, and comprehensive testing programs are important for determining the most cost-effective odor control methods. Regardless of the technologies implemented, there are ongoing costs for preventing and controlling odors that must be included in the operational budget of the wastewater authority.

BIBLIOGRAPHY

1. US EPA. (1985). *Design Manual, Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants*. U.S. Government Printing Office, Washington, DC.
2. Thistlewayte, D.K.B. (1972). *The Control of Sulphides in Sewerage Systems*. Ann Arbor Sciences and Publishers, Ann Arbor, MI.
3. WEF. (2004). *Control of Odors and Emissions from Wastewater Treatment Plants*. WEF Manual of Practice No. 25, Water Environment Federation, Alexandria, VA, pp. 5–7, 133–146, 239–293.
4. Tchobanoglous, G., Burton, F.L., and Stensel, H.D. (2003). *Wastewater Engineering Treatment and Reuse*, 4th Edn. Metcalf and Eddy/McGraw Hill, Boston, pp. 1650–1693.
5. Pomeroy, R.D. and Bowlus, F.D. (1946). Progress report on sulfide control research. *Sewerage Works J.* **18**(4): 597–640.
6. WPCF. (1976). *Chlorination of Wastewater*. Manual of Practice No. 4, Water Pollution Control Federation, Washington, DC.
7. WPCF. (1969). *Design and Construction of Sanitary and Storm Sewers*. Manual of Practice No. 9, Water Pollution Control Federation, Washington, DC.
8. Duggan, S.W. (1980). *A Perspective on Hydrogen Sulfide in Sewers*. Presented at New Jersey Water Pollution Control Association Technology Transfer Seminar, November 19, 1980.

ULTRAFILTRATION—COMPLEXATION IN WASTEWATER TREATMENT

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GENERAL INTRODUCTION

General

Wastewater treatment represents one of the most important fields of study today in the wide subject of pollution problems solving. A "rational hydrologic resource management" is necessary because of the world's increased demand of water, particularly in these last years, owing to a lack of this resource (1). As a result, the main challenge is to create new resources and to fully reuse the existing ones (2). In particular, water frequently contains numerous ionic solutes, many of which are not desirable, and it is used either for residential or industrial purposes.

In the last fifty years, pressure-driven membrane processes have become a routine technique for the removal of environmentally relevant and hazardous substances from aqueous systems (3–10). A membrane can be defined as a selective barrier between two phases (5,11). Transport through the membrane takes place when a driving force is applied. The main goals of such processes are: a) concentration of a solute by removing the solvent, b) purification of a solution by removing nondesirable components, and c) fractionation of liquid or gaseous mixtures.

The separation of solutes with ionic dimensions can be accomplished by using the reverse osmosis operation, but this will result in high operative costs, low permeate flow rate, and low ions selectivity. In order to overcome these problems, the hybrid ultrafiltration-complexation process was introduced (12–17). It was named polymer-assisted ultrafiltration (PAUF) or polymer-enhanced ultrafiltration (PEUF). This process can be applied for various purposes such as the treatment of waste effluents, groundwater, and seawater (13–15,18,19). The advantages of this method are the low energy requirements involved in UF, the conceptual simplicity, the modularity typical of membrane processes, the high permeate flow rate, the high removal efficiency because of effective binding while reducing the initial waste volume significantly, the selectivity achieved when an appropriate complexing agent is considered, and the optimal quality of treated water (6,16,20–22).

The separation process will be successful if the polymer meets the following requirements: good solubility, high selectivity, regeneration possibility, chemical and mechanical stability, low toxicity, high molecular weight with low viscosity, and low cost (12).

The complexation-ultrafiltration technique is mainly applied today in the separation of metal ions from aqueous solutions, covering processes ranging from production of potable water to leaching and recovery of metals from washing water of contaminated soil or from ores to detoxification of process water and wastewater, also for water recycling and reuse (23–27). Indeed, metal contamination is a dangerous cause of water pollution and it constitutes a big health hazard (28–34). Some metal ions play an essential role in many biological processes, and their deficiency, unusual accumulation or imbalance, may lead to biological troubles, e.g., Cu^{2+} ion is an essential nutrient, but when people are exposed to copper levels of above 1.3 mg/l for short periods of time, stomach and intestinal problems occur. Long-term exposure to Cu^{2+} leads to kidney and liver damage (35,36), producing DNA mutation, evidence of its cancerogeneous character.

In the following, the application of PAUF technique is reported with particular focus on metal removal from water.

Historical Background

In 1980, Nguyen et al. (37) considered the application of ultrafiltration to the concentration and separation of solutes of low molecular weight in water. Their results showed a high rejection of these species by complexing them with a suitable soluble macromolecule. Furthermore, they demonstrated that it is possible to separate a specific cation from a mixture by using a polymer that shows a marked selectivity for one cation.

Another similar approach was published in 1982 by Renault et al. (38), which studied the recovery of chromium from effluents by using ultrafiltration.

In 1984, Buffle and Staub (39) gave a fundamental contribution to increase research interest on PAUF method with a work in which they applied the ultrafiltration for measurement of complexation equilibrium constants of metal ions in water in natural conditions. Thus, the coupling of the terms complexation and ultrafiltration was used.

In successive years, several research efforts were made to study mainly the technical and economical feasibility of PAUF to meet the limits fixed by pollution laws for metal removal from water of various origins.

Tabatabai et al. (17) studied the feasibility in the removal of Ca^{2+} and Mg^{2+} ions from hard water by using the sodium polystyrene sulfonate (PSS) polymer (water softening). They demonstrated (with some economical considerations) that the PSS needs to be recovered from the retentate and regenerated appropriately to be reused.

Juang and Shiau (20) studied the metal removal from aqueous solutions using chitosan-enhanced membrane filtration, and in two other works (2,40), Juang and Chiou considered the problem of technical feasibility on the use of PAUF for brackish water softening and wastewater treatment by using three weakly basic, water-soluble polymers like chitosan, polyethylenimine (PEI), and poly(diallyl dimethylammonium chloride) to remove ions like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cu^{2+}, and Zn^{2+}.

An et al. (28) evaluated the ability of crab shell (practically chitosan) to remove heavy metals from aqueous solutions by comparison with several sorbents. They found, for crab shell heavy metals, removal capacity higher than cation exchange resins, zeolite, powered activated carbon, and granular activated carbon. Besides, this process is selective, removing Pb and Cr in preference to Cd and Cu.

Barron-Zambrano et al. (23) investigated the separation of mercury from aqueous solutions using PEI as polymeric complexing agent. They considered the development of a two-stage process: The first one enables mercury concentration and the production of a purified stream, whereas the second one was required to separate the mercury from the polymer and to recycle the polymer (chemical regeneration).

Steenkamp et al. (35) considered the copper(II) removal from polluted water with alumina/chitosan composite membrane, giving attention prevalently to the problems related to the synthesis of the composite support and to the factors that influence metal removal efficiency, like pore radii variation with temperature and powder mixtures used and chitosan coating thickness.

Vieira et al. (41) studied the metal removal from wastewater of the pulp and paper industry. Zakrzewska-Trznadel et al. (42) tested the application of PAUF for radioactive waste processing purposes. Their results showed that this process could be an alternative to reverse osmosis.

Canizares et al. (18) studied a semicontinuous laboratory-scale application of polymer-enhanced ultrafiltration for the recovery of lead and cadmium from aqueous effluents. They emphasized that this process includes two stages: a) metal retention, where a permeate stream free of heavy metals is obtained and b) polymer regeneration, where the polymer is regenerated in order to be reused. The pH for metal retention and polymer regeneration and the binding capacity to know the metal amount that can be treated are also important parameters.

FUNDAMENTALS OF POLYMER-ASSISTED ULTRAFILTRATION

The idea of the PAUF process is that ultrafiltration can be used for removal of ions from aqueous streams, provided that they are preliminarily bound to water-soluble polymers (2,12,43,44). The unbound ions pass through the membrane, whereas the polymers and their complexes are retained (13,14,42,45).

Low-molecular-weight species such as metal ions can be bound to macromolecules by intermolecular forces, mainly ionic interaction and complex binding, or the combination of both.

Formation of complexes is significantly more selective than ionic interactions. An example of this binding mechanism is the complexation reaction among the polymeric agent (PEI), the proton (H^+), and the metal cation (Cu^{2+}), which is represented by the equilibrium equations:

$$\mathrm{PEI} + \mathrm{n\,H_2O} \Longleftrightarrow \mathrm{PEIH_n^{n+}} + \mathrm{n\,OH^-} \tag{1}$$

$$\mathrm{PEI} + \mathrm{a\,Cu^{2+}} \Longleftrightarrow \mathrm{PEICu_a^{2a+}} \tag{2}$$

where $0 \le \mathrm{n} \le \bar{\mathrm{n}}$ and $0 \le \mathrm{a} \le \bar{\mathrm{a}}$ with $\bar{\mathrm{n}}$ equal to the number of monomers contained in a single polymeric chain and $\bar{\mathrm{a}}$ representing the maximum complexation ratio of the polymers with copper ions ($\bar{\mathrm{a}} = \frac{\bar{\mathrm{n}}}{4}$ for PEI-Cu complex because of Cu^{2+} tetra-coordination with four nitrogen of PEI). In particular, considering that commercial PEI, widely used in literature, has a polymeric chain of MW 60 kDa and considering that a monomeric unit $-CH_2-CH_2-NH-$has MW 43.062 Da, $\bar{n} = 1393$ is obtained (30).

An ionic interaction mechanism can be described, for example, in the removal of dihydrogen arseniate ion with a polymer R^+Cl^-, by the following reactions:

$$\mathrm{R^+Cl^-} \Longleftrightarrow \mathrm{R^+} + \mathrm{Cl^-} \tag{3}$$

$$\mathrm{R^+} + \mathrm{H_2AsO_4{}^-} \Longleftrightarrow \mathrm{RH_2AsO_4} \tag{4}$$

This is an ion-exchange reaction, similar to that which takes place in anion-exchange resin. In another case, the water-soluble polymers polyacrylic acid (PAA) and polyacrylic acid sodium salt (PAASS) interact with copper cation by ion-exchange reactions, described by the following equations:

$$\mathrm{PAA} + \mathrm{n\,Cu^{2+}} \Longleftrightarrow \mathrm{PAACu_n} + \mathrm{2n\,H^+} \tag{5}$$

$$\mathrm{PAASS} + \mathrm{m\,Cu^{2+}} \Longleftrightarrow \mathrm{PAACu_m} + \mathrm{2m\,Na^+} \tag{6}$$

Ionic exchange interaction mechanism has low selectivity and the disadvantage to release another ion (H^+ or Na^+ in this case) in the feed solution, so that to remove an ion from an aqueous solution, another one must be released. In contrast, reactions such as in Eq. 2 do not present this disadvantage.

It should be taken into account that, in general, solid resins and water-soluble polymers have similar functional groups, which would result in similar chemical properties, e.g., the ability to bind certain ions. These analogies in the properties can be used in order to predict the behavior of an unknown hydrophilic polymer if the properties of the functional group of the resin are known.

The PAUF process can be economically more feasible if the polymer could be regenerated, releasing the metal to separate, and be reused. The general scheme of the overall process is represented in Fig. 1.

Polymer regeneration could be carried out by three major methods (12):

1. *Chemical regeneration* means the change of pH of the retentate in order to cleave the polymer–metal bond (21,30,46);
2. *Electrochemical regeneration* means the electrolysis of the retentate resulting in a deposition of the metal on an electrode, whereas the polymeric agent remains in the solution (44);

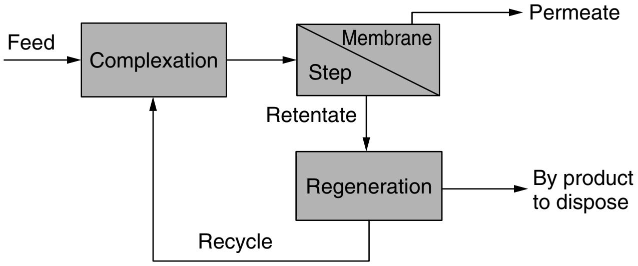


Figure 1. Flowsheet of PAUF separation process.

3. *Thermal regeneration* could be also possible if the polymer-metal bond can be cleaved by heating the retentate, but it has found no practical application so far.

SOME STUDIES OF PAUF IN THE REMOVAL OF METAL IONS FROM AQUEOUS SYSTEMS

In the following, attention will be focused on the application of the complexation-ultrafiltration process in the removal of the model ion copper(II) from aqueous systems, using water-soluble polymers as chelating agents.

Copper(II) Removal from Water by Using Polyethylenimine (30)

The mechanism of the water-soluble polymer PEI—copper interaction can be described by the previously reported equilibrium reactions (1) and (2). In those reactions, a competition exists between Cu^{2+} and H^+ for the polymer because, depending on pH, the PEI is able to complex copper ions by means of Eq. (2), but, at low pH, it stays in aqueous solution in the $PEIH_n^{n+}$ form incapable to interact with copper.

Thus, the first step in the application of the complexation ultrafiltration technique consists in the determination of optimal chemical conditions (pH) for copper complexation (bound) and de-complexation (release) at isothermal conditions (e.g., temperature of 25 °C). To quantify the copper-polyethylenimine (Cu-PEI) complex formation, the spectrophotometric technique was used by reading at 620 nm wavelength.

The complexation-decomplexation process was quantified by plotting vs. the pH the complexation percentage $C\% = (ABS/ABS_{max}) \times 100$, where ABS_{max} is the maximum value of the absorbance that corresponds the maximum amount of complex (100%). The results, reported in Fig. 2, show that PEI is able to complex copper ion at pH 6 or higher, whereas the decomplexation happens at pH < 3.

Similar results were obtained by working at different polymer concentrations observing that maximum binding pH does not depend on polymer concentration. This behavior agrees with the chemical mechanism of polymer-copper interactions (Eqs. 1–2). Indeed, at high pH, the complexation reaction (2) takes place.

To determine the binding capacity of PEI (maximum copper amount (mg) that can be complexed by a fixed amount (1 g) of polymer), some complexation tests were carried out with a polymer concentration of 150 mg/l and changing copper concentration at a fixed pH ($\sim$6). The obtained value of the binding capacity was 0.333 mg Cu^{2+}/mg PEI. It must be observed that a high-binding capacity means a lower cost of the PAUF process.

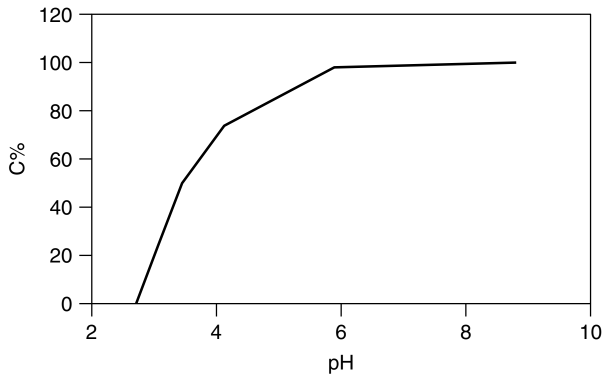


Figure 2. Cu-PEI complex formation $C\%(= (ABS/ABS_{max}) \times 100)$ vs pH in complexation tests of PEI (150 mg/l) with copper (50 mg/l).

Ultrafiltration tests were carried out by using five different membranes (Table 1), two operative transmembrane pressures (2 and 4 bar), pH ca. 6, and five different weight concentrations of PEI and Cu^{2+} with the same ratio (150/50, 270/90, 375/125, 480/160, 600/200).

Working at increasing PEI and Cu^{2+} concentrations and maintaining the same ratio, it is permitted to simulate the increase of retentate concentration in a hypothetical industrial plant where the permeate, free of metals, is withdrawn using the PAUF technique.

It was obtained that simultaneously increasing copper and polymer concentrations (ratio $PEI/Cu^{2+} = 3$ fixed) in the retentate, the separation efficiency (R%) decreased, resulting in an increase of copper and polymer concentrations in the permeate and a little decrease of permeate flux. As a result of increased concentration in the retentate, rejection first decreased, but then increased, because of the formation of a selective dynamic layer (by concentration polarization), which caused a little decrease of permeate flux too, because of mass transfer resistance increase.

It should be observed that an optimal PAUF process should produce a high permeate flux (J_P) and a low copper concentration (C_p). So, in order to compare membrane performances, an appropriate parameter Jp/Cp was introduced. This parameter has no dimensional significance, but it answers the previous requirements to optimize PAUF processes by choosing the membrane that gives the highest ratio.

To evaluate the possibility of polymer regeneration, some UF tests were carried out (operative conditions:

Table 1. Some Characteristics of the UF Membranes Tested in the PAUF Process

Membrane Type	Material	Cut-off (kDa)	Producer	Water Flux [l/h × m^2] (2–4 bar)
Iris 10	Poly ether sulphone (PES)	10	Tech-Sep	33.85–55.00
FS 40 PP	Fluoride-polypropylene	40	Dow	220.0–397.7
GR 40 PP	Polysulphone-polypropylene	40	Dow	220.0–444.3
Iris 30	Poly ether sulphone (PES)	30	Tech-Sep	114.2–207.3
PAN 40	Polyacrylonitrile	40	Tech-Sep	291.1–528.9

PEI = 150 ppm; Cu = 50 ppm; pH = 3) withdrawing the permeate at established time and analyzing copper and TOC (Total Organic Carbon) concentrations. Obtained data showed that all the copper passed through the membrane, whereas the polymer remained in the retentate (rejection of 95% with PAN 40 kDa membrane); that means a good possibility of polymer regeneration, recovery, and reuse.

Comparison of Copper(II) Removal from Waters by Using Various Polymers (21)

Some water-soluble polymers, such as polyetilenimine (PEI), polyacrylic acid (PAA), polyacrilic acid sodium salt (PAASS), and poly(dimethylamine–co–epichlorohydrin–co–ethylenediamine) (PDEHED) as chelating agents (Table 2), have been tested by using the Cu^{2+} as model ion.

Optimal Chemical Conditions. For PAA and PAASS, an ionic interactions mechanism, such as the equilibrium reactions (5) and (6), occurs. It is influenced by the pH: at low pH, the protonation of carboxylic group of the polymer is favored, whereas at higher pH complexation, the reaction is shifted right, meaning macromolecular complex formation with the metal ion. The interaction between the copolymer PDEHED and copper ion is more complicated: both the lone pair of the nitrogen in dimethylamine and ethylenediamine monomers and the oxygen of epichlorohydrin could bind copper with both complex bond and ionic interactions.

From Fig. 3 it can be observed that copper ion is complexed by PEI, PAA or PAASS, and PDEHED at pHs higher than 6, 4.6, and 8, respectively. The decomplexation reactions took place at pH < 3.

Binding capacity was 0.333 mg Cu^{2+}/mg polymer for PEI and PAA. At pH 8.5, working with a polymer concentration of 50 mg/l and changing copper concentration, a binding capacity of 2 mg Cu^{2+}/mg PDEHED was obtained; at higher ratios, a cloud solution was observed, probably because of limited complex solubility.

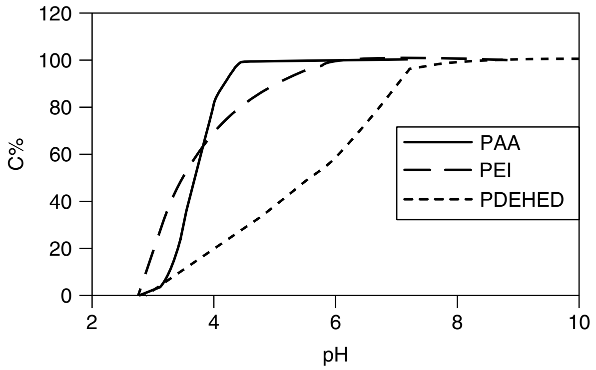


Figure 3. Comparison of Cu-polymer complex formation C% (= $(ABS/ABS_{max}) \times 100$) vs pH in complexation tests of PEI (150 mg/l), PAA (150 mg/l), and PDEHED (150 mg/l) with copper (50 mg/l).

Ultrafiltration Tests. Ultrafiltration tests were realized at two transmembrane pressures (2 and 4 bar), by using five different membranes, and determining flux and rejection. Copper concentration was fixed at 50 mg/l to simulate the treatment of the same pollution load.

The results, summarized in Table 3, show that the fluxes (J_P) obtained with the PDEHED are lower than that registered using PEI and PAA. Regarding the separation efficiency, measured by R%, this is in the order PDEHED > PAA > PEI. This behavior could be caused by the higher membrane fouling and/or polarization concentration caused by the copolymer.

Inspection of membranes at the end of the experimental runs showed a thin layer on the filtering surface: the cake was cerulean with the color of polymer-copper complexes, and it appeared like an incrustation in the case of PDEHED, whereas for PAA and PEI it was a simpler deposit easily removable.

The polymer PDEHED is useful if the objective of wastewater treatment is to obtain a complete copper removal. In opposition, the polymer PAA with the

Table 2. Some Polymeric Binding Agents

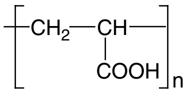
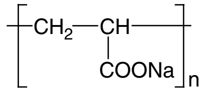
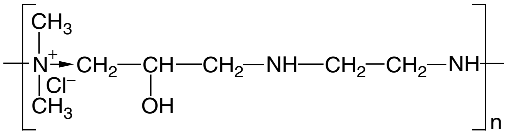
Polymer	General Formula	Average Molecular Weight (kDa)
Polyacrylic acid (PAA)	 $\left[-CH_2-CH(COOH)-\right]_n$	100
Polyethylenimine (PEI)		60
Polyacrylic acid, sodium salt (PAASS)	 $\left[-CH_2-CH(COONa)-\right]_n$	30
Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (PDEHED)	 $\left[-N^{+}(CH_3)_2Cl^{-}\rightarrow CH_2-CH(OH)-CH_2-NH-CH_2-CH_2-NH-\right]_n$	75

Table 3. Results of Ultrafiltration Tests Using: PEI (150 mg/l) and Cu^{++} (50 mg/l) at pH = 6.2; PAA (150 mg/l) and Cu^{++} (50 mg/l) at pH 4.6; PDEHED (50 mg/l) and Cu^{++} (50 mg/l) at pH = 8.5

	Membrane	Iris 10 kDA		Iris 30 kDa		PANGKSS HV3/T		PANGKSS HV2/T		UTC 60 ROPUR	
Polymer	Pressure [bar]	J_p [l/hm^2]	R%	J_p [l/hm^2]	R%	J_p [l/hm^2]	R%	J_p [l/hm^2]	R%	J_p [l/hm^2]	R%
PDEHED	2	93.08	100.0	110.0	99.9	122.7	99.9	131.2	99.9	50.8	100.0
	4	55.0	99.9	67.7	99.9	71.9	99.8	71.9	99.8	50.8	100.0
PEI	2	120.58	99.0	156.5	98.7	241.2	99.1	253.9	99.1	29.6	99.9
	4	173.47	98.9	232.7	98.5	262.3	98.7	262.3	98.6	63.5	99.9
PAA	2	105.78	99.1	156.5	98.3	258.1	99.5	275.0	99.6	25.4	100.0
	4	143.85	99.5	190.4	99.3	220.0	99.5	215.8	99.5	50.8	99.9

membrane PAN GKSS HV2/T can be used when very low metal concentration is not required because of the higher flux (rejection 99.6% and permeate flux 275 l/h·m^2 at 2 bar). Indeed, it is better operating at transmembrane pressure of 2 bar rather than at 4 bar because the little increase of the permeate flux obtained at steady state for PEI and PAA polymers does not justify the higher costs (e.g., electrical energy and cooling).

Data of the optimization parameter J_p/C_p for the transmembrane pressure of 2 bar, for the PEI and PAA polymers, showed that PAN GKSS membranes gave the best combination of the two parameters. Furthermore, a higher J_p/C_p for PAA was registered, meaning more interesting performances in copper removal from waters. The optimization parameter for PDEHED has no practical significance, in this case, because of copper concentration next to the zero.

Membrane Washing and Reuse. The possibility of membrane reuse in the complexation-ultrafiltration process was evaluated by carrying out three UF runs in series by using the polymer PDEHED, which gave the highest fouling. Each run was composed by four steps in sequence:

1. membranes characterization;
2. UF test carried out until reaching steady-state conditions;
3. washing of membranes and system with tap water for 2 hours without recycle (open loop);
4. washing of membranes and system with 20 l of demineralized water without recycle; and
5. return to (1).

Steps 3 and 4 were carried out at maximum cross flow and minimum transmembrane pressure to avoid further cake compaction during membrane washing.

The results showed that, after a flux decrease was observed in the second run, membrane performance remained the same in the third run, which is interesting for a long-time use of the same membrane.

CONCLUSION

The experimental work available in the literature on the PAUF process show that satisfactory results were obtained by applying it in the separation and concentration of metallic cations from wastewaters. This technique combines both the advantages of classical adsorption (i.e., ion exchange and complexation interactions) method for metal removal from aqueous systems and of membrane processes.

The chemical fundamentals of the process have to be preliminarly studied in order to find the optimal chemical conditions of: 1) pH for the metal retention stage (complexation) and for the polymer regeneration stage (decomplexation) and 2) polymer-binding capacity (loading ratio = g metal/g polymer).

These results have to be transferred in the realization of the two stages of metal separation and recovery process: (1) metal retention, where a permeate stream free of heavy metals can be obtained, and (2) polymer regeneration, where the polymer is regenerated in order to be recycled.

Several factors influence the separation of the target substance, such as membrane type, composition of water to treat, pH, binding capacity of the polymer, polymer adsorption on the membrane (fouling), and hydrodynamics.

The complexation-ultrafiltration technique could be competitive in the near future provided a significant knowledge on the main process parameters are realized: (1) design and preparation of polymeric binding agents with the desired properties (good solubility, high selectivity, regeneration possibility, chemical and mechanical stability, low toxicity, high molecular weight with low viscosity, and low cost); (2) proper membrane choice; (3) accurate approach to the fluid dynamics and to the chemistry of the process; (4) appropriate study of polymer regeneration; and (5) appropriate study on membrane washing and reuse.

The complexation-ultrafiltration process is a relatively new separation technique, but the results reported in the literature clearly indicate its potential in wastewater treatment with some reasonable technological improvements.

BIBLIOGRAPHY

1. Asano, T. and Levine, D. (1996). Wastewater reclamation, recycling and reuse: past, present and future. *Wat. Sci. Technol.* **33**: 1–14.

2. Juang, R.S. and Chiou, C.H. (2001). Feasibility of the use of polymer-assisted membrane filtration for brackish water softening. *J. Membr. Sci.* **187**: 119–127.
3. Scott, K. (1995). *Handbook of Industrial Membranes*. Elsevier Advanced Technology, Oxford, UK.
4. Aptel, P. and Vial, D. (1992). In: *Membranes in Water Treatment and Potabilization*. C. Haber and E. Drioli (Eds.). Proc. Membrane Separation Processes, Rio de Janeiro, Brazil, p. 291.
5. Mulder, M. (1996). *Basic Principles of Membrane Technology*, 2nd Edn. Kluwer Academy Publishers, Dordrecht, the Netherlands.
6. Uludag, Y., Ozbelge, H.O., and Yilmaz, L. (1997). Removal of mercury from aqueous solutions via polymer enhanced ultrafiltration. *J. Membr. Sci.* **129**: 93–99.
7. Molinari, R., Argurio, P., and Romeo, L. (2001). Studies on interactions between membranes (RO and NF) and pollutants (SiO_2, $NO_3{}^-$, Mn^{++} and Humic Acid) in water. *Desalination* **138**: 271–281.
8. Oussedik, S. et al. (2000). Enhanced ultrafiltration of bovine serum albumin with pulsed electric field and fluidized activated alumina. *Desalination* **127**: 59–68.
9. Huotari, H.M., Huisman, I.H., and Trägårdh, G. (1999). Electrically enhanced crossflow membrane filtration of oily waste water using the membrane as cathode. *J. Membr. Sci.* **156**: 49–60.
10. Toyomoto, K. and Higuchi, A. (1992). Microfiltration and ultrafiltration, In: *Membrane Science and Technology*. Y. Osada and T. Nakagawa (Eds.). Marcel Dekker, New York, Chap. 8, p. 289.
11. Hwang, S.T. and Kammermeyer, K. (1975). *Membranes in Separations*. Wiley Interscience, New York.
12. Geckler, K.E. and Volchek, K. (1996). Removal of hazardous substances from water using ultrafiltration in conjunction with soluble polymers. *Env. Sci. Technol.* **30**: 725–734.
13. Volchek, K., Krantsel, E., Zhilin, Yu., Shtereva, G., and Dynersky, Yu. (1993). Polymer binding/ultrafiltration as a method for concentration and separation of metals. *J. Membr. Sci.* **79**: 253–272.
14. Rumeau, M., Persin, F., Sciers, V., Persin, M., and Sarrazin, J. (1992). Separation by coupling ultrafiltration and complexation of metallic species with industrial water soluble polymers. Application for removal or concentration of metallic cations. *J. Membr. Sci.* **73**: 313–322.
15. Volchek, K., Keller, L., Velicogna, D., and Whittaker, H. (1993). Selective removal of metal ions from groundwater by polymeric binding and microfiltration. *J. Membr. Sci.* **89**: 247–262.
16. Tabatai, A., Scamehorn, J.F., and Christian, S.D. (1995). Water softening using polyelectrolyte-enhanced ultrafiltration. *Sep. Sci. Technol.* **30**: 211–224.
17. Tabatabai, A., Scamehorn, J.F., and Christian, S.D. (1995). Economic feasibility study of polyelectrolyte-enhanced ultrafiltration (PEUF) for water softening. *J. Membr. Sci.* **100**: 193–207.
18. Canizares, P., Perez, A., Camarillo, R., and Linares, J.J. (2004). A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents. *J. Membr. Sci.* **240**: 197–209.
19. Bodzek, M., Korus, I., and Loska, K. (1999). Application of the hybrid complexation-ultrafiltration process for the removal of metal ions from galvanic wastewater. *Desalination* **121**: 177–121.
20. Juang, R.S. and Shiau, R.C. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *J. Membr. Sci.* **165**: 159–167.
21. Molinari, R., Argurio, P., and Poerio, T. (2004). Comparison of polyethylenimine, polyacrylic acid and poly(dimethylamine–co–epichlorohydrin–co–ethylenediamine) in Cu^{2+} removal from wastewaters by polymer–assisted ultrafiltration. *Desalination* **162**: 217–228.
22. Bisset, W., Jacobs, H., Koshti, N., Stark, P., and Gopalan, A. (2003). Synthesis and metal ion complexation properties of a novel polyethyleneimine N-methylhydroxamic acid water soluble polymer. *Reactive Functional Polymers* **55**: 109–119.
23. Barron-Zambrano, J., Laborie, S., Viers, Ph., Rakib, M., and Durand, G. (2002). Mercury removal from aqueous solution by complexation-ultrafiltration. *Desalination* **144**: 201–206.
24. Thompson, J.A. and Gordon, J. (1999). Using water-soluble polymers to remove dissolved metal ions. *Filtration Sep.*: 28–29.
25. Kruithof, J.C. and Kopper, H.M.M. (1989). Experiences with groundwater treatment and disposal of the eliminated substances in the Netherlands. *Aqua.* **38**: 207–216.
26. Bohdziewicz, J. (2000). Removal of chromium ions (VI) from underground water in the hybrid complexation-ultrafiltration process. *Desalination* **129**: 227–235.
27. Alpatova, A., Verbych, S., Bryk, M., Nigmatullin, R., and Hilal, N. (2004). Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation-ultrafiltration process. *Sep. Purif. Technol.* **40**: 155–162.
28. An, H.K., Park, B.Y., and Kim, D.S. (2001). Crab shell for the removal of heavy metals from aqueous solution. *Water Research* **35**: 3551–3556.
29. Mulligan, C.N., Yong, R.N., and Gibbs, B.F. (2001). Heavy metal removal from sediments by biosurfactants. *J. Hazardous Materials* **85**: 111–125.
30. Molinari, R., Gallo, S., and Argurio, P. (2004). Metal ions removal from wastewater or washing water from contaminated soil by ultrafiltration–complexation. *Water Research* **38**: 593–600.
31. Mulligan, C.N., Yong, R.N., and Gibbs, B.F. (2001). Heavy metal removal from sediments by biosurfactant. *J. Hazardous Materials* **85**: 111–125.
32. Yurlova, L., Kryvoruchko, A., and Kornilovich, B. (2002). Removal of Ni(II) ions from wastewater by micellar enhanced ultrafiltration. *Desalination* **144**: 255–260.
33. Korus, I., Bodzek, M., and Loska, K. (1999). Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation ultrafiltration process. *Sep. Purif. Technol.* **17**: 111–116.
34. Aliane, A., Bounatiro, N., Cherif, A.T., and Akretche, D.E. (2001). Removal of chromium from aqueous solution by complexation-ultrafiltration using a water soluble macroligand. *Water Research* **35**: 2320–2326.
35. Steenkamp, G.C., Keizer, K., Neomagus, H.W.J.P., and Krieg, H.M. (2002). Copper(II) removal from polluted water with alumina/chitosan composite membranes. *J. Membr. Sci.* **197**: 147–156.
36. Petrov, S. and Nenov, V. (2004). Removal and recovery of copper from wastewater by a complexation-ultrafiltration process. *Desalination* **162**: 201–209.

37. Nguyen, Q.T., Aptel, P., and Neel, J. (1980). Application of ultrafiltration to the concentration and separation of solutes of low molecular weight. *J. Membr. Sci.* **6**: 71–82.
38. Renault, M., Aulas, F., and Rumeau, M. (1982). Recovery of chromium from effluents using ultrafiltration. *Chem. Eng. J.* **23**: 137.
39. Bufle, J. and Staub, C. (1984). Measurements of complexation properties of metal ions in natural condition by ultrafiltration: measurement of equilibrium constants for complexation of zinc by synthetic and natural ligands. *Anal. Chem.* **56**: 2837–2842.
40. Juang, R.S. and Chiou, C.H. (2000). Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers. *J. Membr. Sci.* **177**: 207–214.
41. Vieira, M., Tavares, C.R., Bergamasco, R., and Petrus, J.C.C. (2001). Application of ultrafiltration-complexation process for metal removal from pulp and paper industry wastewater. *J. Membr. Sci.* **194**: 273–276.
42. Zakrzewska-Trznadel, G. and Harasimowicz, M. (2002). Removal of radionuclides by membrane permeation combined with complexation. *Desalination* **144**: 207–212.
43. Juang, R.S. and Shiau, R.C. (2000). Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers. *J. Membr. Sci.* **177**: 207–214.
44. Villoslada, I.M. and Rivas, B.L. (2003). Retention of metal ions in ultrafiltration of mixtures of divalent metal ions and water-soluble polymers at constant ionic strength based on Freundlich and Langmuir isotherms. *J. Membr. Sci.* **215**: 195–202.
45. Blocher, C. et al. (2003). Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater. *Water Research* **37**: 4018–4026.
46. Molinari, R., Poerio, T., and Argurio, P. (2004). Ultrafiltration-Complexation for copper-citric acid chelates removal from washing solutions of contaminated soil. *J. Appl. Electrochem.* in press.

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