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# Environmental Engineering

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## 16.1 Introduction

### Environmental Engineering and the Role of Mechanical Engineers

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The subject of environmental science and management is vast and interdisciplinary, ranging from highly technical matters such as the design of emission control equipment to socioeconomic matters such as the valuation of the impacts of pollution. The goal is to prevent or reduce undesirable impacts of human activities on the environment. Within this endeavor there are several different areas where mechanical engineers can make important contributions. One type of contribution concerns the design of equipment, in particular for the control of emissions; an example is an electrostatic precipitator to reduce emissions of particulates from the flue gas of a boiler or furnace. Another type of contribution concerns the modeling of the dispersion of pollutants in the environment. This chapter covers air pollution, surface water pollution, and groundwater pollution. Since space is limited and since mechanical engineers are most likely to be involved in air pollution analysis and abatement projects, the emphasis is on air pollution problems.

## Environmental Burdens and Impacts

*Ari Rabl*

As general guidance to the field of environmental engineering, it may be helpful to present the most important environmental burdens and impacts in the form of a matrix, as in Figure 16.1.1. Burdens, e.g., the emission of a pollutant, are listed in the column on the left; impact categories are listed as a row at the top. Each element in this matrix corresponds to a specific impact of a specific burden. An X indicates that the impact from the corresponding burden is likely to be significant. Particulate air pollution, for instance, has been shown to cause a significant increase in mortality.

As an added feature we have indicated the spatial and temporal extent to the burdens. The classic air pollutants (particulates, $NO_x$, and $SO_x$) are dispersed over distances on the order of a thousand kilometers, and they affect essentially only the present generation; thus, the second and third columns show the letters R (for regional) and P (for present generation). Global warming from greenhouse gases, on the other hand, affects the entire globe and will persist over decades or centuries, hence the letters G (for global) and P, F (for present and future generations).

The classification in Figure 16.1.1 is not without ambiguities or problems. For example, we have indicated the impact of greenhouse gases as “climate change” only, even though this category includes such effects as deaths from flooding. The relative importance of impacts may change with improved scientific understanding and with the evolution of societal preferences. One should also note that the assignment of effects to causes is in many cases quite uncertain; for instance, the observed mortality from air pollution could be due to particulates or due to $SO_2$.

Some impacts, especially thermal pollution and noise, can be highly site dependent. The cooling water from a power plant, for instance, could damage the ecosystem of a river or it could be used to improve the output of a fishery.

Each of the categories in Figure 16.1.1 could be broken down into subcategories:

- Health
    - Mortality
    - Injury
    - Cancer
    - Respiratory illness
- Natural environment
    - Recreational value of land (including forests)
    - Recreational value of water (including fishing)
    - Biodiversity
- Agricultural environment
    - Crops
    - Cattle (milk, meat, fur, …)
    - Wood production by forests
    - Commercial fishing
- Man-made environment
    - Functional buildings
    - Historical buildings
    - Other objects (bridges, cars, …)
    - Noise

| | **Impacts** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Extent** | | | | **Environment** | | |
| **Burdens** | **Space** | **Time** | **Climate** | **Health** | **Natural** | **Agricultural** | **Man-Made** |
| **Primary air-pollutants** | | | | | | | |
| $CO_2$ | G | P, F | X | | | | |
| $CH_4$ | G | P, F | X | | | | |
| Other greenhouse gases | G | P, F | X | | | | |
| Particulates | R | P | | X | | | X |
| $SO_2$ | R | P | | X | X | X | X |
| $NO_x$ | R | P | | X | X | X | X |
| CO | R | P | | X | | | |
| Heavy metals (Pb, Hg, Cd, …) | R | P, F | | X | X | | |
| Toxic organic compounds (e.g., dioxins) | R | P, F | | X | X | | |
| VOC (volatile organic compounds, etc.) | R | P | | X | | | |
| **Secondary air pollutants** | | | | | | | |
| $O_3$ (from NO + VOC) | R | P | X | X | X | | |
| Acid rain (from $NO_x$, $SO_x$) | R | P | | X | X | X | X |
| Aerosols (from $NO_x$, $SO_x$, etc.) | R | P | X | X | X | X | X |
| **Liquid residues** | | | | | | | |
| Heavy metals (Pb, Hg, Cd, …) | L, R | P, F | | X | X | | |
| Toxic organic compounds (e.g., dioxins) | L, R | P, F | | X | X | | |
| COD (chemical oxygen demand) | L, R | P, F | | X | X | X | |
| BOD (biological oxygen demand) | L, R | P, F | | X | X | X | |
| **Solid residues** | L | P, F | | X | X | X | |
| **Other** | | | | | | | |
| Thermal | L | P | | | X | | |
| Noise, odor | L | P | | | | | |

**Impacts:** X = potentially important; blank = usually not important. **Extent:** L = local (up to tens of kilometers); P = present generation; R = regional (hundreds to thousands of kilometers); G = global; F = future generations.

**FIGURE 16.1.1** Overview of environmental burdens and major impact categories, with approximate indication of typical geographic extent and typical importance of impact.

# 16.2 Benchmarks and Reference Conditions

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## Natural Environment

### Air Basins

Unpolluted air is an idealization, but its composition has been defined as indicated in Table 16.2.1. Unfortunately, measurements of truly unpolluted air were not and can never be made because measurement techniques and even the interest in measurements did not exist when air was unpolluted. Now even the most remote sites have mildly polluted air.

**TABLE 16.2.1 Gaseous Composition of Unpolluted Air (dry basis)**

| | ppm (vol) | μg/m³ |
|---|---|---|
| Nitrogen | 780,000 | $8.95 \times 10^8$ |
| Oxygen | 209,400 | $2.74 \times 10^8$ |
| Water | — | — |
| Argon | 9,300 | $1.52 \times 10^7$ |
| Carbon dioxide | 315 | $5.67 \times 10^5$ |
| Neon | 18 | $1.49 \times 10^4$ |
| Helium | 5.2 | $8.50 \times 10^2$ |
| Methane | 1.0–1.2 | $6.56–7.87 \times 10^2$ |
| Krypton | 1.0 | $3.43 \times 10^3$ |
| Nitrous oxide | 0.5 | $9.00 \times 10^2$ |
| Hydrogen | 0.5 | $4.13 \times 10^1$ |
| Xenon | 0.08 | $4.29 \times 10^2$ |
| Organic vapors | ~0.02 | — |

Although measurements of the undisturbed atmosphere were not made, we can gain some insight into trends of air pollutant burden growth by examining emissions over the last century. Figure 16.2.1 shows the growth of emissions of the classical air pollutant species since 1900. The latter two panels of the figure show that emissions from regulated sectors in the United States have abated in the past 20 years. Those regulations are described later. Note that Table 16.2.1 uses two sets of units for gaseous pollutants, one volumetric, the other mass based. To convert from one to the other the ideal gas law is used with the result (at 1 atm and 25°C):

$$1 \text{ ppm} = \text{MW} * 40.9 \ \mu\text{g/m}^3$$

where MW is the molecular weight.

### Surface Water Basins

Human activity has also dramatically altered the distribution, quantity, and quality of Earth's water, especially since the industrial revolution. Accurate measurement of many water impurities, particularly trace impurities, has only become possible in the latter part of the 20th century. Given the quantities and wide distribution of human-generated wastes delivered directly or indirectly (via atmospheric deposition or surface runoff and erosion) to water bodies, recent water quality surveys might not be representative of truly "natural" conditions. As an example, a "pristine," undeveloped alpine lake may show traces of plutonium that are residuals of 1950s through 1960s atmospheric testing of nuclear weapons. Lead from automobile emissions can be detected in the bottom sediments of the Atlantic Ocean, more than 1500 km from the nearest landmass. A tabulation of the averages and ranges of concentrations of many naturally occurring substances detected in minimally impacted waters can serve

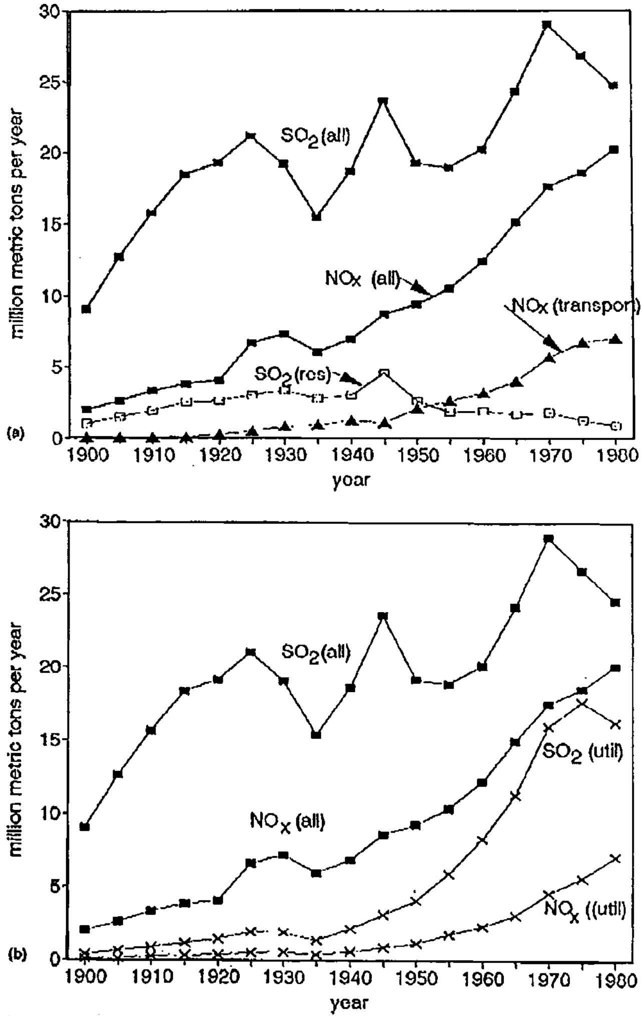

**FIGURE 16.2.1** Trends in U.S. national emmissions of air pollutants. (a) $SO_2$ and $NO_X$ ,1900–1980, all sources, residential $SO_2$ and transportation $NO_X$. (b) $SO_2$ and $NO_X$, 1900–1980, all sources and electric utility sources. (c) $SO_2$ and $NO_X$, 1970–1990, all sources, transportation and electric utility sources. (d) $SO_2$ and $NO_X$, and particulates, 1970–1990. (Data from EPA annual reports; Gschwandtner et al., 1985.)

as a benchmark, admittedly imperfect, against which to compare "polluted" waters, water quality criteria, and regulatory standards.

*Choice of Reference Conditions.* The authors propose as reference conditions, the concentrations of measured impurities in the oceans, "average" rainwaters, and "average" river waters. This choice of reference waters was based on two distinct criteria:

1. Either the volume of water was so large (such as the open oceans) that human activity has had little detectable effect on average water quality conditions, or
2. The waste input is small and the water body is rapidly and continuously renewed by unpolluted sources (such as a tributary to a major river).

The major and minor constituents of water and their quantities are easily presented in tables. The use of the word "major" indicates materials present or required in large quantities. Table 16.2.2 summarizes data on the constituents of selected natural waters. Note that the concentration data for major constituents

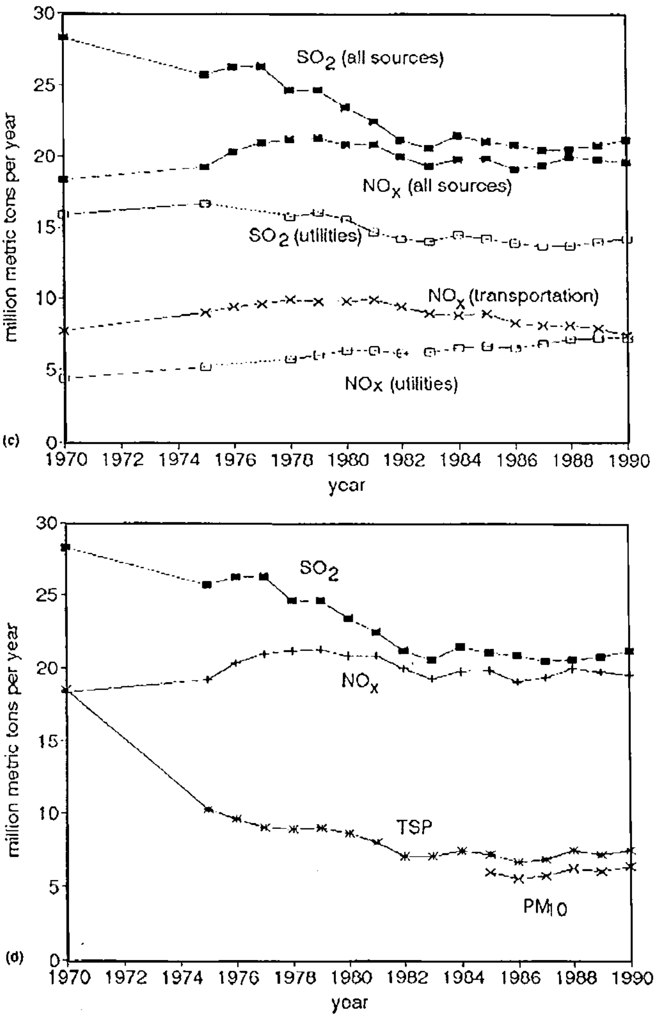

**FIGURE 16.2.1** continued

(Table 16.2.2) is given in milligrams per liter and the concentration data for the minor constituents (Table 16.2.3) is given in micrograms per liter. Inclusion of boron and fluoride as major constituents is somewhat arbitrary and was based on their occurrence at greater than 1 mg/L in seawater. In these tables, individual entries are *average values* reported by U.S. regional or national surveys. *Ranges* are derived from the majority of the data from similar surveys, excluding data obtained from waters apparently contaminated by pollution. Some surveys presented results by stating that “very few” samples exceeded certain concentration values or simply reported measurements as “less than” due to analytical detection limits. These results are preceded by the symbol < in the tables. Although the data given are believed to be representative of water found in natural settings, it should be appreciated that, especially for industrially important trace constituents, the upper limits of the concentration ranges may include some small level of **anthropogenic** inputs.

There are additional categories of natural and contaminant components of water. There are complex, difficult to characterize, organic humic materials in natural water bodies that represent the end point of decay of formerly living organic matter. There are synthetic chemicals by the thousands, produced currently and in the past, by the chemical industry. Some of these compounds and polymers are completely new to the natural environment. Many are considered toxic to aquatic organisms and/or

**TABLE 16.2.2 Major Constituents and Characteristics of Natural Waters (constituent concentrations in mg/L, unless otherwise noted)**

| Constituent | Oceans | Rivers | Rain |
|---|---|---|---|
| $Cl^-$ | 19,000 | 5.8, 7.8 | 0.2–0.6 |
| $Na^+$ | 10,500 | 5.3, 6.3 | 0.2–0.6 |
| $SO_4^{2-}$ | 2,700 | 8.3, 11 | 1.1, 2.2 |
| $Mg^{++}$ | 1,350 | 3.4, 4.1 | 0.3–1.5 |
| $Ca^{++}$ | 410 | 13.4, 15 | 0.05–1.5 |
| $K^+$ | 390 | 1.3, 2.3 | 0.07–0.11 |
| $HCO_3^-$ | 142 | 52, 58 | 1–10 |
| $Br^-$ | 0.67 | <20 | <0.15 |
| $Sr^{++}$ | 8 | 0.06–0.11 | — |
| $SiO_2$ | 6.4 | 10.4, 13 | 0.1 |
| $B^{3-}$ | 4.5 | 0.3 | — |
| $F^-$ | 1.3 | <1 | — |
| pH (units) | 8.2 | 6, 7.2, 7.5 | 5.7 |
| Hardness (total) | — | 10–200 | — |
| Ammonia, as N | — | 0.05–0.5 | — |
| Nitrate, as N | — | 0.1–2.0 | — |
| BOD | — | 2–4 | — |

*Note:* BOD is biochemical oxygen demand, mg/L oxygen; nitrate is $NO_3^-$, ammonia is $NH_3$.

**TABLE 16.2.3 Minor Constituents of Natural Waters (constituent concentrations in µg/L)**

| Constituent | Oceans | Rivers | Rain |
|---|---|---|---|
| N | 670 | 0–1000 | 0–620 |
| C (organic) | 100 | 3, 6, 19 | — |
| P | 90 | 10–30 | — |
| Ba | 20 | 43, 45 | — |
| Zn | 10 | 5–45, 10, 20 | 3.6 |
| Ni | 7 | 0.3, 10 | — |
| As | 3 | 0.15–0.45 | 0.45 |
| Cu | 3 | 10 | 2.5 |
| Fe | 3 | 10 | — |
| Mn | 2 | — | — |
| Sb | 0.3 | 0.54 | — |
| Ag | 0.3 | 0.3 | 0.001–0.1 |
| Hg | 0.2 | <0.3 | 0.2 |
| Cd | 0.11 | 1, <10 | — |
| Se | 0.09 | 0.1, 0.2 | — |
| Cr | 0.05 | 0.43, 1.4, 5.8, <10 | 0.1–.02 |
| Pb | 0.03 | <1 | <1 |

humans. For lists of contaminants considered toxic and their effluent limitations, there are many documents available from the U.S. Environmental Protection Agency (USEPA) and other sources.

## Soils and Water Basin Definitions

The unconsolidated sediment that covers a comparatively thin mantle of the land surface in general is referred to as soil. Soils are complex mixtures of solid, liquid, and gases. The solid phase consists of a mineral inorganic fraction that is produced by weathering of rocks or transported material. The predominant inorganic elements are silicon, aluminum, and iron. The organic fraction consists of partially or fully decomposed products of flora and fauna. The liquid phase is the water that occupies the pore spaces between and within grains of the solid material. In its natural form this water, which is referred to as soil water, contains dissolved substances introduced from the solids or transported from the ground surface. The pore spaces that are not occupied by water will be filled by water vapor, gases, and air. The complexity of soil systems derives from the fact that the mixture of the solid, liquid, and gases is very heterogeneous and that the composition of the individual phases and the mixture changes in space and with time.

The soils in their natural environment can be subjected to drastic changes not only as a result of the interaction among the solid, liquid, and gas phases but also by external factors that are controlled by pressure, temperature, and light. The physical and chemical characteristics of the changing solid phase have a significant influence on the thermal behavior, water retention and flow, adsorption and entrapment of chemicals and wastes, and transport of dissolved substances. All of the above processes are of importance in the study, understanding, and solution of problems in environmental sciences and engineering associated with soil contamination.

The physical characteristics of soils as a porous medium are affected by the shape, size and size distribution, and the arrangement of the solid phase or the soil grains. The *shapes* and *sizes* of the soil grains vary widely from small colloids to large sand and gravel. Particles that are less than the arbitrary size of 2 μm are the clay fraction that is formed as a secondary product of weathering of rocks or derived from the transported deposits. These particles are platelike or disk shaped. The non-clay fraction formed from inert minerals and fragments of rock consists of silt, sand, and gravel. In a particle size classification used by agricultural scientists that was developed by the U.S. Department of Agriculture (USDA), non-clay particles that are in the size range 2 to 50 μm are classified as silts, in the range 50 to 2000 μm as sands, and above 2000 μm as gravel. In this classification system the sands are further divided into subgroups of very fine, fine, medium, coarse, and very coarse sands. A second system, by the International Society of Soil Science (ISSS) that is also used by agricultural scientists, classifies silts to be in the range 2 to 20 μm, fine sands 20 to 200 μm, and coarse sands 200 to 2000 μm. The American Society of Testing and Materials (ASTM) classifies colloids as particles that are less than 0.1 μm in size.

The surface area of the solid particles contained in a known volume of the soil has a significant influence on the physical and chemical processes that occur on the surfaces of the soil grains. The ratio of the internal solid surface area to the total volume is referred to as the *specific surface*. This parameter is also sometimes expressed as the ratio of the surface area to the mass of the soil grains. This parameter of the soil is affected by the size and shape of the individual soil grains. Because of the platelike or disk-shaped nature of small clay particles, clays in general have very large specific surface compared with the non-clay particles (silts, sand, and gravel). For example, the three common clay minerals kaolinite, illite, and montmorillonite have specific surface of 45, 175, and 800 $m^2$/gm, respectively (Corey, 1994). Because of these enormously large surface areas, the clay fraction in soils has a significant influence on the chemical reactive processes that are controlled by the surface area of the soil grains. The silt and sand fraction will not have a significant influence on the chemical processes, and also the smaller surface areas result in small water retention capacities as compared with clay.

The spaces between the grains that are referred to as intergranular pore spaces control the flow behavior and capacity to hold water by a soil. A physical parameter that is known as the *average porosity* or *porosity* characterizes the secondary pore space enclosed between the aggregates. The porosity of a soil sample is defined as the ratio of the volume of interconnected pores to the total volume of the sample. Soil porosity depends on many factors that include its structure, shape of soil grains, size distribution of the grains, the degree of mixing of the various-sized particles, and the way the soil grains are packed. Under conditions of normal packing the porosities of unconsolidated sand vary in the range 0.39 to 0.41 and soil with structure in the range 0.45 to 0.55. The organic matter in soil binds the inorganic fraction to form larger aggregates. The primary pore spaces within the soil aggregate play a significant role in retardation and attenuation of dissolved chemicals that are contained in the aqueous phase.

The subsurface soil–water environment that exists below the ground surface is divided into two zones, namely, the *unsaturated* or *vadose zone* and the *saturated zone*. In the unsaturated zone pore spaces contain both water and air. The capillary forces created by the surface tension in the water–air interfaces produce water pressures that are less than atmospheric (suction). The water flowing through the unsaturated zone is subjected to capillary driving forces in addition to the gravitational forces. In the saturated zone, the water pores are fully saturated with water and the water pressures are greater than atmospheric. The water in the saturated zone is driven by gravitational forces. The surface that separates the unsaturated and saturated zones is referred to as the *water table*. By definition, the water pressure at the water table is atmospheric. The location of the water table below the ground surface at waste and spill sites becomes critical in determination of the fate and transport of pollutants in the subsurface soil–water environment as described later. Figure 16.2.2 shows the essentials of the situation schematically.

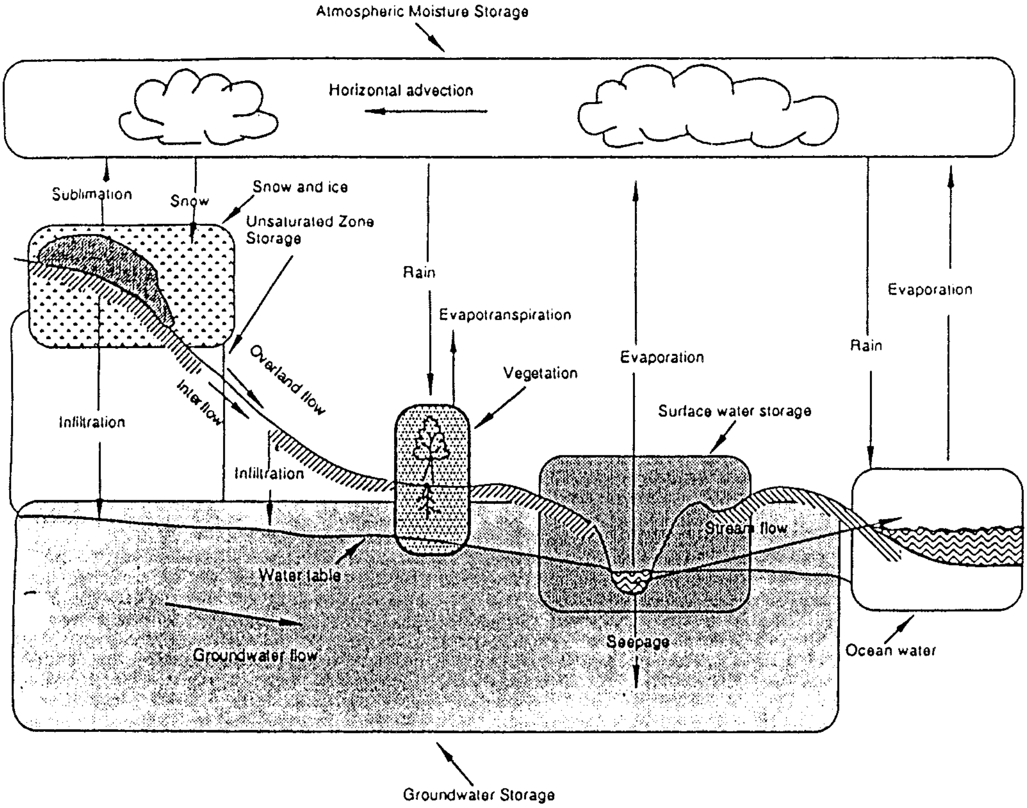

**FIGURE 16.2.2** A column of Lagrangian boxes simulating atmospheric dynamics.

## Acceptable Levels of Pollutants

### Water

*Criteria vs. Standards.* The *objective* of water quality control programs, for example, is to protect current or potential *beneficial uses* of water. Criteria define the specific characteristics necessary to protect such uses. Criteria are not absolute, but are based on a combination of experience, current scientific knowledge, and the judgment of experts. Toxicological data for many of the water components often are limited. There may be results of tests for acute, or immediate, impact to organisms (including humans), but little information on impact on reproduction, long-term health or tolerance at low concentrations, organism adaptability, acclimatization, or interaction with other substances. General criteria are intended to protect sensitive species subjected to long-term exposure and may be overly conservative in specific situations. The aquatic life column of Table 16.2.4 presents typical, continuous, maximum concentration criteria for freshwaters intended to support a variety of aquatic life. Surface water quality criteria and their

**TABLE 16.2.4 Water Quality Criteria and Standards (inorganic contaminants in μg/L)**

| | Beneficial Use or Protection Category | | |
|---|---|---|---|
| **Constituent** | **Aquatic Life** | **Irrigation** | **Drinking Water** |
| B | — | 750, 500–3,000 | — |
| F | — | 1,000 | 4,000[a] |
| Ammonia-N | 20[b] | — | — |
| Nitrite-N | — | — | 1,000 |
| Nitrate-N | — | 5,000–30,000 | 10,000 |
| Ba | — | — | 2,000 |
| Zn | 110 | 2,000 | 5,000[c] |
| Ni | 160 | 200 | — |
| As | 190 | 100 | 50 |
| Cu | 12 | 200, 100–1,000 | 1,300[c] |
| Fe | 1,000 | 5,000 | 300[c] |
| Mn | — | 200 | 50[c] |
| Sb | — | — | 6 |
| Ag | 3[d] | — | — |
| Hg | 0.012, 0.05[e] | — | 2 |
| Cd | 1.1 | 10 | 5 |
| Se | 5 | 20 | 50 |
| Cr | 11 | 100 | 100 |
| Pb | 3.2 | — | 15 |
| pH, units | No vertebrates below 4–4.5 | — | 6.5–8.5 |

[a] Considered beneficial in drinking water at somewhat lower concentrations.

[b] Temperature and pH dependent, only unionized form ($NH_3$) is toxic to aquatic life.

[c] Secondary standards based on use impacts (tastes, staining), not health related.

[d] Controversial, based on toxicity of $Ag^+$, rarely present in natural waters.

[e] Extremely low levels partly due to food chain bioaccumulation potential.

relationship to permitted discharges are further discussed later in this chapter. The irrigation criteria given in Table 16.2.4 are intended to protect the yields of agricultural crops.

Due to resource limitations (time, money, data, or a shortage of knowledgeable experts), conservative criteria are often adopted as *standards*. Standards development should, however, include considerations of actual local needs and conditions, economics, technical feasibility, and the defined objectives of environmental policy. In contrast to criteria, standards are usually incorporated into laws and regulations and are often absolute. Either standards are violated or they are not.

Summarized as simple, USEPA (1979) definitions follow:

1. *Water Quality Criterion:* That concentration of a water quality measure that will meet a specific water use.
2. *Water Quality Standard:* The translation of a water quality criterion into a legally enforceable mass discharge of effluent limitation.

The drinking water column of Table 16.2.4 presents a subset of the current U.S. National Standards for drinking water supplied to the public. The health-based standards are enforceable. It should be noted that the drinking water standards list in Table 16.2.2 is not comprehensive. Maximum concentration levels (MCLs) for some inorganics, microbial contaminants, and the many regulated toxic organics have been omitted. Many drinking water MCLs are controversial because they rely on dose–response models which cannot be directly verified at the low levels of exposure that are typical.

## Air

Tables 16.2.5 to 16.2.9 summarize the current U.S. ambient air quality standards for carbon monoxide, sulfur dioxide, nitrogen dioxide, ozone, and particulate matter. These criteria represent myriad effects depending on the receptor, species of pollutant, and duration and severity of impact. These criteria are

**TABLE 16.2.5 U.S. Ambient Air Quality Criteria for Carbon Monoxide**

| CoHb in Blood, % | Associated Human Symptoms |
|---|---|
| 80 | Death |
| 60 | Loss of consciousness; death if exposure is continued |
| 40 | Collapse on exercise; confusion |
| 30 | Headache, fatigue; judgment disturbed |
| 20 | Cardiovascular damage; electrocardiographic abnormalities |
| 5 | Decline (linear with increasing CoHb level) in maximal oxygen uptake of healthy young men undergoing strenuous exercise; decrements in visual perception, manual dexterity, and performance of complex sensorimotor tasks |
| 4 | Decrements in vigilance (i.e., ability to detect small changes in one's environment that occur at unpredictable times); decreased exercise performance in both healthy persons and those with chronic obstructive pulmonary disease |
| 3–6 | Aggravation of cardiovascular disease (i.e., decreased exercise capacity in patients with angina pectoris, intermittent claudication, or peripheral arteriosclerosis) |

CoHb = carboxy hemoglobin.

*Source:* Henderson, Y. and Haggard, H.W., *Noxious Gases,* Chemical Catalog Co., New York, 1927; and USEPA, Air Quality Criteria for Carbon Monoxide, EPA/600/8-90/045F, Research Triangle Park, NC, December 1991.

**TABLE 16.2.6 U.S. Ambient Air Quality Criteria for Sulfur Dioxide**

| Concentration of $SO_2$ in Air (ppm) | Exposure Time | Human Symptoms and Effects on Vegetation |
|---|---|---|
| 400 | — | Lung edema; bronchial inflammation |
| 20 | — | Eye irritation; coughing in healthy adults |
| 15 | 1 hr | Decreased mucociliary activity |
| 10 | 10 min | Bronchospasm |
| 10 | 2 hr | Visible foliar injury to vegetation in arid regions |
| 8 | — | Throat irritation in healthy adults |
| 5 | 10 min | Increased airway resistance in healthy adults at rest |
| 1 | 10 min | Increased airway resistance in people with asthma at rest and in healthy adults at exercise |
| 1 | 5 min | Visible injury to sensitive vegetation in humid regions |
| 0.5 | 10 min | Increased airway resistance in people with asthma at exercise |
| 0.5 | — | Odor threshold |
| 0.5 | 1 hr | Visible injury to sensitive vegetation in humid regions |
| 0.5 | 3 hr | U.S. National Secondary Ambient Air Quality Standard promulgated in 1973 |
| 0.2 | 3 hr | Visible injury to sensitive vegetation in humid regions |
| 0.19 | 24 hr[a] | Aggravation of chronic respiratory disease in adults |
| 0.14 | 24 hr | U.S. National Primary Ambient Air Quality Standard promulgated in 1971[b] |
| 0.07 | Annual[a] | Aggravation of chronic respiratory disease in children |
| 0.03 | Annual | U.S. National Primary Ambient Air Quality Standard promulgated in 1971[b] |

[a] In the presence of high concentrations of particulate matter.

[b] *Sources:* Air Quality Criteria for Particulate Matter and Sulfur Oxides, final draft, USEPA, Research Triangle Park, NC, December 1981; Review of the National Ambient Air Quality Standards for Sulfur Oxides: Assessment of Scientific and Technical Information, Draft OAQPS Staff Paper, USEPA, Research Triangle Park, NC, April 1982.

descriptive and are used for emission and air quality standards that are summarized briefly. As better data become available, these tables may change.

**TABLE 16.2.7 U.S. Air Quality Criteria for Nitrogen Dioxide**

| Concentration of $NO_2$ in Air (ppm) | Exposure Time | Human Symptoms and Effects on Vegetation, Maerials, and Visibility |
|---|---|---|
| 300 | — | Rapid death |
| 150 | — | Death after 2 or 3 weeks by bronchiolitis fibrosa obliterans |
| 50 | — | Reversible, nonfatal bronchiolitis |
| 10 | — | Impairment of ability to detect odor of $NO_2$ |
| 5 | 15 min | Impairment of normal transport of gases between the blood and lungs in healthy adults |
| 2.5 | 2 hr | Increased airway resistance in healthy adults |
| 2 | 4 hr | Foliar injury to vegetation |
| 1.0 | 15 min | Increased airway resistance in individuals with bronchitis |
| 1.0 | 48 hr | Slight leaf spotting of pinto bean, endive, and cotton |
| 0.3 | — | Brownish color of target 1 km distant |
| 0.25 | Growing season | Decrease of growth and yield of tomatoes and oranges |
| 0.2 | 8 hr | Yellowing of white fabrics |
| 0.12 | — | Odor perception threshold of $NO_2$ |
| 0.1 | 12 weeks | Fading of dyes on nylon |
| 0.1 | 20 weeks | Reduction in growth of Kentucky bluegrass |
| 0.05 | 12 weeks | Fading of dyes on cotton and rayon |
| 0.03 | — | Brownish color of target 10 km distant |
| 0.003 | — | Brownish color of target 100 km distant |

**TABLE 16.2.8 U.S. Ambient Air Quality Criteria for Ozone**

| Concentration of $O_3$ in Air (ppm)[a] | Human Symptoms and Vegetation Injury Threshold |
|---|---|
| 10.0 | Severe pulmonary edema; possible acute bronchiolitis; decreased blood pressure; rapid weak pulse |
| 1.0 | Coughing; extreme fatigue; lack of coordination; increased airway resistance; decreased forced expiratory volume |
| 0.5 | Chest constriction; impaired carbon monoxide diffusion capacity; decrease in lung function without exercise |
| 0.3 | Headache; chest discomfort sufficient to prevent completion of exercise; decrease in lung function in exercising subjects |
| 0.25 | Increase in incidence and severity of asthma attacks; moderate eye irritation |
| 0.15 | For sensitive individuals, reduction in pulmonary lung function; chest discomfort; irritation of the respiratory tract, coughing, and wheezing. Threshold for injury to vegetation |
| 0.12 | U.S. National Primary and Secondary Ambient Air Quality Standard, attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is equal to or less than 1, as determined in a specified manner |

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**TABLE 16.2.9 U.S. Ambient Air Quality Criteria for Particulate Matter**

| **Concentration of Particulate Matter in Air ($\mu$g m$^{-3}$)** | | | | |
|---|---|---|---|---|
| **TSP < 25 $\mu$m** | **TP < 10 $\mu$m** | **FP < 2.5 $\mu$m** | **Exposure Time** | **Human Symptoms and Effects on Visibility** |
| 2000 | — | — | 2 hr | Personal discomfort |
| 1000 | — | — | 10 min | Direct respiratory mechanical changes |
| — | 350 | — | | Aggravation of bronchitis |
| | 150 | — | 24 hr | U.S. Primary National Ambient Air Quality Standard as of September 1987 |
| 180 | 90 | — | | Increased respiratory disease symptoms |
| | 150 | — | 24 hr | U.S. Primary National Ambient Air Quality Standard as of September 1987 |
| 110 | 55 | — | 24 hr | Increased respiratory disease risk |
| | 50 | — | Annual geometric mean | U.S. Primary National Air Quality Standard as of September 1987 |
| | 50 | — | Annual geometric mean | U.S. Secondary National Ambient Air Quality Standard as of September 1987 |
| — | — | 22 | 13 weeks | Usual summer visibility in eastern U.S., nonurban sites |

TSP = total suspended particulates; TP = thoracic particulates; FP = fine particulates.

# 16.3 Sources of Pollution and Regulations

## Sources

*Jan F. Kreider, Nevis Cook, Tissa Illangasekare, and*
*Ronald R. Hewitt Cohen*

### Air

Air pollutants are found in the form of gases (e.g., $SO_2$) and particulate matter (e.g., fine dust). They are emitted into the atmosphere from natural sources (e.g., volcanoes) and *anthropogenic* sources (e.g., industrial activities). These pollutants are called "primary" because they are directly emitted from local sources. Primary pollutants may undergo chemical reactions that result in the subsequent formation of other species called "secondary" pollutants (e.g., $O_3$).

Air pollution is found at all spatial scales, ranging from a few meters (e.g., indoor pollution) to local, urban, regional, and global scales (Milford and Russell, 1993). *Indoor pollution* is of great concern because a large fraction of our time is spent indoors. Indoor sources of pollutants include combustion processes, aging materials (e.g., formaldehyde emitted from particleboard and plywood), and radon — a natural indoor pollutant which migrates through the soil and may penetrate and accumulate inside buildings. The *local scale* ranges from 100 m to a few kilometers. At this scale, pollution dynamics are dominated by atmospheric diffusion and the role of primary pollutants. The local scale is the one where we experience major exposure to toxic substances and flammable compounds during catastrophic and emergency releases.

The *urban scale* ranges from 10 to 100 km and is characterized by both primary and secondary pollutants. In fact, characteristic residence times are on the order of 1 or a few days, thus, allowing enough time for chemical transformation to play a role. Two types of urban smog are well known: the "London" smog and the "Los Angeles" smog. The former is characterized by stagnant, foggy meteorological conditions in winter which allow a buildup, over a few days, of $SO_2$ and particulate matter. The latter, which has become the most common type of atmospheric pollution throughout the cities of the world, is a **photochemical** smog associated with clear, sunny days. Photochemical smog is a mixture of many gaseous compounds and particulate matter, among which the two most important constituents are ozone (a colorless secondary pollutant) and fine secondary particulate matter (such as sulfates, nitrates, and organic particles), which is responsible for most of the visual haze.

The *regional scale* ranges from hundreds to thousands of kilometers (the upper regional scale is also called *continental scale*). Characteristic residence times are on the order of 1 week. At this scale, pollution dynamics are dominated by chemical transformation and ground deposition phenomena. Acidic deposition, often referred to as *acid rain,* is a phenomenon in which acid substances, such as sulfuric and nitric acid, are brought to Earth by dry and wet deposition. Some lakes are very sensitive to acidic deposition because of their limited buffering capacity. *Global air pollution* is characterized by relatively unreactive compounds, such as $CO_2$, methane ($CH_4$), and chlorofluorocarbons (CFCs). The long lifetime of these pollutants allows their global dispersion and accumulation.

Air pollution at any scale creates several adverse effects. Air pollution can just be a nuisance (e.g., odors) or be aesthetically offensive (e.g., visibility impairment). Some adverse effects, however, are of fundamental importance to the welfare of the population and public health. For example, many pollutants cause respiratory effects; some pollutants have mutagenic effects; others have shown carcinogenic effects; some pollutants also have synergistic effects (e.g., the damage of $SO_2$ to the human respiratory system can be greatly enhanced by the presence of fine particles).

In the rest of this chapter, an overview is presented of analytical and numerical techniques for simulating air pollution phenomena. Air quality modeling is an essential tool for most air pollution studies today. Models can be divided into **deterministic** models, based on fundamental mathematical descriptions of atmospheric processes, and statistical models, based upon semiempirical relationships extracted from data and measurements. Deterministic models, in particular, have become a major tool in providing objective assessment of air pollution scenarios and evaluating the effectiveness of different air pollution control measures. In fact, only deterministic models provide an unambiguous assessment of the fraction of responsibility of each pollution source in each receptor area, thus, allowing the definition and implementation of the most cost-effective cleanup strategy. Statistical models, instead, are useful in situations where deterministic models do not perform well, e.g., for real-time forecasting of air pollution episodes.

### Waterborne

Table 16.3.1 summarizes important sources of surface water pollution species by economic or technical sectors of the U.S. economy. An X indicates a key source and no entry indicates a second-order effect at most. Table 16.3.2 lists groundwater pollution sources by cause, extent and waste type.

### Soil and Groundwater

Various waste products and chemicals are generated from industrial, agricultural, commercial, and domestics activities. Unmonitored and uncontrolled long-term application on the land, accidental spillage, and improper storage and disposal result in these chemicals and wastes acting as potential sources of soil and groundwater contamination. La Grega et al. (1994) use an engineering classification system in which hazardous wastes are grouped under six categories, namely, inorganic aqueous waste, organic aqueous waste, organic liquids, oils, inorganic sludges/solids, and organic sludges/solids. In addition to these, pathogens and nuclear wastes act as sources of contamination. As most of these materials are fully or partially soluble in water, they ultimately will contaminate the water phase contained within the soil pores and the water passing through the soil both in the unsaturated and saturated zones of the subsurface. Figure 16.3.1 shows in schematic form how groundwater pollution occurs.

Inorganic aqueous wastes generated from manufacturing activities involving galvanizing, metal finishing, electroplating, etc. mostly contain acids, alkalis, or concentrated solutions of inorganic wastes such as heavy metals. Organic aqueous wastes are liquids that primarily contain mixtures of dilute concentrations of organic substances such as pesticides. Organic liquid wastes are complex mixtures or concentrated solutions of **organic compounds**. A common example of organic liquid wastes is halogenated solvents that are used in metal degreasing. Most of the oily wastes are derived from petroleum. Oils are used as fuels, lubricating oils in engines, and cutting oils in manufacturing. Inorganic sludges/solids wastes are produced from wastewater treatment, smelters, coking, and metal fabrication. Tars and sludges that are produced from manufacturing activities are some of the examples of wastes that are in the form of organic sludges.

Waste materials and chemicals are released to the soil and groundwater from various sources. The most common sources are leaking underground chemical storage tanks, septic tanks, municipal landfills, industrial landfills, surface impoundments, and abandoned hazardous waste sites. In addition, injection wells, regulated hazardous waste sites, land application, road salting, saltwater intrusion, and oil and gas brine pits contribute to soil and groundwater contamination.

The most frequent use of underground tanks is for storage of gasoline in service stations. Hazardous wastes and chemicals and oils are also stored in buried tanks at industrial sites, farms, and homes. The potential for leakage exists when these tanks corrode internally or externally. In addition, chemicals can leak from pipe joints or holes in the pipes that are connected to the tanks.

Older landfills that were not properly designed for containment of liquids or leachates were used to dispose of garbage, sludges from wastewater treatment plants, construction wastes and debris, incinerator ash, waste from foundries, and many other industrial and domestic hazardous and nonhazardous waste products. The chemicals in the landfill become a source of contamination when rain or surface water infiltrating through the landfill produces leachate. These leachates containing the dissolved constituents of the waste, eventually contaminate the underlying soil and groundwater. Modern well-designed landfills have synthetic liners and leachate-collection systems.

Surface impoundments in the form of open pits, lagoons, or ponds are designed to accept liquid wastes or mixed solids and liquids. The chemical wastes in these temporary storage sites are treated and

**TABLE 16.3.1 Sources of Water Pollution vs. Contaminant Emission Categories**

| | General Emissions Type or Category | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Pollution Source** | **BOD** | **Pathogens** | **TSS** | **Turbidity** | **TDS** | **Nutrients N, P** | **Synthetic Organics** | **Volatile Organics** | **Metals** | **pH** |
| Sewage | X | X | X | — | — | X | — | — | — | — |
| Mining operation | — | — | X | X | X | — | — | — | X | X |
| Timber operation | — | — | X | X | — | — | — | — | — | — |
| Agriculture | — | X | — | X | X | — | — | — | — | — |
| Food processing | X | — | X | — | X | — | — | — | — | X |
| Chemical manufacturing | X | — | — | — | — | — | X | X | X | X |
| Textiles manufacturing | X | — | X | X | X | — | — | — | — | X |
| Primary metals | — | — | — | — | — | — | — | — | X | X |
| Pulp and paper | — | — | X | X | X | — | — | — | — | X |
| Petroleum refining | X | — | X | — | — | X | — | X | X | X |
| Rubber/plastics | X | — | X | — | X | — | — | — | — | X |
| Septic systems | — | X | — | — | — | X | — | — | — | — |
| Injection wells | — | — | — | — | X | — | X | X | X | X |
| Sewage sludge | — | X | — | — | — | X | — | — | X | — |
| Urban runoff | — | X | — | X | X | — | X | X | X | — |
| Landfill leachate | X | — | — | — | X | X | — | — | — | — |

*Notation:* BOD = biochemical oxygen demand; TSS = total suspended solids; TDS = total dissolved solids; synthetic organics = synthetic organic compounds; volatile organics = volatile organic compounds; metals = industrial metals; pH = high (alkaline) or low (acid) pH.

**TABLE 16.3.2 Groundwater Pollution Sources**

| Source | Cause | Extent | Chemical/Wastes |
|---|---|---|---|
| Underground storage tanks | Hole due to internal and external corrosion leaks chemical into soil and groundwater | • 2.5 million<br>• 47 states<br>• 35% of 800,000 fuel tanks leaked | Gasoline<br>Oil<br>Hazardous chemicals<br>Waste products |
| Landfills | Rainwater leaching chemicals to groundwater | • 2,395 open dumps<br>• 24,000–36,000 closed or abandoned landfills<br>• 75,000 on-site industrial landfills<br>• 12,000–18,000 municipal landfills contain hazardous wastes | Garbage and trash<br>Sludge<br>Incinerator ash<br>Foundry waste<br>Hazardous substances |
| Surface impoundments | Direct infiltration to the saturated zone of aquifer | • 180,000 waste impoundments (1982)<br>• 37,000 municipal<br>• 19,400 agricultural<br>• 27,912 industrial<br>• 25,000 mining<br>• 65,688 brine pits for oil and gas<br>• Industrial sites evaluated 95% within 1 mile of drinking wells, 70% unlined, 50% on top of aquifers | Settling ponds from municipal wastewater and sewage treatment<br>Animal feed lots and farms<br>Oil and gas industries<br>Mining<br>Paper<br>Chemical operation |
| Waste-disposal injection wells | Direct dumping through wells to aquifers | • Groundwater contamination in 20 states<br>• Millions of tons through thousands of wells | Toxic<br>Hazardous<br>Radioactive<br>Metals<br>Wood Preservatives<br>Petroleum |
| Septic systems | Surfacing and flooding due to failure; leaching into aquifers | • 22 million in U.S.<br>• 0.5 million installed every year<br>• 30% of population served | Variety of organic and inorganic compounds<br>Fecal coliform<br>Nitrates and nitrites<br>Trichloroethylene, benzene, and methylene chloride |
| Agricultural waste | Leaching through unsaturated zone to groundwater | • 50,000 pesticides with 600 active ingredients<br>• 10 million t of nitrogen | Nitrates<br>Salts<br>Dissolved solids |
| Land application | Leachates reaching groundwater | • Major threat to groundwater in 20 states<br>• 40% of hazardous wastes in California treated by land farming | Heavy metals<br>Toxic chemical<br>Nitrogen<br>Pathogens |
| Radioactive contaminants | Potential migration to groundwater | • Massive production of radioactive isotopes after World War II | Uranium<br>Plutonium |

After Bedient, P.B., Rifai, H.S., and Newell, C.J. 1994. *Ground Water Contamination: Transport and Remediation*, Prentice Hall, Englewood Cliffs, NJ, 541.

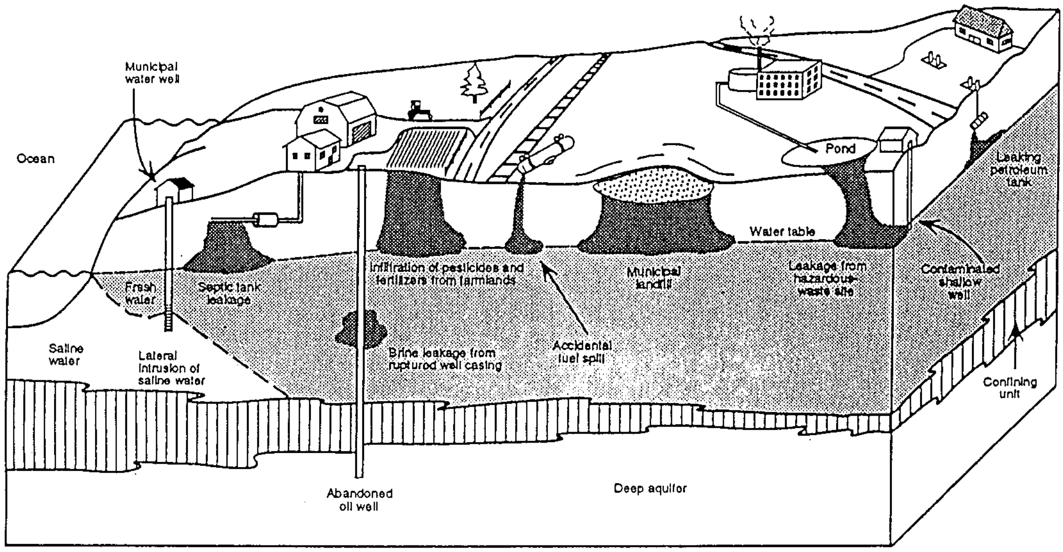

**FIGURE 16.3.1** Mechanisms of groundwater contamination (From Fetter, 1993).

discharged or allowed to evaporate or infiltrate into the ground. In addition, to store and dispose of wastewater and products from sewage treatment, surface impoundments are used in paper, mining, and oil and gas industries. They are also used in farms and large feed lots. In unlined impoundments, the liquids leak, and when undetected, can result in soil and groundwater contamination in large zones of the subsurface.

Because of the large number of septic tanks that are in operation in homes, small businesses, service stations, laundries, and industry, septic tanks have become a major source of soil and groundwater contamination. When these systems fail, the sludges or septage floods the drainage field and leachates that are generated act as a source of contamination. The discharges from septic tanks contain many organic and inorganic chemical products, suspended solids, fecal coliform, pathogenic bacteria and viruses, nitrates, and nitrites. Industrial septic systems used in commercial operations discharge hazardous waste chemicals that include synthetic organics (e.g., trichloroethylene, tetrachloroethylene, toluene, etc.) and heavy metals (e.g., lead, copper, and zinc).

Injection wells that are drilled into deep aquifers or aquifers that are not used for water supply are used to discharge liquid wastes into the subsurface. Large volumes of toxic, hazardous, and radioactive wastes that are generated in chemical, petroleum, metals, mining, and wood-treatment industries are disposed of using this method. The contamination of aquifers that are used for drinking water can occur when the injection wells are not designed properly and are placed in formations where the hydrogeolgic conditions are not well known or understood.

Many types of agriculture-related activities use chemicals and produce wastes that contaminate soil and groundwater. Among these products are pesticides, fertilizer, and feed lot waste. Various types of pesticides are used in farming, golf courses, gardens, and parks to control insects and weeds. Many of the modern-day pesticides are biodegradable, but some of the stable ones are carried by rain and irrigation water through the soil to the groundwater. Fertilizers primarily contain nitrogen, potassium, and phosphorus. Because of comparatively high mobility in soil, nitrogen leachates are the primary contaminant of concern that is associated with application of fertilizers. Waste generated at large feed lots can introduce nitrogen, bacteria, and salts to the underlying aquifers. In addition to the above sources, the salts that get accumulated in soils from long-term application of irrigation water act as a source of soil and groundwater degradation.

In a treatment and disposal method known as land treatment, the wastewater and sludges that are generated from treatment plants and industrial operations are directly applied on the ground surface. Contamination of the soil and groundwater occurs when heavy metals, toxic chemicals, nitrogen, and pathogens leach through the unsaturated zone.

Another source of soil contamination is the radioactive wastes that are produced in the weapons and nuclear industries. These wastes are primarily associated with the elements uranium and plutonium. The ionizing radiation in the form of alpha and beta particles and gamma rays are damaging to human and animal life. As these contaminants follow a first-order exponential decay law, they remain hazardous for very long time periods on the order of hundreds to thousands of years. Table 16.3.2 summarizes several of the key sources of groundwater pollution, their extent and the major associated pollutants.

## Pollutant Monitoring

*Jan F. Kreider and Tissa Illangasekare*

### Groundwater

Contaminants that are released to the aqueous phase from the soil or external sources move with the flowing groundwater creating a solute plume. Monitoring the groundwater flow velocity and the propagation of the solute plume is necessary to design schemes and strategies to protect the quality of groundwater that is used for drinking.

Monitoring wells are installed in aquifers to measure water pressure and to sample groundwater water quality. Wells in general consist of a standpipe with a screened interval. The screened interval allows for the aquifer water to flow into the well pipe. The water pressures are used to determine the head gradients, which in turn can be used to estimate the magnitude and direction of groundwater flow. Water samples that are collected at monitoring wells can be used to obtain information on the quality of groundwater.

Piezometric head is the sum of pressure and the elevation heads. The pressure head at any point in the aquifer intercepted by the screen is the height of the water surface in the well bore (or standpipe) above the point on the screen. The elevation head at a point is the elevation of the point above or below a datum. The gradient of the piezometric head determines the magnitude and direction of groundwater flow. By measuring the piezometric heads at many monitoring wells it is possible to draw the contour lines of equal piezometric head or potential. A flow net is obtained by constructing a set of flow lines that are orthogonal to the equipotential lines. The groundwater flow direction at a point is determined by drawing a tangent to the flow line passing through the point. By constructing the flow net so that the intersection of equipotential lines and the flow lines form curvilinear squares, it is possible to estimate the groundwater flow velocities and discharge in an aquifer. The monitoring well data can also be used to calibrate a groundwater model that then can be used to estimate and monitor groundwater flow.

Groundwater samples collected from monitoring wells can be analyzed in the laboratory to determine the chemical contents. Probes can be inserted into the monitoring wells for the *in situ* measurement of conductivity and pH.

*Process Emissions Monitoring*. Methods and instrumentation for the monitoring of industrial waste discharge streams are discussed in detail in the USEPA *Handbook for Sampling and Sample Preservation of Water and Wastewater*. ASTM publishes a frequently updated *Annual Book of ASTM Standards* that extensively details recommended sampling techniques.

The topic of sampling is complex and includes sampling timing and frequency; sample preservation (until analyses can be done); sample preprocessing (i.e., filtering to separate particulate and dissolved components); questions of whether waste streams are continuously monitored for particular environmental variables or whether discrete samples are taken; whether a single “grab” sample is taken or a series of samples in time or space are retrieved and composted into a single “representative” sample; whether there is a single, worker-sampled, grab sample of an automated, continuous sampling apparatus; whether there is retention of volatile compounds for later analysis. Additionally, there are issues of laboratory analytical techniques, quality control, and quality assurance from the moment of sampling through the reporting of the data, acceptable detection limits, sample contamination, materials used to sample particular chemicals. The only way to account for all these variables is to know thoroughly the data-reporting requirements of the industrial discharge permits or agreements. Also, the objectives of the sampling and the compounds of concern will dictate the entire structure of the sampling regime. The authors will discuss, briefly, some of the above topics.

The ideal characteristics of a process waste discharge stream for monitoring are steady, uniform flow that is chemically homogeneous throughout the cross section. Under such conditions, several grab samples over the day may yield representative results. In many industries, the waste streams vary due to process switching, change of shifts of workers, and cleaning and preparation of process equipment and machinery. Several specified times a day a local beer brewery flushes process wastes from the floor using high-pressure hoses. Occasional grab sampling might miss completely this pulse of waste load to the treatment system. There are continuous sampling devices that take a grab sample at specified time periods, then rotate to another sample bottle in preparation for the next sample. There are more-sophisticated samplers that draw in a sample at time intervals proportional to stream discharge. Often, the type and frequency of discharge sampling is specified in the discharge permit. For best results, the sampling planner or coordinator should know the plant operation cycles in order to be able to characterize the time variation of discharges.

The material of which a sampling device and storage vessel is constructed must be matched to the materials sampled. Some organics require the use of tetrafluoroethylene (Teflon) tubing and glass storage vials that have been washed with an organic-free cleanser. Using the wrong tubing may result in the leaching of plasticizers into the sample. It is recommended that metal sampling devices *not* be used for collection of metal-laden discharge samples that require later analysis for metal ions. Samplers must be washed between samplings to avoid sample cross contamination.

*Environmental Quality Monitoring.* Most of the mechanics and issues of sampling discussed just above for monitoring discharges hold true for environmental sampling, i.e., after the discharge has entered a stream or lake. Detailed sampling plans must be prepared. Existing data is gathered (from company files; land use maps; USEPA; U.S. Geological Survey gauging and water quality station results; state departments of environment, resources, and health; other federal and local agencies). It helps to have site characteristics prior to the inception of the waste discharge.

The data collection for environmental monitoring often is governed by legal considerations concerning the validity and admissibility of the data. To this end, a quality assurance/quality control (QA/QC) plan must be prepared according to USEPA or state guidelines. These plans will specify the frequency of taking duplicate samples (taken at approximately the same time and place), split samples (one sample is split into two, separate containers), spiked samples (an additional injection of chemicals anticipated to be in the environmental sample are added to a duplicate sample, and the recovery of that known amount of spike is reported). A good QA/QC operation will ensure that the best effort is being made to

1. Obtain representative samples,
2. Use appropriate sampling methods,
3. Use appropriate analytical methods,
4. Ensure adequate records of chain of custody of samples, and
5. Develop a sound and acceptable database.

The USEPA can be contacted to send *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (or QAPPS — pronounced “kwaps”).

Other documents that may be required include

1. Sampling plans;
2. Site background information;
3. Planned sampling locations;

4. Planned sampling methodology and sample preservation (some chemicals decay on exposure to light, microbes may induce decomposition of organic compounds at ambient temperatures, chemically reduced compounds may oxidize on exposure to a head space of air, volatile compounds may escape from an insufficiently sealed vial, solid materials may dissolve, or dissolved materials may precipitate);
5. Health and safety plans;
6. Plans for sample-handling procedures and chain of custody of samples;
7. Request forms for sample analyses;
8. Frequency and format of data reports.

### Air Quality Monitoring

Air quality monitoring has many of the same goals and general techniques as water quality monitoring. A stationary monitoring network should yield the following information:

1. Background concentration
2. Highest concentration levels
3. Representative levels in populated areas
4. Impact of local sources
5. Impact of remote sources
6. Relative impact of natural and anthropogenic sources

Spatial scales range from micro- (up to 100 m) to regional scales (tens to hundreds of kilometers). Site selection is a key part of network design because microclimates can affect readings and cause them to be nonrepresentative of the region.

Mobile monitoring is useful when sites not monitored with the fixed network need assessment. The key drawback of such systems is the sparsity of equipment suitable for reliable and durable mobile monitoring. Remote sensing offers a second alternative to stationary networks.

Quality assurance is a continuous concern of monitoring systems. Good instrumentation installation and maintenance practice with careful record keeping is essential.

Space precludes presentation of further details on air quality monitoring, but Boubel et al. (1994) has a thorough overview.

# 16.4 Regulations and Emission Standards

## Water

### *Nevis Cook and Ronald R. Hewitt Cohen*

The Clean Water Act (CWA) of 1972 and its amendments establish the framework of current U.S. water pollution control. This act is sometimes referred to as the Federal Water Pollution Control Act Amendments after the original 1965 act which the CWA amended. The objective of the CWA is to "restore and maintain the chemical, physical, and biological integrity of the nation's waters." The CWA regulates both nonpoint (runoff from farmlands, roads, and city streets) and point sources (discharges from pipes conveying pollutants to surface waters) of water pollution. The discussions in this chapter are limited to regulation of point sources of pollution to *surface* waters. Discharges to groundwaters are regulated under the Safe Drinking Water Act (SDWA) underground injection control (UIC) program and are beyond the scope of this chapter. The discussion is still quite broad, since all domestic and industrial wastewater discharges are considered point sources under the CWA.

*Discharge Permits*. The CWA prohibits point source discharges to surface waters unless a *discharge permit* is obtained. Permits typically are issued at the state level and are known as state pollution discharge elimination standards (SPDES) permits. If the state has not taken over this responsibility, national (NPDES) permits are issued by the USEPA. The permit for each point source prescribes allowable discharges in terms of amount and concentration of flows and pollutants. In some cases, an industrial facility may avoid obtaining its own permit by discharging into the local public sewer system. Control of these *indirect discharges* is accomplished by requiring publicly owned treatment works (POTWs) receiving such discharges to enter into formal *pretreatment agreements* with industrial users of the sewer. Such pretreatment agreements are intended to prevent industrial discharges to POTWs which would represent a hazard to the sewer system or its workers, interfere with treatment operations or sewage sludge disposal, or pass through the treatment process causing a violation of the POTW discharge permit.

*Permitted Discharges*. Prior to the CWA of 1972, point source water pollution control laws were established at the state level and permitted discharge of pollutants on a discharger-by-discharger and water-body-by-water-body basis. This approach worked poorly in most states, demonstrating the need for enforceable *federal minimum effluent standards*. For this reason, the CWA and subsequent amendments have established *technology-based* national minimum pretreatment and discharge standards. Technology-based standards reflect the current state of the art with respect to controlling specific pollutant discharges from specific pollution sources. Since technology-based standards represent the capabilities of typical "well-operated" facilities and are not issued on the basis of in-stream water quality, it is not surprising that in some cases compliance with national minimum standards does not adequately protect all potential uses of a water body. In such cases the uses of the receiving water body are said to be *water quality limited,* and *local discharge limits*, more stringent than national limits, may be imposed. In addition, pretreatment agreements reflect the capabilities of local treatment works with respect to pass through, destruction, or partitioning of nondegradable toxic metal pollutants into POTW sludges. Following the development of local water quality–based limits, these are compared with national minimum technology-based standards and the more restrictive criteria are imposed as discharge permit or pretreatment limitations. Further considerations with respect to setting permit values are presented below.

Industrial dischargers may obtain an industrial NPDES permit and directly discharge wastewater to a receiving water body. Alternatively, where municipal sewer service is available, industries may choose to negotiate a pretreatment agreement with the local sewer authority permitting discharge of industrial wastewater to the sewer system. Most industrial facilities employing either discharge option (direct or indirect) are subject to national technology-based minimum effluent standards. In addition, more-stringent standards may be imposed at the state or local level.

State permits containing discharge constraints more stringent than the national minimum standards are commonly derived from local water quality considerations. Ideally, local water quality–based standards are developed from science-based use protection criteria, wastewater flow data, and actual receiving water characteristics (such as low-flow conditions for streams). Rational direct discharge permits to streams or rivers can be developed by application of the following procedure: convert use-based, in-stream quality criteria to standards according to local policy; obtain data on upstream water quality and low-flow conditions (conditions at which the waste assimilative capacity of a stream is at a minimum) and determine potential for dilution of the wastewater flow by the receiving water body; compute the allowable water quality–based industrial discharge on a pollutant-by-pollutant basis and compare with national minimum standards; finally, impose permit restrictions according to the most stringent of the two types of standards developed.

Development of water quality–based permits for direct discharges to lakes, estuaries, bays, or oceans follows a procedure similar to that outlined above. However, estimates of mixing patterns and the dilution potential of these water bodies are likely to be more difficult because of the complex flow patterns involved. Water quality–based pretreatment standards for discharges to sewers also follow the same general procedure. However, in this case, the application of use criteria, policy, and potential for in-stream dilution lead to a pollutant-by-pollutant permit for the *local* POTW. Based on this permit and the removal capabilities of the treatment facility, maximum allowable (usually daily) loading of pollutants arriving at the plant is determined on a pollutant-by-pollutant basis. Allowable loads are then allocated to the various municipal and industrial users of the sewer. Setting water quality–based pretreatment standards is obviously complicated by the presence of multiple sewer uses and users. Thus, POTWs receiving significant industrial discharges are required to set up formal programs to negotiate industrial pretreatment agreements and monitor compliance.

## Air

### *Jan F. Kreider*

The U.S. Clean Air Act Amendments of 1977 set forth two air quality standard types:

- Primary (protect health)
- Secondary (protect health and prevent other adverse impacts)

Table 16.4.1 summarizes the present primary and secondary standards in the U.S. The amendments also specified for certain geographical areas further standards to prevent significant deterioration (PSD areas). These are standards that are to be considered increments over baseline air quality but are more stringent than secondary or primary standards in most cases. Table 16.4.2 lists these PSD standards.

**TABLE 16.4.1 U.S. Federal Primary and Secondary Ambient Air Quality Standards**

| Pollutant | Type of Standard | Averaging Time | Frequency Parameter | Concentration μg/m³ | Concentration ppm |
|---|---|---|---|---|---|
| Sulfur oxides (as sulfur | Primary | 24 hr | Annual maximum | 365 | 0.14 |
| | | 1 year | Arithmetic mean | 80 | 0.03 |
| dioxide) | Secondary | 3 hr | Annual maximum | 1,300 | 0.5 |
| Particulate matter >10 μm | Primary | 24 hr | Annual maximum | 150 | — |
| | | 24 hr | Annual geometric mean | 50 | — |
| | Secondary | 24 hr | Annual maximum | 150 | — |
| | | 24 hr | Annual geometric mean | 50 | — |
| Carbon monoxide | Primary and secondary | 1 hr | Annual maximum | 40,000 | 35.0 |
| | | 8 hr | Annual maximum | 10,000 | 9.0 |
| Ozone | Primary and secondary | 1 hr | Annual maximum | 235 | 0.12 |
| Nitrogen dioxide | Primary and secondary | 1 year | Arithmetic mean | 100 | 0.05 |
| Lead | Primary and secondary | 3 months | Arithmetic mean | 1.5 | — |

**TABLE 16.4.2 U.S. Federal PSD Concentration Increments**

| Pollutant | Increment ($\mu$g m$^3$) |
|---|---|
| **Class I areas** | |
| Particulate matter | |
| TSP, annual geometric mean | 5 |
| TSP, 24-hr maximum | 10 |
| Sulfur dioxide | |
| Annual arithmetic mean | 2 |
| 24-hr maximum | 5 |
| 3-hr maximum | 25 |
| Nitrogen dioxide | |
| Annual arithmetic mean | 2.5 |
| **Class II areas** | |
| Particulate matter | |
| TSP, annual geometric mean | 19 |
| TSP, 24-hr maximum | 37 |
| Sulfur dioxide | |
| Annual arithmetic mean | 20 |
| 24-hr maximum | 91 |
| 3-hr maximum | 512 |
| Nitrogen dioxide | |
| Annual arithmetic mean | 25 |
| **Class III areas** | |
| Particulate matter | |
| TSP, annual geometric mean | 37 |
| TSP, 24-hr maximum | 75 |
| Sulfur dioxide | |
| Annual arithmetic mean | 40 |
| 24-hr maximum | 182 |
| 3-hr maximum | 700 |
| Nitrogen dioxide | |
| Annual arithmetic mean | 50 |

# 16.5 Mitigation of Water and Air Pollution

This section discusses the methods for abating or mitigating air and water pollution burdens on the environment. Because mechanical engineers are most concerned with air pollution control systems and civil engineers deal with water treatment systems, this section emphasizes the air pollution mitigation side.

## Overview

*Jan F. Kreider*

There are several methods for controlling air- or waterborne pollution:

- Process change
- Fuel change
- Pollution removal and disposal
- Pollution prevention

*Process change* includes everything from modifications that reduce emissions to substitution of a less polluting one for a more polluting one. The latter could be classified as pollution prevention, described shortly. In many cases, for example, in the steel industry, it has proved most economical to replace completely old plants with totally new ones. Likewise, complete substitution has been widely adopted in the pulp and paper industry.

*Fuel change* as a control strategy is based on the fact that airborne pollutants often are related to the combustion aspects of a process. For example, coal-fired power plants emit $SO_2$ because coal contains sulfur. Substitution of natural gas for coal eliminates any sulfur in the fuel and, therefore, any oxides of sulfur in the stack gases.

Fuel changes must consider fuel supply, capital cost, and competition for clean fuels among many industries before an engineering design decision can be made. Life cycle methods that consider all parts of the life of a plant are necessary. For example, a nuclear power plant may produce very low emission electricity but after decommissioning may cause long-term waste disposal problems.

*Pollution removal* is necessary when process or fuel changes cannot provide adequate emission control. A physical, chemical, or electrical feature of the pollutant to be removed must differ from those types of characteristics of the carrying gas or liquid stream. An example is a baghouse or electrostatic precipitator for particulate emissions. Not only collection of pollutants but also disposal of the collected pollutant must be considered by the design engineer. A whole systems viewpoint is necessary for a successful pollution removal design.

Pollutant disposal is governed by different criteria depending on whether it is hazardous or not. Hazardous waste disposal is covered by the Resource Conservation and Recovery Act of 1976, which established the Office of Solid Waste with the USEPA. On the other hand, nonhazardous waste disposal is governed by the states. Table 16.5.1 categorizes the ultimate disposal methods for classes of hazardous wastes. Many of the methods apply for nonhazardous wastes as well.

*Pollution prevention* is the ultimate solution to abatement. This can be accomplished at the source by various technical means, depending on process specifics. This approach is currently the most commonly used term by the USEPA. The Pollution Prevention Act of 1990 stated these policies:

- Prevent or reduce pollution at the source whenever possible;
- Recycle to the environment pollution that cannot be prevented in a safe manner whenever possible;
- Pollution that can neither be prevented nor recycled should be treated in as environmentally safe a manner as possible;
- Disposal or other release into the environment should be used as only a last resort.

**TABLE 16.5.1 Ultimate Waste Disposal Methods**

| Process | Purpose | Wastes | Problems (Remarks) |
|---|---|---|---|
| Cementation and vitrification | Fixation<br>Immobilization<br>Solidification | Sludges<br>Liquids | Expensive |
| Centrifugation | Dewatering<br>Consolidation | Sludges<br>Liquids | — |
| Filtration | Dewatering<br>Volume reduction | Sludges<br>Liquids | Expensive |
| Thickening (various methods) | Dewatering<br>Volume reduction | Sludges<br>Liquids | — |
| Chemical addition (polyelectrolytes) | Precipitation<br>Fixation<br>Coagulation | Sludges<br>Liquids | Can be used in conjunction with other processes |
| Submerged combustion | Dewatering | Liquids | Acceptable for aqueous organics |
| **Major Ultimate Disposal Methods** | | | |
| Deep well injection | Partial removal from biosphere<br>Storage | Oil field brines; low toxicity, low-persistence wastes; refinery wastes | Monitoring difficulty; need for special geological formations; groundwater contamination |
| Incineration | Volume reduction<br>Toxicity destruction | Most organics | If poor process control, unwanted emissions produced<br>Can produce $NO_x$, $SO_x$, halo acids |
| Recovery | Reuse | Metals<br>Solvents | Sometimes energy prohibitive |
| Landfill | Storage | Inert to radioactive | Volatilization |
| **Major Waste Disposal Methods** | | | |
| Land application | Isolation | | Leaching to groundwater |
| Land burial | Dispersal | | Access to biota |
| Ocean disposal | Dispersal<br>Dilution<br>Neutralization<br>Isolation(?) | Acids, bases<br>Explosives<br>Chemical war agents<br>Radioactive wastes | Contact with ocean ecosystem; containers unstable |
| **Minor Disposal Methods** | | | |
| Biological degradation | Reduction of concentration<br>Oxidation | Biodegradable organics | Most hazardous wastes do not now qualify |
| Chemical degradation (chlorination) | Conversion<br>Oxidation | Some persistent pesticides | — |
| Electrolytic processes | Oxidation | Organics | — |
| Long-term sealed storage | Isolation<br>Storage | Radioactive | How good are containers? |
| Salt deposit disposal | Isolation<br>Storage | Radioactive | Are salt deposits stable in terms of waste lifetimes? |

## Air Pollution Control

*Jan F. Kreider*

The most common method of meeting emission standards in industries that must control air pollution is by *pollution removal*. This section describes the most widely used approaches. Table 16.5.2 lists the important characteristics of control systems for airborne pollutants.

Dry particulate matter is removed by

**TABLE 16.5.2 Key Characteristics of Pollution Control Devices and/or Systems**

| Factor Considered | Characterisitc of Concern |
|---|---|
| General | Collection efficiency |
| | Legal limitations such as best available technology |
| | Initial cost |
| | Lifetime and salvage value |
| | Operation and maintenance costs |
| | Power requirement |
| | Space requirements and weight |
| | Materials of construction |
| | Reliability |
| | Reputation of manufacturer and guarantees |
| | Ultimate disposal/use of pollutants |
| Carrier gas | Temperature |
| | Pressure |
| | Humidity |
| | Density |
| | Viscosity |
| | Dewpoint of all condensables |
| | Corrosiveness |
| | Inflammability |
| | Toxicity |
| Process | Gas flow rate and velocity |
| | Pollutant concentration |
| | Variability of gas and pollutant flow rates, temperature, etc. |
| | Allowable pressure drop |
| Pollutant (if gaseous) | Corrosiveness |
| | Inflammability |
| | Toxicity |
| | Reactivity |
| Pollutant (if particulate) | Size range and distribution |
| | Particle shape |
| | Agglomeration tendencies |
| | Corrosiveness |
| | Abrasiveness |
| | Hygroscopic tendencies |
| | Stickiness |
| | Inflammability |
| | Toxicity |
| | Electrical resistivity |
| | Reactivity |

- Filters — baghouse, fixed beds, or mats
- Electrostatic precipitators — plate-type, tube-type; see Figure 16.5.1
- Inertial collectors — cyclones and baffles; see Figure 16.5.2
- Scrubbers — wet or dry

Table 16.5.3 lists the key characteristics of these technologies, where they are best applied, and annual operating, capital, and maintenance costs in $1994. Of course, a design is needed upon which a quotation for final cost studies can be based.

Liquid droplets and mists are controllable by

- Filters — more loosely knit than for dry filters
- Electrostatic precipitators — wetted wall type
- Inertial collectors — cyclones and baffles
- Venturi scrubbers

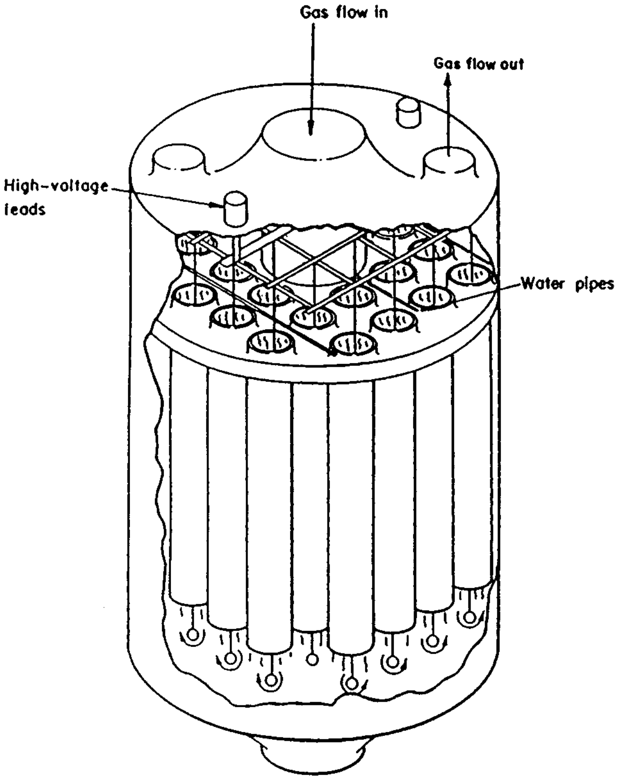

**FIGURE 16.5.1** Wet-wall eledtrostatic precipitator with tubular collection electrodes. (From Oglesby, S., Jr., and Nichols, G. B., in *Air Pollution*, 3rd ed., Vol. IV, A. C. Stern, Ed., p.238, Academic Press, New York, 1977. With permission.)

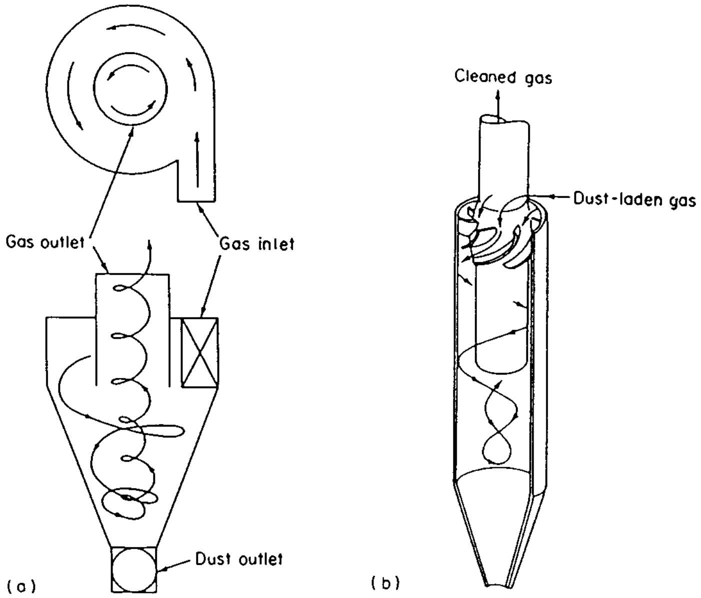

**FIGURE 16.5.2** (a) Tangential inlet cyclone. (b) Axial inlet cyclone.

**TABLE 16.5.3 Comparison of Particulate Removal Systems**

| Type of Collector | Particle Size Range (μm) | Removal Efficiency | Space Required | Max. Temp. (°C) | Pressure Drop (cm $H_2O$) | Annual cost (U.S. $\$$/year/m$^3$)[a] |
|---|---|---|---|---|---|---|
| Baghouse (cotton bags) | 0.1–0.1 | Fair | Large | 80 | 10 | 28.00 |
| | 1.0–10.0 | Good | Large | 80 | 10 | 28.00 |
| | 10.0–50.0 | Excellent | Large | 80 | 10 | 28.00 |
| Baghouse (Dacron, nylon, Orlon) | 0.1–1.0 | Fair | Large | 120 | 12 | 34.00 |
| | 1.0–10.0 | Good | Large | 120 | 12 | 34.00 |
| | 10.0–50.0 | Excellent | Large | 120 | 12 | 34.00 |
| Baghouse (glass fiber) | 0.1–1.0 | Fair | Large | 290 | 10 | 42.00 |
| | 1.0–10.0 | Good | Large | 290 | 10 | 42.00 |
| | 10.0–50.0 | Good | Large | 290 | 10 | 42.00 |
| Baghouse (Teflon) | 0.1–1.0 | Fair | Large | 260 | 20 | 46.00 |
| | 1.0–10.0 | Good | Large | 260 | 20 | 46.00 |
| | 10.0–50.0 | Excellent | Large | 260 | 20 | 46.00 |
| Electrostatic precipitator | 0.1–1.0 | Excellent | Large | 400 | 1 | 42.00 |
| | 1.0–10.0 | Excellent | Large | 400 | 1 | 42.00 |
| | 10.0–50.0 | Good | Large | 400 | 1 | 42.00 |
| Standard cyclone | 0.1–1.0 | Poor | Large | 400 | 5 | 14.00 |
| | 1.0–10.0 | Poor | Large | 400 | 5 | 14.00 |
| | 10.0–50.0 | Good | Large | 400 | 5 | 14.00 |
| High-efficiency cyclone | 0.1–1.0 | Poor | Moderate | 400 | 12 | 22.00 |
| | 1.0–10.0 | Fair | Moderate | 400 | 12 | 22.00 |
| | 10.0–50.0 | Good | Moderate | 400 | 12 | 22.00 |
| Spray tower | 0.1–1.0 | Fair | Large | 540 | 5 | 50.00 |
| | 1.0–10.0 | Good | Large | 540 | 5 | 50.00 |
| | 10.0–50.0 | Good | Large | 540 | 5 | 50.00 |
| Impingement scrubber | 0.1–1.0 | Fair | Moderate | 540 | 10 | 46.00 |
| | 1.0–10.0 | Good | Moderate | 540 | 10 | 46.00 |
| | 10.0–50.0 | Good | Moderate | 540 | 10 | 46.00 |
| Venturi scrubber | 0.1–1.0 | Good | Small | 540 | 88 | 112.00 |
| | 1.0–10.0 | Excellent | Small | 540 | 88 | 112.00 |
| | 10.0–50.0 | Excellent | Small | 540 | 88 | 112.00 |
| Dry scrubber | 0.1–1.0 | Fair | Large | 500 | 10 | 42.00 |
| | 1.0–10.0 | Good | Large | 500 | 10 | 42.00 |
| | 10.0–50.0 | Good | Large | 500 | 10 | 42.00 |

[a] Includes water and power cost, maintenance cost, operating cost, capital, and insurace costs (in $\$$ 1994).

Finally, gaseous pollutants can be controlled using

- Absorption materials — wet scrubber, packed tower, or bubble tower; see Figure 16.5.3, for example;
- Adsorption materials — porous media such as activated charcoal, silica gel, and alumina;
- Condensers — widely used in the chemical process industries;
- Chemical conversion to contaminants — oxidize hydrocarbons to $CO_2$ and $H_2O$, for example.

Table 16.5.4 compares gaseous pollutant removal systems.

Cataloging of industry-specific designs is beyond the scope of this handbook because of space limitations. The reader is referred to Boubel et al. (1994) for details. One must make an inventory of emissions and then identify the most appropriate control methods based on operating and capital costs considerations. For example, Table 16.5.5 shows common emissions and control methods for the petrochemical industry. The energy, power generation, incineration, ferrous and nonferrous metallurgical, agricultural, and mineral/mining industries produce considerable emissions that must be controlled in accordance with federal regulations.

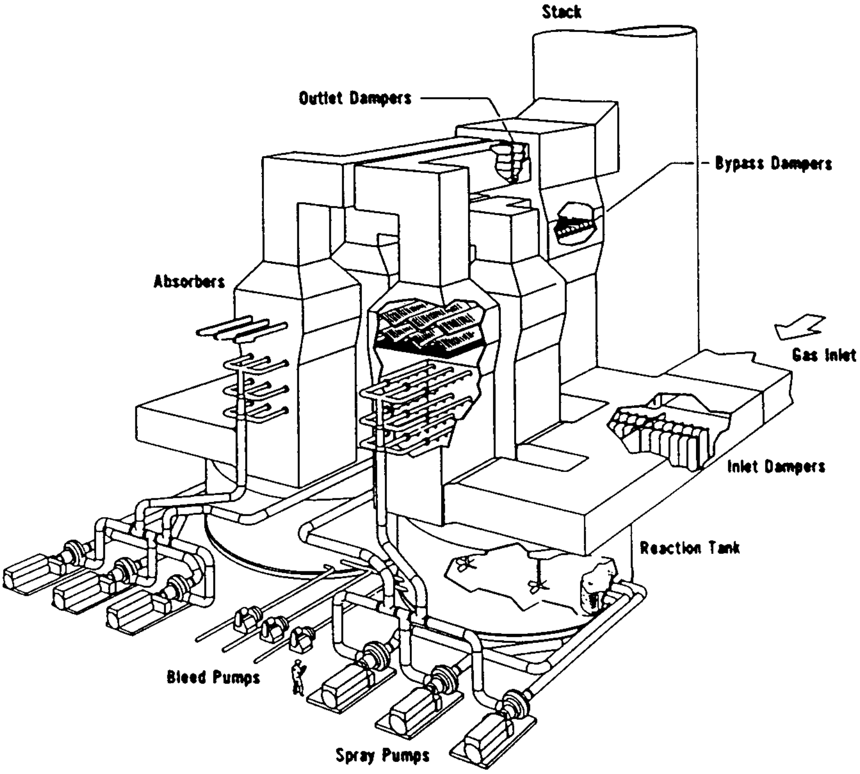

**FIGURE 16.5.3** Cutaway drawing of a flue gas desulfurization spray tower absorber. (Courtesy of CE Power Systems, Combustion Engineering, Inc.)

**TABLE 16.5.4 Comparison of Gaseous Pollutant Removal Systems**

| Type of Equipment | Pressure Drop (cm $H_2O$) | Installed Cost (U.S. \$/m$^3$) | Annual Operating Cost (U.S. \$/m$^3$) |
|---|---|---|---|
| Scrubber | 10 | 9.80 | 14.00 |
| Absorber | 10 | 10.40 | 28.00 |
| Condenser | 2.5 | 28.00 | 7.00 |
| Direct flame afterburner | 1.2 | 8.20 | 8.40 + gas |
| Catalytic afterburner | 2.5 | 11.60 | 28.00 + gas |

## Water Pollution Control

*Nevis Cook and Ronald R. Hewitt Cohen*

Control of waterborne pollutants is at present undertaken by nine distinct techniques:

- Biological oxidation
- Chemical oxidation
- Chemical reduction
- Conventional treatment
- Precipitation
- Air stripping
- Activated carbon

**TABLE 16.5.5 Air Pollution Emissions and Controls: Petrochemical Processes**

| Petrochemical Process | Air Pollutant Emissions | Control Methods in Use |
|---|---|---|
| Ethylene oxide (most emissions from purge vents) | Ethane, ethylene, ethylene oxide | Catalytic afterburner |
| Formaldehyde (most emissions from exit gas stream of scrubber) | Formaldehyde, methanol, carbon monoxide, dimethyl ether | Wet scrubber for formaldehyde and methanol only; afterburner for organic vent gases |
| Phthalic anhydride (most emissions from off-gas from switch condensers) | Organic acids and anhydrides, sulfur dioxide, carbon monoxide, particulate matter | Venturi scrubber followed by cyclone separator and packed countercurrent scrubber |
| Acrylonitrile (most emissions from exit gas stream from product absorber) | Carbon monoxide, propylene, propane, hydrogen cyanide, acrylonitrile, acetonitrile | Thermal incinerators (gas-fired afterburners or catalytic afterburners) |
| | $NO_x$ from by-product incinerator | None |
| Carbon black (most emissions from exit gas stream from baghouse, some fugitive particulate) | Hydrogen, carbon monoxide, hydrogen sulfide, sulfur dioxide, methane, acetylene | Waste heat boiler or flare (no control for $SO_2$) |
| | Particulate matter (carbon black) | Baghouse |
| Ethylene dichloride (most emissions from exit gas stream of solvent scrubber) | Carbon monoxide, methane, ethylene, ethane, ethylene dichloride, aromatic solvent | None at present, but could use a waste heat boiler or afterburner, followed by a caustic scrubber for hydrochloric acid generated by combustion |

- Ion exchange
- Reverse osmosis

Table 16.5.6 summarizes these approaches and their applications by contaminant type. The letter A in the table indicates the best available technology, whereas a B indicates an alternative that may apply to a subclass of industries. The reader is referred to the notes to the table for further details.

**TABLE 16.5.6 General Effectiveness of Treatment Technology vs. Contaminant Type**

| Constituent | Biological Oxidation | Chemical Oxidation | Chemical Reduction | Conventional Treatment | Precipitation | Air Stripping | Activated Carbon | Ion-Exchange | Reverse Osmosis |
|---|---|---|---|---|---|---|---|---|---|
| BOD | A | — | — | — | — | — | — | — | — |
| COD | B | B | — | — | — | — | B | — | — |
| MOs[a] | — | A | — | A | A | — | — | — | I |
| Turb.[b] | — | — | — | A | B | — | — | I | I |
| TDS[c] | — | — | — | — | — | — | — | A | A |
| Ca, Mg | — | — | — | — | A | I | — | A | A |
| Fe, Mg | — | P | I | B | A | I | — | I | I |
| $NH_3$ | A | B | — | — | — | B | — | B | B |
| $NO_3^-$ | — | — | A | — | — | — | — | B | B |
| Me++[d] | — | — | — | B | A | — | — | A | A |
| Cr | — | I | P | B | A | — | — | A | A |
| As, Se | — | P | I | B | A | — | — | A | A |
| CN | — | A | — | — | — | I | — | — | B |
| Phenols | B | A | — | — | — | — | B | — | — |
| SOC[e] | B | B | — | — | — | — | A | — | A |
| VOC[f] | B | B | — | — | — | A | B | — | B |

**A** = treatment technology commonly applied to reduce contaminant to acceptable levels; perhaps best conventional technology. **B** = treatment technology that has been used to remove a particular contaminant, but might not be fully effective under all conditions. **I** = substance could interfere with efficient removal of other contaminants. **P** = pretreatment required if technology is to be used.

[a] MO = microbiological contaminants including pathogenic bacteria, protozoa, and viruses.

[b] Turb. includes fine colloidal matter and suspended solids, for true suspended solids use sedimentation.

[c] Total dissolved solids (TDS) includes removal of the highly soluble ions: $Na^+$, $K^+$, $Cl^-$, $SO_4^{2-}$.

[d] Includes the valence +2 transition metals: $Cu^{++}$, $Ni^{++}$, $Pb^{++}$, $Zn^{++}$.

[e] SOC = synthetic organic compounds, including pesticides.

[f] VOC = volatile organic compounds, including solvents.

# 16.6 Environmental Modeling

## Air Pollution Dispersion Modeling

*Paolo Zannetti*

To understand air pollution, it is mandatory, at any scale, to simulate correctly the dispersion characteristics of the emissions. Therefore, the role of meteorology is essential. Pollutants are typically transported by two types of flows: an "ordered" flow, which is characterized by average wind speed and direction, and a semirandom, turbulent flow, which is characterized by wind fluctuations. All dispersion models aim at simulating these two components. As further discussed below, dispersion modeling techniques can be categorized into four general classes: (1) Gaussian models; (2) Eulerian grid models; (3) Lagrangian box models; and (4) Lagrangian particle models.

### Gaussian Models

All Gaussian models assume that the concentration of pollutants maintains a Gaussian distribution in space. The Gaussian distribution, as illustrated in Figure 16.6.1, is a symmetrical bell-shaped distribution which is described at any given point $x$ by two parameters: the location of the peak (in this case, the centerline of the plume indicated by the segmented line) and the standard deviation (in this case, the spread of the plume mass about its center). Therefore, the dilution rate of the plume is fully characterized by the two standard deviations, $\sigma_y$ and $\sigma_z$, expressed as a function of the downwind distance, $x$.

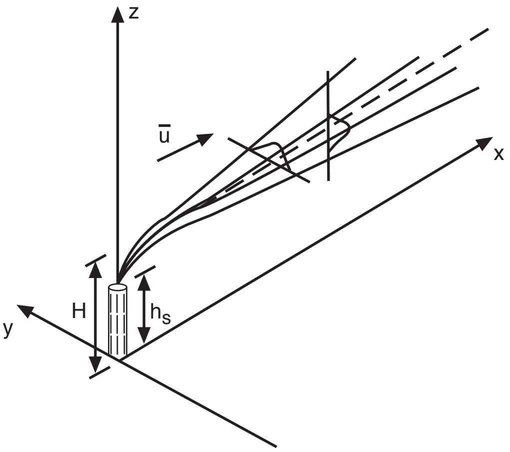

**FIGURE 16.6.1** The Gaussian plume in a wind-oriented coordinate system (i.e., the wind is blowing toward the $x$ axis). The plume is released from a source located at (0, 0, $h_s$) and possesses an initial buoyancy. Therefore, the plume behaves as if it were originated from (0, 0, $H$), where $H$ is the effective emission height and $\delta h = H - h_s$ is the plume rise. The plume is advected by the average wind speed $\bar{\mathbf{u}}$ and expands in the horizontal and the vertical direction while maintaining a Gaussian distribution along both.

In mathematical notation, the Gaussian plume formula in Figure 16.6.1 can be written as

$$c = \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}_{\square}}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)_{\square}^2\right]\exp\left[-\frac{1}{2}\left(\frac{H-z}{\sigma_z}\right)^2\right] \tag{16.6.1}$$

where $c$ is the concentration computed at the receptor ($x$, $y$, $z$), Q is the emission rate, $\bar{\mathbf{u}}$ is the average horizontal wind speed, $H$ is the effective emission height, and $\sigma_y$ and $\sigma_z$ are functions of the downwind distance, *x,* with parameters that vary with the meteorological conditions (in fact, the stronger the turbulence intensity of the atmosphere, the larger the growth rate of $\sigma_y$ and $\sigma_z$ with $x$).

As can easily be seen, Equation (16.6.1) refers to a stationary state (i.e., $c$ is not a function of time), uses meteorological parameters that must be considered homogeneous and stationary in the modeled area (i.e., between the source and the receptors at which concentrations are computed), and cannot work in calm conditions where the wind speed approaches zero (in general, the wind speed cannot be less than 1 m/sec when Equation (16.6.1) is applied). In spite of these limitations, the simplicity of the Gaussian approach, its relative ease of use, and, especially, the elevation of this methodology to the quantitative decision-controlling level in the United States (USEPA, 1978) have stimulated research aimed at removing some of the limitations of the Gaussian theory in modeling the real-world situations.

Equation (16.6.1) has been modified and expanded to incorporate, among others, the following factors: ground reflection, multiple reflections, hourly simulations, deposition and decay, chemical transformation, fumigation, complex terrain, gravitational settling, calm conditions, nonstationary and nonhomogenous conditions, and long-term simulations. We summarize below some of these improvements.

Reflection terms can be added to Equation (16.6.1) to account for partial or total reflection of concentration at the ground. Similarly, reflection can be added at the top of **the planetary boundary layer, PBL** (typically, about 500 to 1000 m above the ground). If both reflections are implemented, the plume is trapped inside the PBL. Equation (16.6.1) is generally applied for periods of 1 hr. This allows the incorporation of time-varying emission and meteorological parameters. Chemistry and decay can be incorporated by introducing exponential decay terms (for example, it can be assumed that an emission of primary gaseous $SO_2$ is transformed into particulate matter $SO_4^{2-}$ at a rate of 1% per hour). Gravitational settling will affect a plume of primary particulate matter. In this case, the plume centerline can be tilted to account for the settling velocity of the particles, which is a function of both particle size and density.

In addition to the Gaussian plume model, Gaussian segment and puff models can be used (Zannetti, 1986a). These models break up the plume into independent elements (plume segments or puffs) whose initial features and time dynamics are a function of time-varying emission and meteorological conditions encountered by the plume elements. These techniques allow us to account properly for nonhomogeneous, nonstationary conditions. Gaussian puff models, in particular, have the additional advantage of being able to simulate calm or low-wind conditions.

Complex terrain conditions affect the plume dynamics, both the motion of the centerline trajectory and the growth of $\sigma_y$ and $\sigma_z$. Finally, the Gaussian plume model equation can be rewritten in a way to simulate long-term concentration averages (e.g., annual averages) by incorporating the joint frequency of occurrence of a predetermined set of emission and meteorological conditions.

### Other Models

Eulerian grid models (Lamb [from Longhetto], 1980) simulate pollutant diffusion by superimposing a grid over the computational domain and numerically solving a mass-balance equation (typically, a partial differential equation, PDE, or a set of PDEs) in each grid cell at each time step. This is also called numerical integration. In general, the smaller the grid and time intervals, the more accurate the numerical solution.

Difficulties may be encountered in simulating atmospheric diffusion with the K-theory. In particular, the application of the K-theory to simulate vertical dispersion during daytime, unstable meteorological conditions is highly questionable. To improve the simulation ability of Eulerian grid models, equations of high-order moments of concentration, wind, and temperature fluctuations can be solved simultaneously. This approach is called high-order closure and requires the definition of more-complex, nonlinear relationships between the turbulent fluxes and the concentration fields.

Lagrangian box models are mostly used to perform fast simulations of photochemical smog. These models define a set of "boxes" (e.g., a column of boxes as illustrated in Figure 16.6.2) which are advected horizontally according to the local wind speed and direction. Each box encounters emissions along its trajectory. These emissions inject new pollutants inside the box. A full set of chemical reactions inside

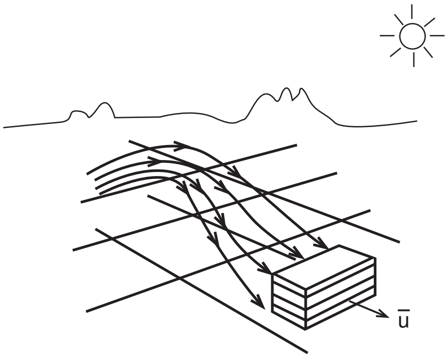

**FIGURE 16.6.2 Lagrangian box modeling.**

each box allows the simulation of the photochemical smog and the formation of secondary pollutants, such as ozone.

Lagrangian particle models provide a very interesting alternative method for simulating atmospheric diffusion. Particle motion can be produced by both deterministic velocities and semirandom pseudovelocities generated using Monte Carlo techniques. In the latter case, the trajectory of a single particle represents a realization from an infinite set of possible solutions, and, if enough particles are used, important characteristics can be inferred from the computation of particle **ensemble average** properties.

When using Lagrangian particle models to simulate air pollution, pollutant emissions (both gases and particulate matter) are represented by the injection of fictitious particles into the computational domain. Each particle represents a specified amount of pollution and is moved at each time step by a pseudovelocity that is time and space dependent. Zannetti (1990) discusses alternative modeling approaches in more detail than is possible here.

## Atmospheric Chemistry

Atmospheric chemistry deals essentially with four major issues (Seigneur, 1987): (1) photochemical smog in sunny, urban areas; (2) **aerosol** chemistry; (3) acidic deposition; and (4) air toxics. Chemical reactions can be simulated in two ways: (1) with simple first-order terms (e.g., a decay term) and (2) with a full chemical reaction scheme.

First-order terms for simulating atmospheric chemistry can be easily incorporated into any of the models previously discussed. For example, a radioactive pollutant with a specified decay rate (or half-life) can be simulated by introducing the following multiplicative term in any concentration equation

$$\exp(-t/T) \qquad (16.6.2)$$

where $t$ is the travel time and $T$ is the time scale of the decay (easily related to the half-life of the chemical species). Similarly, chemical transformation from a primary to a secondary pollutant (e.g., from gaseous $SO_2$ to sulfate particulate matter, $SO_4^{2-}$) can be accomplished by introducing two exponential terms— $[\exp(-t/T)]$ and $[1 - \exp(-t/T)]$ — having the effect of simultaneously decreasing the $SO_2$ concentration and increasing the $SO_4^{2-}$ concentration as time increases. First-order schemes, though relatively simple, may use parameters that are space and time dependent; for example, the $SO_2$-to- $SO_4^{2-}$ conversion rate may vary as a function of relative humidity and solar radiation.

Photochemical smog, which in the past only affected large cities at low latitudes, such as Los Angeles, has become today the most important and common air pollution problem in urban areas throughout the world. Overall, the photochemical smog reactions can be summarized as

$$\text{ROG} + \text{NO}_x + \text{sunlight} \rightarrow \text{O}_3,\ \text{PAN},\ \text{HCHO},\ \text{HNO}_3,\ \text{PM},\ \ldots \qquad (16.6.3)$$

where ROG are primary reactive organic gases and $NO_x$ include primary NO and mostly secondary $NO_2$. This smog includes carbon monoxide (CO), ozone ($O_3$) formaldehyde (HCHO), peroxyacetyl nitrate (PAN), nitric acid ($HNO_3$), particulate matter (PM; especially secondary particles, such as nitrates and organic particles), and other products.

A full chemical reaction scheme is required to simulate complex phenomena, such as the photochemical smog described above, and can be incorporated today only inside Eulerian grids or Lagrangian box models. A typical reaction set, applied in each grid cell at each time step, can be written in terms of linear combinations:

$$\sum_{m=1}^{M} r_{nm} C_m \rightarrow \sum_{m=1}^{M} p_{nm} C_m \qquad n = 1, 2, \ldots, N \tag{16.6.4}$$

where $M$ species participate in $N$ reaction steps, $c_m$ is the concentration of the $m$th species, and $r_{nm}$ and $p_{nm}$ are numerical constants. Each reaction rate is generally expressed as a product of the concentrations of the species involved, with a temperature-dependent rate constant.

The main difficulty in using Equation (16.6.4) to simulate the photochemical smog is the treatment of **organic compounds**. In fact, due to the very large number, organic species cannot all be included explicitly. Three different types of gas-phase chemical mechanisms are generally used: (1) surrogate mechanisms, which use the chemistry of one or two compounds in each class of organics to represent the chemistry of all species in that class; (2) lumped mechanisms, in which the grouping of chemical compounds is done on the bases of their similar structure and reactivity; and (3) the carbon bond approach, which splits each organic molecule into functional groups using the assumption that the reactivity of the molecule is dominated by the chemistry of each functional group. Each classification technique necessarily introduces a simplification and, therefore, a potential simulation error.

Some key reactions involve the **photolysis** of such species as $NO_2$, HCHO, and nitrous acid (HONO). These one-specie reactions require the calculation of the photolysis rate constant which is a function of, among other things, of solar elevation and temperature.

Aerosol chemistry is particularly difficult to simulate and computationally expensive. However, inclusion of aerosol dynamics within air quality models is of primary importance because of the health effects associated with fine particles in the atmosphere, visibility impairment, and the acid deposition problem. Simple first-order reaction terms can be used to simulate the transformation of $SO_2$ into sulfates and $NO_x$ into nitrates. These terms can be included in any model. However, a comprehensive simulation of aerosol processes can only be performed within an Eulerian grid or a Lagrangian box model and must include the following fundamental equation of aerosol dynamics (Milford and Russell, 1993) which describes aerosol transport, growth, coagulation, and sedimentation

$$\frac{\delta n}{\delta t} + \nabla \cdot \bar{\mathbf{u}} n + \frac{\delta l}{\delta \nu} = \frac{1}{2}\int_0^{\nu} \beta(\bar{\nu}, \nu - \bar{\nu}) n(\bar{\nu}) n(\nu - \bar{\nu})\, d\bar{\nu} - \int_0^{\infty} \beta(\bar{\nu}, \nu) n(\bar{\nu}) n(\nu)\, d\bar{\nu} - \nabla \cdot \mathbf{C} n \tag{16.6.5}$$

where $n$ is the particle size distribution function, $\bar{\mathbf{u}}$ is the wind velocity, $I$ is the droplet current that describes particle growth and nucleation due to gas-to-particle conversion, $\nu$ is the particle volume, $\beta$ is the rate of particle coagulation, and $\mathbf{C}$ is the sedimentation velocity.

The simulation of heterogeneous and aqueous-phase chemistry is of key importance for regional-scale acid deposition and **stratospheric** ozone models, but is usually neglected in urban photochemical applications where the main goal is the simulation of **tropospheric** ozone.

## Deposition

Chemical species are removed from the atmosphere by two mechanisms: reaction and deposition. While chemical reactions may produce new pollutants, deposition is the real process in which the atmosphere cleans itself. Some pollutants are highly reactive and, consequently, have short lifetimes. For example, ozone has a typical lifetime of 2 min and, therefore, its concentration will drop unless it is continuously regenerated. Other pollutants have longer lifetimes. For example, $SO_2$ has a typical lifetime of 13 days. Therefore, under certain circumstances, it can easily accumulate during multiday episodes (e.g., the "London" smog). Finally, there are pollutants with very large lifetimes. Because of their low reactivity, they do not cause adverse effects on human health but, nevertheless, can diffuse on a global scale and affect the thermal balance of the Earth. Methane and carbon dioxide are a good example, both with a typical lifetime of 7 years.

Deposition terms can be introduced in any model discussed above. For example, dry deposition can be described by the following formula

$$F_i = V_d c_i \tag{16.6.6}$$

where $F_i$ is the flux of a species $i$ to the ground, $c_i$ is the concentration of the species $i$ at some reference height (e.g., 1 m), and $V_d$ is the deposition velocity. The term $V_d$ has been measured under various meteorological conditions and for a number of surface types (Wesley et al., 1985). Therefore, the calculation of $F_i$ is straightforward.

Wet deposition (i.e., precipitation scavenging) depends upon the intensity and size of raindrops. Fog and cloud droplets can also absorb gases, capture particles, and accelerate chemical reactions. Wet deposition is quantified by computing the wet flux of pollution to the surface. This calculation requires the estimate of the washout coefficient, which can be inferred (Scott, 1982) as a function of storm type and precipitation amounts.

Because of dry and wet deposition, acidic components such as sulfuric acid particles, particulate nitrate, and nitric acid gas are transferred from the atmosphere to the Earth. Areas which are tens and hundreds of kilometers downwind of large $SO_2$ and $NO_x$ sources (e.g., power plants and smelters) suffer the greatest impact.

## Statistical Models

Statistical models are often used in air pollution studies. They include frequency distribution studies, time series analysis, Kalman filters, receptor-modeling techniques, and others. A general distinction between statistical and deterministic approaches is that air pollution deterministic models initiate their calculations at the pollution sources and aim at the establishment of cause/effect relationships, while statistical models are characterized by their direct use of air quality measurements to infer semiempirical relationships. Although very useful, especially for real-time short-term forecasting, statistical models are generally unable to provide cause/effect relationships, with the exception of receptor modeling.

The basic concept of the receptor-modeling approach is the apportionment of the contribution of each source, or group of sources, to the measured concentrations without reconstructing the dispersion pattern and trajectory of the pollutants. Typically, receptor models start with *observed* ambient aerosol concentrations measured at a receptor and seek to apportion the concentrations among several source types (e.g., industrial, transportation, soil, etc.), based on the known chemical composition (i.e., the chemical fractions) of source and receptor materials.

In mathematical notation, the concentration $c_{ik}$ of the species $i$ in the $k$th sample at a certain monitoring station can be written as

$$c_{ik} = \sum_{j=1}^{p} a_{ij} D_{jk} E_{jk} \tag{16.6.7}$$

where $p$ sources (or groups of sources) are assumed to contribute to $c_{ik}$, $a_{ij}$ is the fractional amount of the component $i$ in the emission from the $j$th source, $D_{jk}$ is the atmospheric dispersion term, and $E_{jk}$ is the emission rate (i.e., $D_{jk}E_{jk} = S_{jk}$ is the total contribution of the source $j$ to the $k$th sample at the receptor location). Dispersion models assume $a_{ij}$, $D_{jk}$, and $E_{jk}$ to be known (or obtainable from emission and meteorological data) and estimate the output $c_{ik}$. For receptor models, the concentrations $c_{ik}$ and source "profiles" $a_{ij}$ are measured instead, and the $D_{jk}E_{jk}$ products are computed as a model result.

## Ground Water Pollution Modeling

*Tissa Illangasekare*

### Saturated Groundwater Flow

The description of the exact movement of fluid particles in a porous medium is difficult (or impossible) as it is not practical to define exactly the flow domain that is described by the geometry of the internal solid surfaces. The problem can be treated at the molecular level, microscopic level, or macroscopic level.

The treatment of the behavior of a system of molecules using theories of classical fluid mechanics is extremely difficult because of the large number of molecules involved and the difficulties in identifying all forces and defining the exact pore geometry. Instead of treating individual molecules, the statistical properties of a very large number of molecules may be inferred from laws governing the motion of individual molecules. Still, this approach will also have similar limitations with respect to the need to define the exact pore geometries. A coarser treatment at the microscopic level where fluid is treated as a continuum is feasible, but most applications in groundwater flow may not require this level of refinement. This approach will also require the accurate definition of the pore geometry.

A coarse level of averaging at the macroscopic level that is referred to as the *representative elementary volume (REV)* is used in most applications in porous media flow analysis. Porous medium is defined as a portion of a space occupied partly by a solid phase (solid matrix) and partly by voids. The voids in general are occupied by one (single phase) or more fluid phases (multiphase). This level of treatment assumes that the solid phase is distributed throughout the problem domain and it should be possible to define an REV such that no matter where we place it within the porous media domain, it will contain both solids and voids.

At the macroscopic scale, the rate at which the water flow in a soil is quantified using a variable that is referred to as the *Darcy velocity* or *specific discharge*. This variable, which has the dimensions of velocity, is defined as the discharge per unit gross area of soil that includes both the pore space and the grains in a flow section. For incompressible fluids a relationship that is referred to as *Darcy's law* expresses the Darcy velocity in terms of a parameter referred to as hydraulic conductivity, $K$, and the gradient of the piezometric head, $h$. Darcy's law for saturated flow (a single fluid filling the pore space) in soils is given by

$$\mathbf{q} = -K\nabla h \tag{16.6.8}$$

where $\mathbf{q}$ is the specific discharge or Darcy velocity ($L/T$) and $h$ is the piezometric head ($L$).

In groundwater flow, as the velocities are generally very small, the velocity head is neglected and the driving head becomes the sum of the elevation and the pressure heads. The piezometric head is defined as

$$h = h_z + h_p = z + \frac{p}{\rho g} \tag{16.6.9}$$

where $\rho$ is the density of water.

In anisotropic aquifers where the hydraulic conductivity changes with flow direction, $\mathbf{K}$ is a second-rank tensor given as

$$\left[K\right] = \begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix} \tag{16.6.10}$$

It can be shown that it is always possible to find three mutually orthogonal directions in space such that

$$K_{ij} \neq 0 \text{ for all } i = j$$

$$K_{ij} = 0 \text{ for all } i \neq j$$

These directions in space are called the principal directions of the anisotropic porous medium. When principal directions are parallel to the axes of the coordinate system, the tensor reduces to a hydraulic conductivity vector given as,

$$[K] = \begin{bmatrix} K_{xx} & 0 & 0 \\ 0 & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{bmatrix} \tag{16.6.11}$$

For conservation of mass,

$$-\nabla \cdot \rho \mathbf{q} = \frac{\partial n\rho}{\partial t} \tag{16.6.12}$$

For homogeneous, incompressible fluid and a nondeformable porous medium,

$$\nabla \cdot \mathbf{q} = 0 \tag{16.6.13}$$

Introducing head, the mass conservation equation can be written as

$$\nabla \mathbf{q} + S_s \frac{\partial h}{\partial t} = 0 \tag{16.6.14}$$

where $S_s$ is the specific storage, defined as the volume of water added to storage, per unit volume of porous medium, per unit rise in piezometric head. This is given as

$$S_s = \rho g(\alpha + n\beta) \tag{16.6.15}$$

where $\beta$ is the compressibility of water and $\alpha$ is the compressibility of the soil matrix.

Combining Darcy's law and the equation of mass conservation, the general equation of saturated groundwater flow is obtained as

$$\nabla \cdot K \nabla h = S_s \frac{\partial h}{\partial t} \tag{16.6.16}$$

The initial and boundary value problem obtained by combining the above second-order partial differential equation with the initial head in the aquifer and the head or flux conditions at the aquifer boundary is solved to obtain the unknown head in the aquifer. The head distribution can then be used with Darcy's law to obtain the groundwater flow velocity in the aquifer.

### Solute Transport in Groundwater

Transport of dissolved chemicals in aquifers is generally considered to be the result of two processes, namely, advection and dispersion. Advection is the process by which the solute gets transported due to the average motion of water through the intergranular pore spaces of the porous medium. In the mathematical representation of this process in the REV, a macroscopically average velocity that is referred to as the *average linear pore velocity* is used. An approximate value for this average pore water velocity for granular material based on macroscopic variables is given as

$$v = \frac{q}{n} \tag{16.6.17}$$

where $n$ is the effective porosity. The average liner pore water velocity is also referred to as the *average solution velocity.*

The advective solute transport is given by

$$\mathbf{J_a} = Cq \tag{16.6.18}$$

where $\mathbf{J}_a$ is the vector of solute mass flux (mass per unit time per unit area, [$MT^{-1}L^{-2}$]) and C is the mass concentration of solute per unit volume of the solution ($ML^{-3}$).

Dispersion is the result of two processes that occur in the pore scale, namely, molecular diffusion and mechanical (or hydrodynamic) mixing. Due to molecular diffusion the solute will move from the high-concentration to low-concentration regions in the fluid phase. Fick's first law modified to account for the presence of the solid phase is used to represent the solute flux as a function of the concentration gradient by

$$J_d = -nD_d \cdot \nabla C \tag{16.6.19}$$

where $\boldsymbol{J_d}$ is diffusive flux, [$MT^{-1}L^{-2}$], $n$ is the porosity, $\boldsymbol{D_d}$ [$L^2T^{-1}$], a second-rank tensor is the effective diffusion coefficient of the solute in the porous medium and C is the solute concentration, [$M/L^{-3}$].

The component of dispersion due to mechanical mixing is the result of velocity variation at the microscopic scale. These velocity variations are the result of three basic mechanisms that occur within the pores: (1) viscous shear forces that produce velocity gradients across flow channels, (2) pores size variations produce pore channels with different sizes transmitting water at different pore velocities, and (3) the changing flow directions due to the tortuosity of the flow channels. The combined effect of these variations results in the solute being mixed at the macroscopic scale and producing mass flux along decreasing concentration gradients. As this process is analogous to the diffusion in the microscopic scale, an equation similar to the Fick's first law is used to describe mass flux due to mechanical mixing. This analogous equation is given as

$$J_m = -nD_m \cdot \nabla C \tag{16.6.20}$$

where $J_m$ is the flux due to mechanical mixing, [$MT^{-1}L^{-2}$] and $D_m$ is the coefficient of hydrodynamic (mechanical) dispersion.

The total flux due to molecular diffusion and hydrodynamic dispersion is given as

$$J = J_d + J_m \tag{16.6.21}$$

Substituting for $J_d$ and $J_m$, we have

$$J_m = -n\left(D_d + D_m\right) \cdot \nabla C \tag{16.6.22}$$

Define the dispersion coefficient $D$ as

$$D = D_d + D_m \tag{16.6.23}$$

Equation (16.6.24) reduces to

$$J = -n(D) \cdot \nabla C \tag{16.6.24}$$

In a three-dimensional system the dispersion coefficient is a second-order tensor that takes the form,

$$[D] = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix} \tag{16.6.25}$$

By orienting the x′ axes of the local coordinates at the aquifer point along the direction of groundwater flow (longitudinal direction), the dispersion coefficient tensor can be reduced to

$$[D] = \begin{bmatrix} D_{x'x'} & 0 & 0 \\ 0 & D_{y'y'} & 0 \\ 0 & 0 & D_{z'z'} \end{bmatrix} \tag{16.6.26}$$

The local axes $x'$, $y'$, and $z'$ are the principal axes of dispersion and $D_{x'x'}$, $D_{y'y'}$, and $D_{z'z'}$ are the principal values of the coefficient of dispersion. These coefficients can be expressed in terms of the longitudinal average linear pore velocity as

$$D_{x'x'} = D_d + \alpha_L \bar{v}, \quad \text{etc.} \tag{16.6.27}$$

where $\alpha_L$ and $\alpha_T$ are longitudinal and lateral dispersion coefficients, respectively. The dispersion coefficients that have dimensions of length can be viewed as characteristic lengths of the porous medium at the pore scale. However, in real applications these values are much larger and have been found to depend on the size of the plume (scale dependent).

Combining advective flux given by Equation (16.6.18) and dispersive flux given by Equation (16.6.24) and applying the principal of mass conservation for the solute, one obtains

$$\frac{\partial(nC)}{\partial t} = \nabla \cdot \left(nD \cdot \nabla C - Cq\right) \tag{16.6.28}$$

By substituting the approximation for Darcy's velocity in Equation (16.6.28), the governing equation for solute transport in saturated porous media is obtained as

$$\frac{\partial C}{\partial t} = D \cdot \nabla C - C\bar{v} \tag{16.6.29}$$

The above equation is referred to as the *advection–dispersion equation.* The initial and boundary value problem obtained by combining the above second-order PDE with the initial concentration distribution in the aquifer and the concentration and mass flux at the aquifer boundary is solved to obtain the time and space distribution of the solute concentration in contaminant plumes. It should be noted that to solve the advection–dispersion equation it is necessary to first solve for the groundwater velocities using the groundwater flow equation.

## Surface Water Pollution Transport Modeling

### *Ronald R. Hewitt Cohen and Nevis Cook*

The study of water quality modeling bloomed in the late 1960s and through the 1970s. Administrators and bureaucrats with minimal mathematical and science backgrounds were greatly impressed by presentations of pages of PDEs, and model outputs were often treated as absolute truth. As the field and model users matured, it was recognized that a model is just a group of hypotheses about the way the modeler believes the world works, all put in mathematical terms. The limitations, shortcomings, and difficulties with environmental models are well recognized and accepted. Models are now used as *tools* for decision making and planning.

An industrial facility may want to assess how reducing or increasing the mass or concentration of some pollutant in a discharge will impact the receiving waters. It may be that a dramatic, negative impact might be predicted. Reducing the level of pollutant in the discharge may result in little to no improvement to water quality. Obviously, the results of the modeling effort will dictate the level of effort and cost going toward the treatment of the pollutant.

The same facility may be instructed by the USEPA or the state to control discharges such that water quality criteria in the receiving waters are met. Good models can be used to address the question "what are the implications to the receiving waters if various facility process modifications are applied." Thus, a decision could be made as to the process modifications to be focused upon to match the criteria or standards.

It is not anticipated that every industrial facility has an individual with the capabilities to construct a water quality transport model. There are many models available to run on microcomputers and can be obtained through the USEPA.

## Impact Pathway Methodology

### *Ari Rabl and Peter S. Curtiss*

A step beyond conventional dispersion modeling includes the physical and economic impacts of air pollution. Rational management of the environment requires an assessment of the damage caused by pollution. The logically correct way to analyze environmental impacts is the impact pathway methodology whose principal steps are the following:

- Specification of the relevant technologies and the environmental burdens they impose (e.g., kilograms per second of particulates emitted by the plant);
- Calculation of increased pollutant concentration in all affected regions (e.g., micrograms per cubic meter of particulates, using models of atmospheric dispersion and chemistry);
- Calculation of physical impacts (e.g., number of cases of asthma due to these particulates, using a dose–response function);
- In some cases a fourth step may be called for: the economic valuation of these impacts (e.g., multiplication by the cost of a case of asthma).

The numbers are summed over all receptors (population, crops, buildings, …) that are affected by this pollutant. Formally, the procedure can be represented as an equation for the incremental damage $D$ due to an incremental quantity $Q$ of a pollutant emitted by the plant

$$D = \sum_i f_{dr,i}\Big(f_{\mathrm{disp}-i}(Q)\Big) \tag{16.6.30}$$

where $f_{\mathrm{disp-i}}(Q) = c$ = increase in pollutant concentration for receptor $i$ and $f_{\mathrm{dr},i}(c)$ = dose–response function for receptor $i$; the summation index $i$ runs over all receptors (people, crops, buildings, etc.) of concern.

Which receptors are of concern depends on the circumstances. One can distinguish three kinds of situation:

1. Episodic values (typically for litigation after pollution episodes);
2. Peak values (typically for obtaining a permit for a new plant, by showing that impacts are below a damage threshold or regulatory limit);
3. Expectation values (typically for policy applications such as setting of regulations, by showing that average impacts are acceptable).

For the first two of these the summation will typically be over a limited set of receptors, for instance, the residents in a town. For the third application one will usually want to know the total damage, and the sum should cover all receptors that make a significant contribution to the total.

The notation in Equation (16.6.30) allows the possibility that the impact may be different for different individual receptors. This equation expresses the damage in functional form; hence, this methodology is also known under the name *damage function*. Of course, while this methodology is logically correct, the practical implementation may not always be feasible for lack of appropriate data or models.

The dose–response function

$$Y = f_{dr}(X) \tag{16.6.31}$$

relates the quantity $X$ of a pollutant that affects a receptor (e.g., population) to the physical impact $Y$ on this receptor (e.g., incremental number of deaths). In the narrow sense of the term, $X$ should be the dose actually absorbed by a receptor. But often one uses, as we do in the present section, the term dose–response function in the sense of exposure–response function where $X$ represents the concentration of a pollutant in the ambient air; in that case $f_{dr}(X)$ accounts implicitly for the absorption of the pollutant from the air into the body. Dose–response functions for the classic air pollutants ($NO_x$, $SO_x$, $O_3$, and particulates) are typically of that kind. One can even define aggregated dose–response functions that include more-complicated pathways, for instance, dioxins passing through the food chain, if one interprets the dose–response function to include the aggregated effects of the pathways from a point at the Earth's surface to all final receptors. In the next sections we take a closer look at the major steps of the methodology.

## The Source Term

The first step of the impact pathway analysis is relatively straightforward. One identifies the site and circumstances of a pollution source, e.g., the tons of NO per $kWhr_e$ emitted by particular power plant. For the major air pollutants ($CO_2$, CO, NO, $SO_2$, VOCs, particulate matter) the emission rates for a given technology are quite well known. For the example of power plants the rate of $CO_2$ emission is especially well determined. Emissions of CO, NO, $SO_2$, VOCs, and particulate matter are somewhat less certain, and they can vary with operating conditions. NO emissions, for instance, are likely to increase above the manufacturer's specifications if a selective catalytic reduction unit is not well maintained. There are different grades of oil and coal, and their sulfur content can differ by an order of magnitude; obviously, the emissions of $SO_2$ depend on the quality of the fuel that will be used. Usually, there are strict regulations that enforce an upper limit on the emissions; due to cost constraints power plants are unlikely to operate significantly below these limits.

The situation is less clear with regard to trace pollutants such as lead and mercury, since their content in different grades of coal can vary by much more than an order of magnitude. Furthermore, some of these pollutants are emitted in such small concentrations that their measurement is difficult. The dirtier the fuel, the greater the uncertainty of emissions. Especially with waste incineration, there has been concern over trace pollutants that are emitted into the air.

Probably the most uncertain emissions are emissions from the disposal and storage of wastes, because they depend on events in the future. Solid waste from coal-fired boilers could be dumped into a simple hole in the ground or it could be placed into an engineered landfill with watertight liners; the possible impacts will be totally different. There may or may not be a breach of containment, depending on the quality of construction and management and on natural events such as floods or earthquakes. The main risk from a landfill is the leaching of toxic minerals into groundwater; such risk can be kept negligible by proper construction and management.

### Transport Modes

Pollutants can be emitted to air, water, or soil. The majority of pollutants are first emitted into the air, even if they later pass into the water or the soil. Therefore, most of this section focuses on atmospheric dispersion. Transport in the soil is difficult to model because it can involve complex processes that depend on the physical and chemical properties of the soil at each site. Furthermore, for new installations, such as new landfills, the emissions into the soil are not known in advance; they depend on the integrity of the containment structure over the indefinite future.

Transport by surface water, i.e., rivers, lakes, and the sea, is relatively simple to analyze if fine geographical resolution is not required. Thus, one can divide these bodies of water into a reasonably small number of compartments that are treated as uniformly mixed. For example, a river may be divided into ten sections. A differential equation with empirical coefficients relates the concentration in a section under consideration to the concentration in the section immediately upstream and to the emission into this section. Sedimentation, removal, and decay processes are included.

Similarly, for the dispersion into marine waters one uses a compartment model where each compartment communicates with one or several neighbors, and the volumes and flow rates are known. For instance, in a model used for the analysis of nuclear power plants (EC, 1995c), the European seas have been divided into 34 compartments.

For dispersion in the atmosphere, in general both physical and chemical processes need to be considered (Seinfeld, 1986; Zannetti, 1990). Some pollutants, e.g., $CO_2$, $CH_4$, and $^{133}Xe$, are sufficiently inert chemically that only the physical transport needs to be analyzed. Some are moderately reactive and their chemical transformation needs to be taken into account. $SO_2$, for instance, leads to the formation of $SO_3$, $H_2SO_4$ as well as sulfates (the latter from the interaction with $NH_3$ emitted by, among others, agricultural activities); this can have significant implications for impact analysis on a regional and global scale.* Ozone is a secondary pollutant, formed by the combination of $NO_x$, VOC, and light, and the chemistry is extremely complex.

Even though the modeling of the physical transport of pollutants is difficult, it is far simpler than weather modeling. The reason is that pollutants can be considered a small admixture, passively transported by the currents of the surrounding medium. Such transport is linear: the increase in concentration at a receptor site is proportional to the emission (the only exception arises from secondary pollutants such as ozone whose formation depends on other variables, coupled through nonlinear phenomena).

Furthermore, for most policy applications one needs only expectation values of environmental impacts. While it is well known that chaotic phenomena in the atmosphere render the prediction of the weather impossible beyond a short time, this does not prevent the prediction of expectation values. The climate is much more certain than the weather. For expectation values of air pollution damage it suffices to know the average motion of the surrounding medium from past observations, by contrast to weather modeling where that very motion needs to be predicted in detail.

### Transport in Air

A simple model for atmospheric dispersion is the Gaussian plume, discussed earlier. According to this model the concentration of a pollutant is described by the product of two Gaussian distributions, one for the spread in the vertical direction and one for the spread in the horizontal direction perpendicular to the prevailing wind direction. The plume width parameters are based on empirical correlations and take into account the relevant meteorological conditions.

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* For example, ammonia sulfate aerosols can reduce the impact of global warming (Charlson and Wigley, 1994).

The Gaussian plume is considered adequate for the short range, up to tens of kilometers from the source, even for episodic events (Zannetti, 1990). The use of this model at distances beyond 100 km is generally not recommended, although it is acceptable for the prediction of the average values if correction terms are included for reflection at the surface and at the PBL of the Earth, and if the depletion mechanisms (deposition, chemical transformation, radioactive decay) are correctly accounted for. As an example of dispersion software based on a Gaussian plume, one can cite the ISC model of the USEPA (Wackter and Foster, 1987).

For regional modeling most analysts prefer to rely on more-detailed computer simulations, for example the Harwell Trajectory Model (1993) or the EMEP model of the Norwegian Meteorological Service (Barrett, 1992; Sandnes, 1993; Iversen, 1993). The latter model is used for the official allocation of acid rain budgets among the countries of Europe.

A crucial question concerns the geographic range over which the analysis needs to be extended in order to capture most of the impacts. This involves a balance among the rates of emission, of dispersion, and of removal of a pollutant. A look at the results of long-range transport models for $SO_2$ and NO, for instance, those calculated by EMEP (Sandnes, 1993), shows that these pollutants are transported over hundreds, even thousands of kilometers. This is illustrated in Figure 16.6.3 using the EMEP data for a source at Nantes, assuming uniform receptor density and a linear dose–response function. The range of the analysis must be extended to over 1000 km if one wants to capture 80 to 90% of the total impact. The same holds for any air pollutants with comparable removal rate, as has been confirmed explicitly for radionuclides by Kelly and Jones (1985).

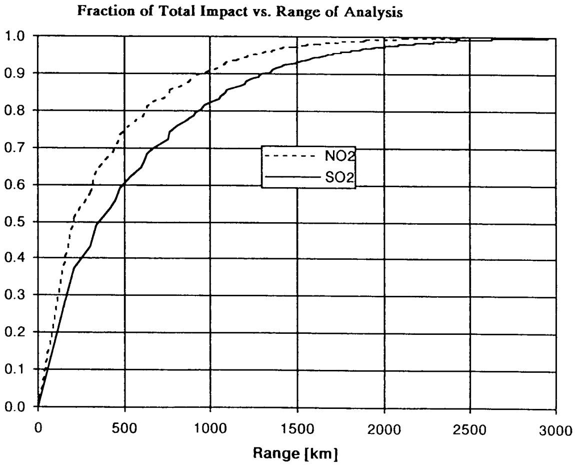


**FIGURE 16.6.3** Fraction of total impact vs. range of analysis, for uniform receptor density and linear dose–response function, based on EMEP data (Barrett, 1994). Wiggles are due to discretization.

## Secondary Pollutants

Many pollutants are transformed into secondary pollutants by chemical reactions in the atmosphere. For example, the reactions shown in Figure 16.6.4 create acid rain (wet deposition of $H_2SO_4$) and ammonium sulfate particulates from $SO_2$.

Another important secondary pollutant is ozone. It is formed when several chemical reactions take place in sequence. The only reaction that forms ozone directly is

$$O + O_2 + M \rightarrow O_3 + M$$

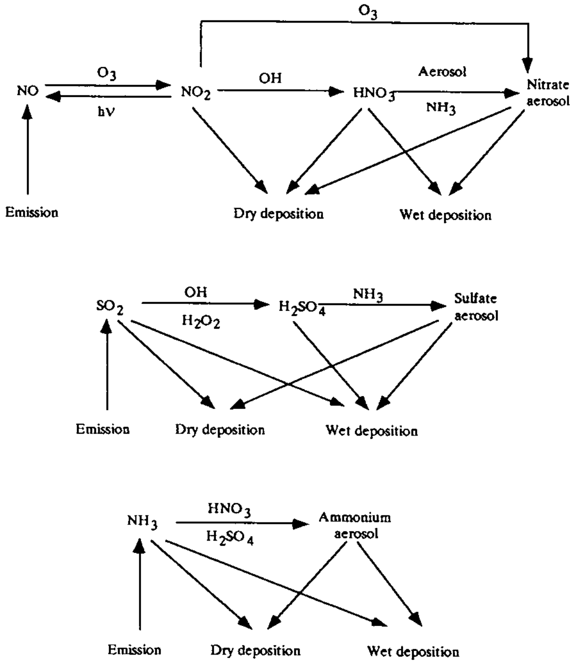


**FIGURE 16.6.4** Chemical reactions included in Harwell Trajectory Model. (From EC, 1995c.)

where M is a molecule such as $N_2$ or $O_2$ whose participation is necessary to conserve energy and momentum. The oxygen atom involved in the formation of ozone is derived from photolysis of $NO_2$ under the action of sunlight (indicated by $h\nu$)

$$NO_2 + h\nu \rightarrow O + NO$$

The presence of VOCs is necessary to prevent the ozone formed from being immediately consumed by NO to produce $NO_2$ in the following reaction:

$$NO + O_3 \rightarrow O_2 + NO_2$$

VOCs enable the transformation of NO into $NO_2$ without consuming ozone. Finally, note also that $NO_2$ plays a double role, since, while being necessary to form ozone, it consumes the radicals needed by VOCs to transform NO into $NO_2$. In fact, an equilibrium is created between these reactions. The concentration of ozone therefore is very dependent on changes in the concentrations of other products, and, due to the complexity of the phenomena, it is observed for example that if VOCs are low (as in the case of an electricity power plant plume), the increase in NO may reduce $O_3$. Figure 16.6.5 shows the influence of the concentrations of nitrogen oxides and VOCs on the concentration of ozone. In particular, we observe the phenomenon mentioned above: the consequence of an increase in NO on atmospheric ozone depends on the concentration of the organic compounds. The ozone content is also strongly dependent on the $[NO_2]$:[NO] ratio. If this ratio is low, the $[O_3]$ content will remain low.

## Dose–Response Functions

*Form of the Dose–Response Function.* By definition, a dose–response function starts at the origin, and in most cases it increases monotonically with dose *X*, as sketched schematically in Figure 16.6.6. At very high doses the function may level off in S-shaped fashion, implying saturation. Dose-response functions are determined from epidemiological studies or from laboratory studies. Since the latter are

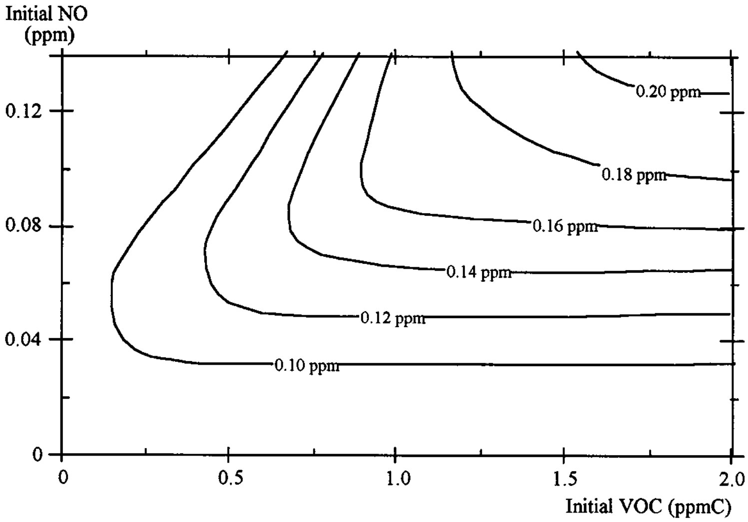


**FIGURE 16.6.5** Isopleth plot for the maximum ozone concentration reached during a fixed length of time as a function of initial NO and VOC concentrations. Details of such a plot depend on site and on weather. (From EPRI 1992.)

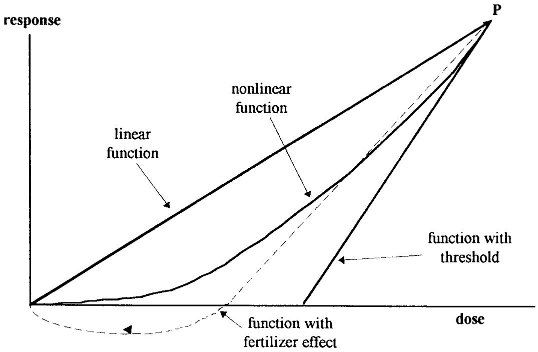


**FIGURE 16.6.6** Possible behavior of dose–response functions at low doses: the four functions shown have the same value at P. For the function with threshold the discontinuity in slope at the threshold is a simplification; in reality there is a smooth transition.

mostly limited to animals, the extrapolation to humans introduces large uncertainties. Another major difficulty is that one needs relatively high doses in order to obtain observable nonzero responses in a sample of realistic size; such doses are usually far in excess of the levels one is concerned with in environmental impact studies. Thus, there is a serious problem of how to extrapolate from the observed data toward low doses. Figure 16.6.6 indicates several possibilities. The simplest is the linear model, i.e., a straight line from the origin through the observed data point(s). Cancer from radioactivity is an example. Linearity also seems to be observed for mortality from fine particulates (Dockery et al., 1993; Dockery and Pope, 1994; Lipfert, 1994).

Another possibility is a straight line down to some threshold, and zero effect below that threshold. Thresholds occur when an organism has a natural repair mechanism that can prevent or counteract damage up to a certain limit. Many dose–response functions for noncancer toxicity are of this type.

There is even the possibility of a "fertilizer effect" at low doses, as indicated by the dashed line in Figure 16.6.6. This can be observed, for example, in the dose–response functions for the impact of $NO_x$ and $SO_x$ on crops: a low dose of these pollutants can increase the crop yield; in other words, the damage is negative. Such a fertilizer effect can occur with pollutants that provide trace elements needed by an organism. It depends on local conditions, in particular the overall balance of nutrients. The fertilizer effect illustrates the link between the understanding of the underlying processes and the choice of the appropriate form for the dose–response function: since N and S are known to be important nutrients for plants, a functional form like the dashed line in Figure 16.6.6 is the most plausible.

If nothing is known about a threshold and a fertilizer effect can be ruled out, the dose–response function could be anywhere between zero and the straight line through the origin, for instance, the curved solid line shown in Figure 16.6.6. *A priori* there is no general rule about the extrapolation to low doses, other than there being no known cases of a dose–response function above the straight line. There is even a case where the same substance causes different cancers according to different dose–response functions, one with and one without threshold. This was established in an experiment (sometimes referred to as the megamouse experiment) in which some 24,000 mice were exposed to the carcinogen 2-acetyl-amino-fluorene at several different dose levels (Frith et al., 1981). The response for liver tumor is linear, whereas the one for bladder tumor has a threshold.

## Site Dependence of Marginal Impacts

From here on we limit ourselves to the important case where the dose–response function $f_{dr}(\mathbf{x},c(\mathbf{x}))$ can be approximated by

$$f_{dr}\left(\mathbf{x},c(\mathbf{x})\right) \approx d(\mathbf{x})c(\mathbf{x}) \quad \text{where} \qquad d(\mathbf{x}) = \frac{df_{dr}\left(\mathbf{x},c(\mathbf{x})\right)}{dc} \tag{16.6.32}$$

is the slope of the dose–response function. With that assumption one can write the damage in the form

$$D = \int dx \int dy \; r(\mathbf{x})d(\mathbf{x})c(\mathbf{x}) \tag{16.6.33}$$

This is obviously exact for any pollutant whose dose–response function is linear, or a straight line with a threshold that is everywhere below the background. It is also valid, regardless of dose–response function, for the evaluation of any marginal impacts, i.e., impacts from small pollutant increments because in that case one can linearize the dose–response function. Since $c(\mathbf{x})$ is linear in the emission, it follows that Equation (16.6.33), and the remainder of this section, are equally applicable to steady-state situations and to emissions that vary with time.

It is instructive to relate the concentration $c(\mathbf{x})$ to the removal rate of the pollutant. There are essentially three mechanisms by which an air pollutant can disappear from the atmosphere (Seinfeld 1986):

1. dry deposition (uptake at the Earth's surface by soil, water, or vegetation);
2. wet deposition (absorption into droplets followed by droplet removal by precipitation);
3. decay or transformation (e.g., decay of radionuclides or chemical transformation of $SO_2$ to $(NH_4)_2SO_4$).

When evaluating the damage of the original pollutant, this pollutant is no longer counted in the equation once it has been transformed; rather from that point on a different dose–response function comes into play for the secondary pollutant. That issue will be addressed below.

The dry deposition rate is proportional to the concentration $c(\mathbf{x})$ at the Earth's surface, and it is customarily written in the form

$$F_{\text{dry}}(\mathbf{x}) = v_{\text{dry}}c(\mathbf{x}) \tag{16.6.34}$$

where $F_{\text{dry}}(\mathbf{x})$ = deposition flux (in $\text{kg/m}^2\cdot\text{sec}$) and $v_{\text{dry}}$ = dry deposition velocity (m/sec).

Wet deposition and decay or transformation can likewise be characterized in terms of fluxes $F_{wet}(\mathbf{x})$ and $F_{trans}(\mathbf{x})$, defined as the rate at which the pollutant is removed by these mechanisms per square meter and per second. Even though in general these fluxes are not proportional to the surface concentration but rather to the average concentration in the air column above *x,* we can write the total removal flux,

$$F(\mathbf{x}) = F_{\text{dry}}(\mathbf{x}) + F_{\text{wet}}(\mathbf{x}) + F_{\text{trans}}(\mathbf{x}) \tag{16.6.35}$$

in terms of the surface concentration $c(\mathbf{x})$ as

$$F(\mathbf{x}) = k(\mathbf{x})c(\mathbf{x}) \tag{16.6.36}$$

if we allow the proportionality constant $k(\mathbf{x})$ to vary with $\mathbf{x}$. The units of $k$ are m/sec, and it could be called removal velocity. Using $F(\mathbf{x})$ and $k(\mathbf{x})$, we can write the damage in the form:

$$D = \int dx \int dy \; r(\mathbf{x}) d(\mathbf{x}) F(\mathbf{x}) / k(\mathbf{x}) \tag{16.6.37}$$

This equation is exact if we interpret Equation (16.6.36) as the definition of $k(\mathbf{x})$.

If the world were homogeneous, with uniform receptor density $r(\mathbf{x}) = r_{\text{uni}}$, uniform dose–response function slope $d(\mathbf{x}) = d_{\text{uni}}$, and uniform removal velocity $k(\mathbf{x}) = k_{\text{uni}}$, the integral in Equation (16.6.37) would be simply

$$D = D_{\text{uni}} = d_{\text{uni}} r_{\text{uni}} \, Q / k_{\text{uni}} \tag{16.6.38}$$

because the surface integral of the removal flux equals the emission

$$Q = \int dx \int dy \; F(\mathbf{x}) \tag{16.6.39}$$

by conservation of matter.

Even though the assumption $k(\mathbf{x}) = k_{\text{uni}}$ may not appear very realistic, especially near a point source, the sensitivity to deviations from uniformity turns out to be surprisingly small, as we will demonstrate below in Figure 16.6.7. The reason is that for typical values of atmospheric dispersion parameters the total impact is dominated by regions sufficiently far from the source that the pollutant can be considered to be vertically well mixed in the PBL, at least as far as expectation values are concerned.

Thus, the simple Equation (16.6.38) can be a useful first estimate, good to an order of magnitude or better, independent of the details of atmospheric dispersion (Curtiss and Rabl, 1996b). It is intuitively plausible that the damage is proportional to the slope $d$ of the dose–response function, to the density $r$ of receptors, and to the emission rate $Q$. Furthermore, it is inversely proportional to the removal velocity $k$. If there were no removal mechanism, the pollutant concentration would increase without limit and the damage would be infinite. This approach can also be adapted for the damage due to a secondary pollutant.

To verify the relevance of Equation (16.6.38) we compare it with real site-dependent results, calculated with the PATHWAYS software package (Curtiss and Rabl, 1995; Curtiss and Rabl, 1996c), which carries out an accurate numerical integration of atmospheric dispersion results over geographic data for population and other receptors. To add substance to the results, we consider a specific impact: the increase in mortality due to $SO_2$ emitted by coal-fired power plants. The dose–response function (based on Sunyer et al., 1996) is linear and can be written in the form:

$$\Delta\text{deaths per year per person} = 5.34 \times \Delta\text{PM}_{10} \text{ concentration } \left(\text{in g/m}^3\right) \qquad (16.6.40)$$

## Example

We consider an annual $SO_2$ output of Q = 1000 ton/year = 30 g/sec. For the atmospheric dispersion we take a curve fit to the EMEP data for a grid cell in the center of France, which yields a removal velocity $k = 0.01$ m/sec. Inserting $Q = 30.9$ g/sec, $k_{\text{uni}} = 0.01$ m/sec, $d_{\text{uni}} = 5.34$ (deaths/year)/(g/m$^3$) and $r_{\text{uni}} = 1.05 \times 10^{-4}$ m$^{-2}$ (for France) into Equation (16.6.38), we obtain

$$D_{\text{uni}} = \frac{5.34 \text{ deaths}/(\text{person}\cdot\text{yr})/(\text{g/m}^3) \times 1.05\text{E-4 persons/m}^2 \times 30.9 \text{ g/sec}}{0.01 \text{ m/sec}} = 1.78 \text{ deaths/yr}$$

This number is shown as the thick solid line in Figure 16.6.7, where the number of deaths per year is plotted vs. emission height $h_e$. The points, connected by lines, show the impacts for five specific sites. We have chosen these sites because there are in fact fossil fuel power plants at these sites (the nearest big city, 25 to 50 km away, is indicated in parentheses). Although the real emissions at the different sites are different, here we have assumed the emissions of the Cordemais plant at all sites to bring out the point of the comparison. The impact is about 2 to 6 times larger than $D_{\text{uni}}$ for the site near Paris and about 0.4 to 0.5 times $D_{\text{uni}}$ for Cordemais, a rural site on the Atlantic Ocean. We also see that there is little variation with stack height.

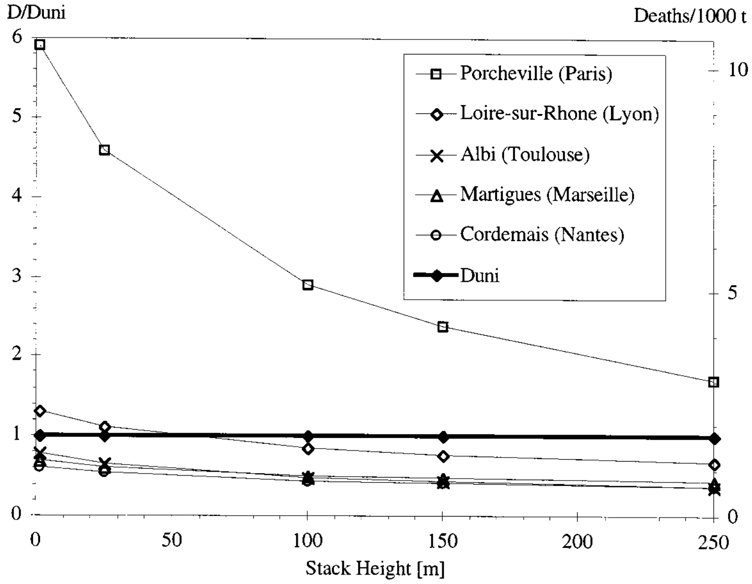


**FIGURE 16.6.7** An example of dependence on site and on height of source: mortality from particulate matter from a coal-fired power plant, for five sites in France and for uniform world model (Equation (16.6.38)). Annual $SO_2$ emission 1000 ton/year.

## Analysis of Uncertainties

By contrast to the relatively small uncertainties and normal (Gaussian) frequency distributions typically encountered in science and engineering, the uncertainties in impact analysis are so large that it would be inappropriate to use error intervals that are additively symmetric about the mean. Instead, one should specify multiplicative intervals, in other words, intervals that are additive on a logarithmic scale. The frequency distributions are not symmetric, with implications that may appear counterintuitive to people not accustomed to them. It is helpful to think in terms of lognormal distributions because they are frequently encountered in impact analysis, analogous to the normal distributions so familiar in the more exact sciences. A variable $x$ has a lognormal distribution if the variable $\ln(x)$ has a normal distribution; in other words, it is normal on a logarithmic scale.

Analogous to the ordinary normal (also known as Gaussian) distribution, which is characterized by two parameters, the mean and the standard deviation, the lognormal distribution can be characterized by the geometric mean and the geometric standard deviation $s_G$. For this distribution the geometric mean is equal to the median: half of the distribution is above, the other half below the median. The geometric standard has a simple interpretation in terms of the 68% confidence interval (a familiar number because for Gaussian distributions 68% of all values are within one standard deviation of the mean): for a lognormal distribution 68% of the values are within the interval $(1/s_G, s_G)$. Likewise, 95% are within the interval $[(1/s_G)^2, (s_G)^2]$. Note, however, that these values are centered around the median rather than the mean; the lognormal distribution is not symmetric. For impacts of primary air pollutants with relatively well-determined dose–response functions, e.g., mortality due to particulates, $s_G$ may be as small as 3. For other impacts, e.g., cancers due to dioxins, the uncertainties could be an order of a magnitude or more.

It is appropriate to note that technical or scientific uncertainties (e.g., uncertainties of emitted quantities or of dose–response functions) are not the only ones. For long-term impacts, such as cancers caused by radioactive waste, one needs to make assumptions about scenarios for the future: what quantities of radionuclides will leak into the environment and how many people will be affected by them. For the estimation of damage costs, there is also the matter of policy/ethical choice, e.g., about discount rate and value of human life.

# 16.7 Global Climate Change

## *Frank Kreith*

There is consensus in the scientific community that continuing the emission of $CO_2$ and other "greenhouse" gases (methane, nitrous oxide, ozone, and chlorofluorocarbons or CFCs) into the atmosphere at current rates will lead to a warming of the Earth. General circulation models of the atmosphere indicate that a doubling of $CO_2$ concentration in the atmosphere will trap sufficient solar radiation to increase the average global temperature by the middle of the 21st century at least 2°C, but possibly as much as 5°C according to the Congressional Research Service (Morrison, 1989). Although critics of these projections argue that the available models do not accurately portray the potential feedback mechanisms from clouds and oceans to warming, and question the amount, timing, and location of the temperature increase, there is agreement that greenhouse gases trap radiation and increase the global temperature. The latest international scientific assessment concluded that "evidence suggests that there is a discernible human influence on global climate" (Watson et al., 1995).

Despite uncertainty over the magnitude, timing, and potential impacts of global warming, there is general agreement that those policies and technologies that reduce the emission of greenhouse gases and have no adverse economic impact should be implemented now. Highest priorities relate to energy conservation, improved efficiency in energy generation, emission reduction from transportation, reforestation, and phasing out of CFCs (see Chapter 9). These proposed actions represent challenges to many facets of mechanical engineering.

## Technical Background

The greenhouse effect is a natural phenomenon and one of the most well established theories in atmospheric science (see Figure 16.7.1). Most of the solar radiation impinging on Earth is in the frequency range below 3 μm. Radiation in this frequency band can readily penetrate Earth's atmosphere and is absorbed by the Earth. But most of the thermal radiation emitted by the Earth is infrared, i.e., in a frequency range above 3 μm, which is partly absorbed and reflected by the atmosphere. Gases in the atmosphere thus prevent part of the radiation emitted by the Earth from escaping into space and trap enough radiation to maintain our climate equilibrium. The atmosphere acts like the glass windows in a greenhouse — hence, the name *greenhouse effect*. Without this effect the Earth would be about 60°F cooler and life as we know it would not exist.

Figure 16.7.2 shows the distribution of the gases in the atmosphere that participate in the greenhouse effect, as well as the industrial sectors emitting them. An increase in the amount of atmospheric greenhouse gases increases the amount of radiation absorbed by the atmosphere and thus reduces the amount of radiation emitted by the Earth that can pass into space. This causes warming of the Earth. Carbon dioxide is the principal greenhouse gas, responsible for over one half of the predicted warming of the Earth. Most of the generation of $CO_2$ results from the burning of fossil fuels. Its primary sources are electric utilities (33%), transportation (31%), industrial processes (24%), and heating and cooling of buildings (12%). Methane, CFCs, ozone, and nitrous oxide constitute the balance of greenhouse emission. Carbon dioxide emissions have increased globally by 25% since the industrial revolution 200 years ago, and there has been an over 10% increase in the last 30 years alone. In the same period, methane concentration has more than doubled (from 800 to 1700 ppb).

Temperature records compiled by the United Kingdom Meteorological Office indicate that the Earth's average temperate has risen roughly 1°F since 1860 (see Figure 16.7.3). Since $CO_2$ is the principal greenhouse gas, estimating its growth is important for future prediction of climate change. Although all fossil fuels emit $CO_2$ when burned, their emission per unit energy produced is not equal. Natural gas is the cleanest fossil fuel. Oil combustion emits between 38 and 43% more $CO_2$ than natural gas, whereas coal combustion contains from 72 to 95% more $CO_2$ per unit energy released than natural gas. Ocean

**FIGURE 16.7.1** Schematic diagram of the greenhouse effect.

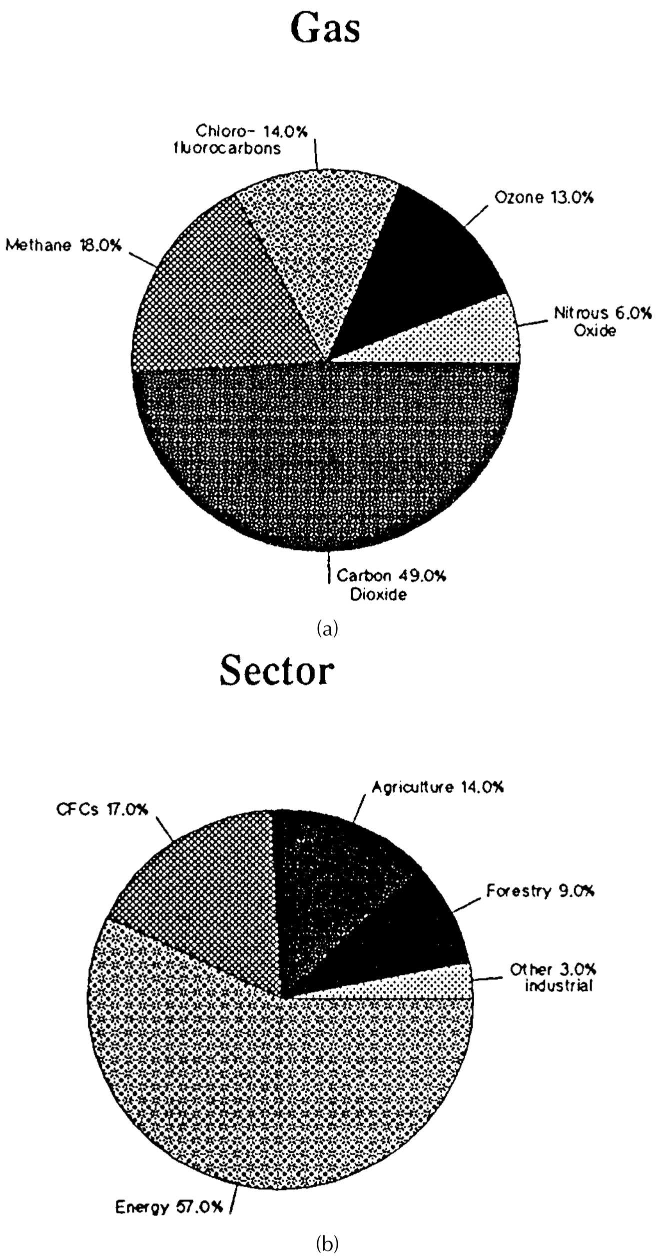
and trees act as carbon sinks because they absorb $CO_2$. Trees absorb $CO_2$ during the process of photosynthesis. Deforestation is important because it not only eliminates a mitigating factor of global warming, but when wood is burned, it too emits carbon dioxide directly into the atmosphere.

## Potential Impacts of Global Climate Change

In its 1989 report to Congress, the USEPA sought to identify the impacts of global warming on specific geographic areas. The agency used simulations from three general circulation models — Goddard Institute for Space Studies (GISS), Geophysical Fluids Dynamics Laboratory (GFDL), and Oregon State University (OSU) — to project the effects of climate change on four regions: Southeast, Great Lakes, Great Plains, and California. The three models are in general agreement that a doubling of carbon dioxide in the atmosphere will increase the temperature, but they differ in magnitude, predicting between 3 and 5°C. Although they concur that annual precipitation will increase, their regional projections vary — the GFDL model predicts reduced precipitation in the Southeast, the GISS in the Great Plains, and the OSU in California. The report acknowledges, however, that the reliability of these regional predictions is limited.

The USEPA assessment of the potential impact of climate change on natural resources and the environment has serious implications for forests, agriculture, water resources, biodiversity, and sea-level rise. The southern boundary of forest species is expected to move northward and drier soils could alter the plant composition with grasslands and hardwoods replacing commercially valuable conifers. Also, fire and pest disturbances could become more frequent. Agricultural productivity would shift northward, causing economic dislocations for farmers in southern states.

One of the most important effects of global warming is a rise in sea level resulting from melting glaciers. Projections of future sea-level rise range from 0.3 to 1.1 m (1 to 3.5 ft) by the end of the next century. A 1-m rise could flood between 26 and 60% of the nation's coastal wetlands and cost up to $100 billion to protect developed areas that would otherwise be flooded.



(a)

(b)

**FIGURE 16.7.2** Greenhouse gas profile. (From U.S. Environmental Protection Agency, 1989.)

## Mitigation Options for Global Warming

There is general agreement that an initial global warming will result from increases in greenhouse gases in the atmosphere, and the position of the U.S. Government, according to the Office of Science and Technology Policy issued in 1996, is that "we collectively must redouble our efforts in identifying the most cost-effective global approaches to reduce emissions in both the near- and long-term utilizing a broad portfolio of actions." However, the scientific uncertainty regarding the timing and severity of future climate impacts and their consequences creates a policy dilemma of what actions should be taken.

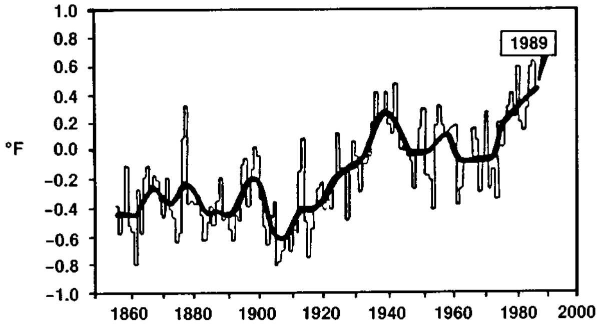


**FIGURE 16.7.3** Global temperature change since 1860. Variation of annual surface temperatures for the world. The solid line shows long-term trends. The planet has warmed an average of almost 1° F. (From United Kingdom Meteorological Office, 1989.)

Because measures to limit greenhouse gas emission require efforts lasting many years and could affect the economic health of a country, the costs of climate policy and the technical means of achieving emission reduction must be considered with the focus on obtaining the largest reduction in potential greenhouse warming at the lowest cost to society. To date, $CO_2$ from combustion of fossil fuels has been the primary focus of attention. A comprehensive look at mitigation options, however, must consider the emission of all greenhouse gases to compare the relative importance of different emissions. The concept of a global warming potential to estimate the $CO_2$-equivalent emission of each of the major greenhouse gases is useful. Table 16.7.1 shows an estimate of greenhouse gas emissions from various human activities.

Various scenarios of the $CO_2$-equivalent reduction achievable by various mitigation measures have been studied. The various mitigation measures were grouped into two categories. The "best practice" technology options shown in Table 16.7.2 can be implemented now at no cost or even at net savings, but they are not used because of institutional and other barriers. Additional options shown in Table 16.7.3 either cost money or have benefits that are not readily quantified or face other implementation obstacles. In this study, no forecasts or scenarios for the future were used, but the results were applied to a 1989 base year.

Inspection of Table 16.7.2 indicates that improved energy efficiency in residential and commercial buildings will reduce demand for fossil fuel and, thereby, also reduce emissions. Conservation measures that reduce the use of electric power are the most significant. For example, improved commercial lighting to reduce the energy consumption by about 45% would not only save money, but if installed in commercial buildings, would result in electricity savings of about 10% from space-conditioning requirements.

The potential for reducing electricity consumption in the industrial sector with currently available technology is about 30%. A case study of energy-intensive industries such as steel mills and petrochemical plants indicates that energy savings of the order of 25 to 30% in direct industrial fuel use may be available economically by investing in more-efficient furnaces, energy recovery systems, and other process equipment. Also, increased use of cogeneration technologies would produce cost-effective $CO_2$ reductions as shown in Table 16.7.2.

The other important sector in which large reductions in greenhouse gas emissions can be achieved is transportation. These reductions in greenhouse gas emissions are largely through improved fuel economy and better transportation management methods that reduce traffic congestion (see Section 10, Transportation).

Mitigation measures outside the energy sector involve landfills, CFC use, agricultural activity, and forests. For example, the collection and combustion of landfill gas could reduce methane emission by about 65%. For a discussion of the other mitigation methods, the reader is referred to the original studies cited.

**TABLE 16.7.1 Estimate of Current Greenhouse Gas Emissions from Human Activity**

| Source | Annual Emissions (Mt/year)[a] World | Annual Emissions (Mt/year)[a] U.S. | $CO_2$-Equivalent (Mt/year)[a] World | $CO_2$-Equivalent (Mt/year)[a] U.S. |
|---|---|---|---|---|
| | *$CO_2$ emissions* | | | |
| Commercial energy | 18,800 | | 18,800 | |
| Tropical deforestation | 2,600 | | 2,600 | |
| Other | 400 | | 400 | |
| **Total $CO_2$** | **21,800** | **4,800** | **21,800** | **4,800** |
| | *$CH_4$ emissions* | | | |
| Rice cultivation | 110 | | 2,300 | |
| Enteric fermentation | 70 | | 1,500 | |
| Fuel production | 60 | | 1,300 | |
| Landfills | 30 | | 600 | |
| Tropical deforestation | 20 | | 400 | |
| Other | 30 | | 600 | |
| **Total $CH_4$** | **320** | **50** | **6,700** | **1,050** |
| | *CFC emissions* | | | |
| **Total CFCs** | **0.6** | **0.3** | **3,200** | **1,640** |
| | *$N_2O$ emissions* | | | |
| Fertilizer use | 1.5 | | 440 | |
| Coal combustion | 1.0 | | 290 | |
| Tropical deforestation | 0.5 | | 150 | |
| Agricultural wastes | 0.4 | | 120 | |
| Land cultivation | 0.4 | | 120 | |
| Fuel and industrial biomass | 0.2 | | 60 | |
| **Total $N_2O$** | **4.0** | **1.4** | **1,180** | **410** |
| **Overall total** | | | **32,880** | **7,900** |

[a] Millions of metric tons based on the estimated global warming potential (GWP) for a 100-year averaging time (6): $CO_2 = 1$, $CH_4 = 21$, $N_2O = 290$, CFC-11 = 3500, CFC-12 = 7300 and CFC-113 = 4200. Values give the $CO_2$-equivalent radiative forcing for an instantaneous injection of 1 kg of gas into the atmosphere. Values for $CH_4$ include the estimated indirect effects of $CO_2$ produced. However, the GWP does not incorporate complex couplings with other greenhouse gases such as stratospheric and tropospheric ozone and their precursor emissions. The GWP thus provides only a preliminary basis for comparing diverse mitigation strategies.

From Ruben, E.S., Realistic Mitigation Options for Global Warming, *Science,* 257, 261–266, 1993. With permission.

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**TABLE 16.7.2 Best-Practice Technology Options Available at Little or No Net Cost that are not Fully Implemented Due to Institutional and Other Barriers**

| Option | $CO_2$-Equivalent Reduction[a] | Net Cost[b] |
|---|---|---|
| | *Residential and commercial energy use* | |
| Electricity efficiency | | |
| 1. White roofs and trees[c] | 32 | –84 |
| 2. Res. lighting[d] | 39 | –79 |
| 3. Res. water heating[e] | 27 | –74 |
| 4. Com. water heating[f] | 7 | –72 |
| 5. Com. lighting[g] | 117 | –71 |
| 6. Com. cooking[h] | 4 | –70 |
| 7. Com. cooling[i] | 81 | –64 |
| 8. Com. refrigeration[j] | 15 | –60 |
| 9. Res. appliances[k] | 72 | –44 |
| 10. Res. space heating[l] | 74 | –39 |
| 11. Com. and Ind. space heating[m] | 15 | –35 |
| 12. Com. ventilation[n] | 32 | 1 |
| Oil and gas efficiency[o] | 300 | –62 |
| Fuel switching[p] | 74 | –90 |
| **Sector total** | **890** | **–62 (–78/–47)** |
| | *Industrial energy use* | |
| Electricity efficiency[q] | 137 | –43 |
| Fuel use efficiency[r] | 345 | –24 |
| New cogeneration[s] | 45 | –18 |
| **Sector total** | **527** | **–28 (–42/–14)** |
| | *Transportation energy* | |
| Light-duty vehicles[t] | 251 | –40 |
| Heavy-duty trucks[u] | 39 | –59 |
| **Sector total** | **290** | **–43 (–21/–75)** |
| | *Power plants* | |
| Coal plants[v] | 45 | –0 |
| Hydroelectric plants[w] | 12 | –0 |
| Nuclear plants[x] | 42 | 2 |
| **Sector total** | **99** | **1 (0/2)** |
| Landfill gas[y] | 230 | **1 (0.4/2)** |

**TABLE 16.7.2 Best-Practice Technology Options Available at Little or No Net Cost that are not Fully Implemented Due to Institutional and Other Barriers (continued)**

| Option | $CO_2$-Equivalent Reduction[a] | Net Cost[b] |
|---|---|---|

Numbers with options refer to steps in Figure 1. Com., commercial; Res, residential; Ind, industrial.

[a] Equivalent $CO_2$ reduction in millions of metric tons based on 1989 fuel and electricity use. [b]Net implemented cost in dollars per ton of $CO_2$-equivalent. Costs are mid-range estimates based on a 6% real discount rate, constant 1989 dollars. Parentheses give low/high range for average cost reflecting real discount rates of 3 to 10% plus uncertainty across different studies or estimates. [c]Plant shade trees and paint roofs white at 50% of residences to reduce air conditioning use and the urban heat island effect by 25%. [d]Replace incandescent lighting (2.5 inside and 1 outside light bulb per residence) with compact fluorescents to reduce lighting energy consumption by 50%. [e]Efficient tanks, increased insulation, low-flow devices, and alternative water heating systems to improve efficiency by 40 to 70%. [f]Residential measures above, plus heat pumps and heat recovery systems to improve efficiency by 40 to 60%. [g]Replace 100% of commercial light fixtures with compact fluorescent lighting, reflectors, occupancy sensors, and day lighting to reduce lighting energy consumption by 30 to 60%. [h]Additional insulation, seals, improved heating elements, reflective pans, and other measures to increase efficiency by 20 to 30%. [i]Improved heat pumps, chillers, window treatments, and other measures to reduce commercial cooling energy use by 30 to 70%. [j]Improved compressors, air barriers, food case enclosures, and other measures to improve efficiency 20 to 40%. [k]Implementation of new appliance standards for refrigeration and use of no-heat drying cycles in dishwashers to improve efficiency of refrigeration and dishwashers by 10 to 30%. [l]Improved and increased insulation, window glazing, and weather stripping along with increased use of heat pumps and solar heating to reduce energy consumption by 40 to 60%. [m]Use measures similar to residential sector to reduce energy consumption by 20 to 30%. [n]Improved distribution systems, energy-efficient motors, and other measures to improve efficiency 30 to 50%. [o]Efficiency measures similar to those for electricity to reduce fossil fuel energy use by 50%. [p]Switch 10% of building electricity use from electric resistance heat to natural gas heating to improve overall efficiency by 60 to 70%. [q]More efficient motors, electrical drive systems, lighting and industrial process modifications to improve electricity efficiency by 30%. [r]Energy management, waste heat recovery, boiler modifications, and other industrial process enhancements to reduce fuel consumption by 30%. [s]An additional 25,000 MW of co-generation plants to replace existing industrial energy systems. [t]Use existing technology to improve fuel economy to 32.5 mpg (CAFE) with no changes in the existing fleet. [u]Use existing technology to improve fuel economy to 18.2 mpg (CAFE) with no changes in the existing fleet. [v]Improve efficiency of existing plants by 3% through improved plant operation and maintenance. [w]Improve efficiency by 5% through equipment modernization and maintenance. [x]Increase the annual average capacity factor of existing plants from 60 to 65% through improved maintenance and operation. [y]Reduce landfill gas generation by 60 to 65% by collecting and burning in a flare or energy recovery system.

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**TABLE 16.7.3 Additional Mitigation Options that are Costly or that have Significant Other Benefits or Costs that are not Readily Quantified. Some of these Options would Face Serious Implementation Obstacles because of Such Factors**

| Mitigation Option | $CO_2$-Equivalent Reduction[a] | Net Cost[b] |
|---|---|---|
| *Industrial energy use* | | |
| Fuel switching[c] | 24 | 60 |
| *Transportation energy use* | | |
| Demand management[d] | 49 | –22 (–50/5) |
| Light-duty vehicle efficiency (change in fleet mix)[e] | 53 | 530 (40/1020) |
| Aircraft engine efficiency[f] | 13 | 360 |
| *Electric supply technology*[g] | | |
| Advanced coal[h] | 200 | 280 |
| Natural gas[i] | 850 | 32 (17/46) |
| Nuclear[j] | 1500 | 49 (28/69) |
| Hydroelectric | 30 | 38 |
| Biomass | 130 | 36 (29/42) |
| Wind | 30 | 79 (33/125) |
| Solar photovoltaic | 400 | 87 |
| Solar thermal | 540 | 160 |
| **Sector total**[k] | **1780** | **50 (30/70)** |
| *Halocarbon use*[l] | | |
| Non-halocarbon substitutes[m] | 302 | 0.02 |
| CFC conservation[n] | 509 | 0.04 |
| HCFC HFC/aerosols, etc.[o] | 248 | 0.6 |
| HFC (chillers)[p] | 88 | 3 |
| HFC (auto air conditioning)[q] | 170 | 5 |
| HFC (refrigerators) | 11 | 11 |
| HCFC (other refrigeration)[r] | 67 | 4 |
| HCFC/HFC (refrigerator insulation) | 14 | 28 |
| **Sector total** | **1409** | **1.4 (0.9/3)** |

**TABLE 16.7.3 Additional Mitigation Options that are Costly or that have Significant Other Benefits or Costs that are not Readily Quantified. Some of these Options would Face Serious Implementation Obstacles because of Such Factors (continued)**

| Mitigation Option | $CO_2$-Equivalent Reduction[a] | Net Cost[b] |
|---|---|---|
| *Domestic agriculture* | | |
| Nitrogenous fertilizers[s] | 126 | 2.5 |
| Paddy rice[t] | 23 | 0.5 |
| Ruminant animals[u] | 84 | 2.0 |
| **Sector total** | **223** | **2 (1/5)** |
| Reforestation[v] | 242 | 7 (3/10) |
| *Other options* | | |
| New industrial technology[w] | 300 | ? |
| New transportation fuels[x] | 1130 | ? |

[a] Equivalent $CO_2$ reduction in millions of metric tons based on 1989 fuel and electricity use. [b]Net implemented cost in dollars per ton of $CO_2$-equivalent. Includes direct costs only. Many of these measures have additional indirect costs that could be significant (see text). Values are mid-range cost estimates based on a 6% real discount rate, constant 1989 dollars. Values in parentheses give low/high range for average cost for real discount rates of 3 to 10% plus uncertainty across different studies or estimates. [c]Switch current coal consumption in industrial plants to natural gas or oil where technically feasible (estimated at 0.6 quadrillion Btu). [d]Estimate 25% of employer-provided parking spaces and tax remaining spaces to reduce solo commuting by 15 to 20%. [e]Improve on-road fuel economy from 32.5 to 46.8 mpg (CAFE) with additional technology measures and downsizing that require changes in the existing fleet mix. [f]Implement improved fan jet and other technologies to improve fuel efficiency by 20%. [g]Potential emission reductions apply only to one technology at a time and are not cumulative. All cost-effectiveness estimates are relative to existing (1989) coal plants. [h]Based on advanced pulverized coal plants. [i]Based on the use of combined cycle systems in place of coal. Co-firing natural gas at existing coal-fired plants has similar costs but lower reduction potential. [j]Based on advanced light-water reactors replacing current fossil-fuel capacity for baseload and intermediate load operation. [k]Based on replacing all fossil fuel plants in the 1989 generating mix. Replacement of coal plants only yields 1470 Mt/year. Remaining potential after maximum demand reductions and plant upgrades is 950 Mt/year. [l]Includes chlorofluorocarbons (CFC), hydrofluorocarbons (HFC), and hydrochlorofluorocarbons (HCFC). [m]Modify or replace existing equipment to use non-CFC materials as cleaning and blowing agents, aerosols, and refrigerants where technically possible. [n]Upgrade equipment and retrain personnel to improve conservation and recycling of CFCs. [o]Substitute cleaning and blowing agents and aerosols with fluorocarbon substitutes. [p]Retrofit or replace all existing chillers to use fluorocarbon substitutes. [q]Replace existing automobile air conditioners with equipment using fluorocarbon substitutes. [r]Replace commercial refrigeration equipment such as used in supermarkets and transportation with equipment using fluorocarbon substitutes. [s]Reduce nitrogenous fertilizer use by 5%. [t]Eliminate all U.S. paddy rice production. [u]Reduce ruminant animal production by 25%. [v]Reforest 28.7 Mha of economically or environmentally marginal crop and pasture lands and nonfederal forest lands. [w]Increase recycling and reduce energy consumption primarily in the primary metals, pulp and paper, chemicals, and petroleum refining industries through new, less energy intensive technology. [x]Based on replacement of highway transport fuels with alternative fuels that emit no greenhouse gases.

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## Defining Terms

**Aerosol:** Small solid particle or liquid droplet suspended in the air.

**Anthropogenic:** Man-made.

**Deterministic:** Dealing with cause and effect.

**Ensemble average:** Theoretical average, i.e., the value that could be expected as the average from an infinite number of realizations.

**Global warming:** The warming of the earth as a result of the atmosphere which traps solar radiation. Currently, the term global warming is used to denote the temperature increase due to carbon dioxide, methane and other greenhouse gases.

**Greenhouse Gases:** Carbon dioxide, methane and other gases resulting from human activities that increase the amount of solar radiation trapped by the atmosphere.

**Numerical advection errors:** Numerical errors generated by finite-difference solutions of transport terms using an Eulerian grid model.

**Organic compounds:** Chemical species containing one or more carbon atoms.

**Photochemical:** Chemical reactions influenced by light.

**Photolysis:** Chemical decomposition by the action of light.

**Planetary boundary layer, PBL:** The atmospheric layer which is affected by the momentum and heat fluxes generated by the Earth surface (typically, the first 500–1000 m of the atmosphere).

**Stratospheric:** Related to the stratosphere, the portion of the atmosphere approximately between 10 to 50 km above the ground.

**Tropospheric:** Related to the troposphere, the lower level of the atmosphere approximately from the surface to 10 km above.

**Wind shear:** The change in wind speed and direction as a function of height.

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## Further Information

For a comprehensive textbook on air pollution modeling, see Zannetti, 1990, above. Shorter reviews of air pollution modeling topics can be found in Zannetti, 1989, below, and Milford and Russell, 1993, above. For a comprehensive review of air pollution issues, see Seinfeld, 1986. For a complete discussion on atmospheric chemistry, see Finlayson-Pitts and Pitts, 1986, below.

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