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15 INORGANIC AIR POLLUTANTS

15.1 INTRODUCTION

This chapter addresses inorganic air pollutants of various kinds, including gases and particles. Organic air pollutants and the photochemical smog formed from them are discussed in Chapter 16.

Inorganic air pollutants consist of many kinds of substances. Many solid and liquid substances may become particulate air contaminants. Another important class of inorganic air pollutants consists of oxides of carbon, sulfur, and nitrogen. Carbon monoxide is a directly toxic material that is fatal at relatively small doses. Carbon dioxide is a natural and essential constituent of the atmosphere, and it is required for plants to use during photosynthesis. However, CO_2 may turn out to be the most significant air pollutant of all because of its potential as a greenhouse gas that might cause devastating global warming. Oxides of sulfur and nitrogen are acid-forming gases that can cause acid precipitation. Several other inorganic air pollutants, such as ammonia, hydrogen chloride, and hydrogen sulfide are also discussed in this chapter.

A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities. Those added in the greatest quantities are CO, SO_2, NO, and NO_2. (These quantities are relatively small compared with the amount of CO_2 in the atmosphere. The possible environmental effects of increased atmospheric CO_2 levels are discussed later in this chapter.) Other inorganic pollutant gases include NH_3, N_2O, N_2O_5, H_2S, Cl_2, HCl, and HF. Substantial quantities of some of these gases are added to the atmosphere each year by human activities. Globally, atmospheric emissions of carbon monoxide, sulfur oxides, and nitrogen are of the order of one to several hundred million tons per year.

As with most aspects of chemistry in the real world, it is somewhat artificial and arbitrary to divide air pollutants between the inorganic and organic realms. For example, inorganic NO_2 undergoes photodissociation to start the processes that convert organic vapors to aldehydes, oxidants, and other substances characteristic of photochemical smog. Oxidants generated in such smog convert inorganic SO_2 to much more-acidic sulfuric acid, the major contributor to acid precipitation. Numerous other examples could be cited to illustrate the interrelationships among air pollutants of various kinds.

15.2 PARTICLES IN THE ATMOSPHERE

Particles in the atmosphere, which range in size from about one-half millimeter (the size of sand or drizzle) down to molecular dimensions, are made up of an amazing variety of materials and discrete objects that may consist of either solids or liquid droplets (Table 15.1). **Particulates** is a term that has come to stand for particles in the atmosphere, although *particulate matter* or simply *particles*, is preferred usage. Particulate matter makes up the most visible and obvious form of air pollution. Atmospheric **aerosols** are solid or liquid particles smaller than 100 µm in diameter. Pollutant particles in the 0.001 to 10 µm range are commonly suspended in the air near sources of pollution, such as the urban atmosphere, industrial plants, highways, and power plants.

Table 15.1 Important Terms Describing Atmospheric Particles

Term	Meaning
Aerosol	Colloidal-sized atmospheric particle
Condensation aerosol	Formed by condensation of vapors or reactions of gases
Dispersion aerosol	Formed by grinding of solids, atomization of liquids, or dispersion of dusts
Fog	Term denoting high level of water droplets
Haze	Denotes decreased visibility due to the presence of particles
Mists	Liquid particles
Smoke	Particles formed by incomplete combustion of fuel

Very small, solid particles include carbon black, silver iodide, combustion nuclei, and sea-salt nuclei formed by the loss of water from droplets of seawater. Larger particles include cement dust, wind-blown soil dust, foundry dust, and pulverized coal. Liquid particulate matter, **mist**, includes raindrops, fog, and sulfuric acid droplets. Some particles are of biological origin, such as viruses, bacteria, bacterial spores, fungal spores, and pollen. Particulate matter may be organic or inorganic; both types are very important atmospheric contaminants.

Chemical Processes for Inorganic Particle Formation

Metal oxides constitute a major class of inorganic particles in the atmosphere. These are formed whenever fuels containing metals are burned. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal:

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \qquad (15.2.1)$$

Organic vanadium in residual fuel oil is converted to particulate vanadium oxide. Part of the calcium carbonate in the ash fraction of coal is converted to calcium oxide and is emitted to the atmosphere through the stack:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \qquad (15.2.2)$$

A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets:

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (15.2.3)$$

When basic air pollutants, such as ammonia or calcium oxide, are present, they react with sulfuric acid to form salts:

$$H_2SO_4(\text{droplet}) + 2NH_3(g) \rightarrow (NH_4)_2SO_4\,(\text{droplet}) \qquad (15.2.4)$$

$$H_2SO_4(\text{droplet}) + CaO(s) \rightarrow CaSO_4(\text{ droplet}) \qquad (15.2.5)$$

Under low-humidity conditions, water is lost from these droplets and a solid salt aerosol is formed.

The preceding examples show several ways in which solid or liquid inorganic aerosols are formed by chemical reactions. Such reactions constitute an important general process for the formation of aerosols, particularly the smaller particles.

15.3 THE COMPOSITION OF INORGANIC PARTICLES

Figure 15.1 illustrates the basic factors responsible for the composition of inorganic particulate matter. In general, the proportions of elements in atmospheric particulate matter reflect relative abundances of elements in the parent material. The source of particulate matter is reflected in its elemental composition, taking into consideration chemical reactions that may change the composition. For example, particulate matter largely from ocean spray origin in a coastal area receiving sulfur dioxide pollution may show anomalously high sulfate and corresponding low chloride content. The sulfate comes from atmospheric oxidation of sulfur dioxide to form nonvolatile ionic sulfate, whereas some chloride originally from the NaCl in the seawater may be lost from the solid aerosol as volatile HCl:

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (15.3.1)$$

$$H_2SO_4 + 2NaCl(\text{particulate}) \rightarrow Na_2SO_4(\text{particulate}) + 2HCl \qquad (15.3.2)$$

The chemical composition of atmospheric particulate matter is quite diverse. Among the constituents of inorganic particulate matter found in polluted atmospheres are salts, oxides, nitrogen compounds, sulfur compounds, various metals, and radionuclides. In coastal areas, sodium and chlorine get into atmospheric par-

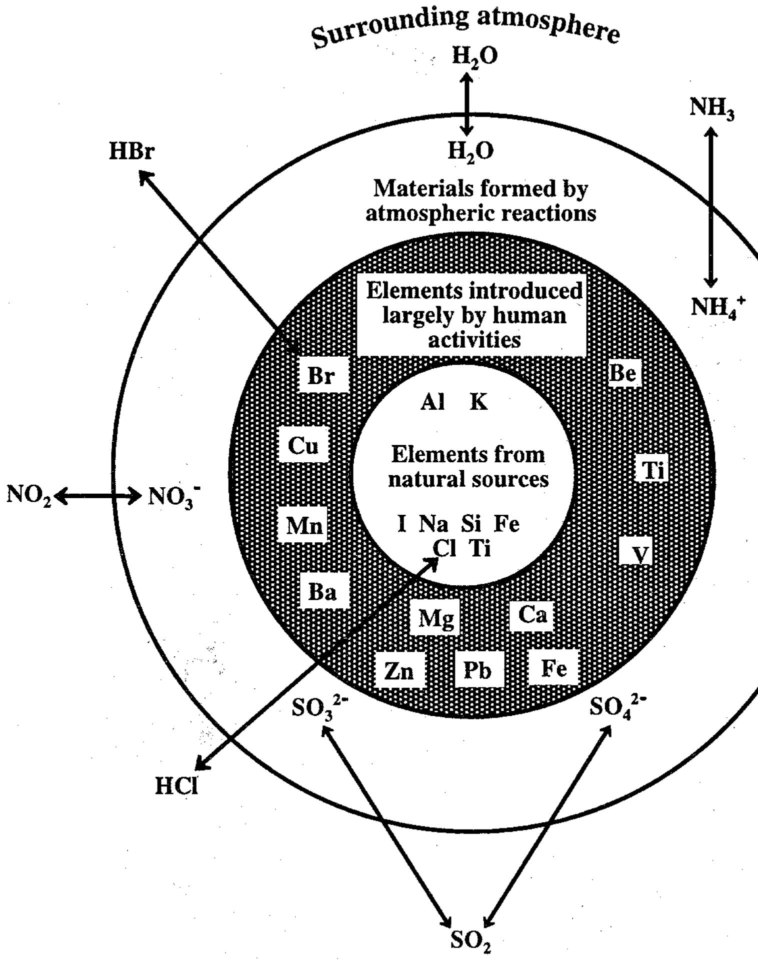

Surrounding atmosphere
H2O
H2O
NH3
NH4+
HBr
Materials formed by atmospheric reactions
Elements introduced largely by human activities
Br
Be
Al K
Cu
Elements from natural sources
Ti
NO2
NO3-
Mn
I Na Si Fe
Cl Ti
V
Ba
Mg
Ca
Zn
Pb
Fe
SO3 2-
SO4 2-
HCl
SO2

Figure 15.1 Some of the components of inorganic particulate matter and their origins.

ticles as sodium chloride from sea spray. The major trace elements that typically occur at levels above 1 µg/m^3 in particulate matter are aluminum, calcium, carbon, iron, potassium, sodium, and silicon; note that most of these tend to originate from terrestrial sources. Lesser quantities of copper, lead, titanium, and zinc, and even lower levels of antimony, beryllium, bismuth, cadmium, cobalt, chromium, cesium, lithium, manganese, nickel, rubidium, selenium, strontium, and vanadium are commonly observed. The likely sources of some of these elements are given below:

- **Al, Fe, Ca, Si**: Soil erosion, rock dust, coal combustion
- **C**: Incomplete combustion of carbonaceous fuels
- **Na, Cl**: Marine aerosols, chloride from incineration of organohalide polymer wastes

- **Sb, Se**: Very volatile elements, possibly from the combustion of oil, coal, or refuse
- **V**: Combustion of residual petroleum (present at very high levels in residues from Venezuelan crude oil)
- **Zn**: Tends to occur in small particles, probably from combustion
- **Pb**: Combustion of leaded fuels and wastes containing lead

Particulate carbon as soot, carbon black, coke, and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations, and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of SO_2 to sulfate.

Fly Ash

Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel. Much of the mineral matter in fossil fuels such as coal or lignite is converted during combustion to a fused, glassy, bottom ash that presents no air pollution problems. Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere. Unfortunately, the fly ash thus released tends to consist of smaller particles, which do the most damage to human health, plants, and visibility.

The composition of fly ash varies widely, depending upon the source of fuel. The predominant constituents are oxides of aluminum, calcium, iron, and silicon. Other elements that occur in fly ash are magnesium, sulfur, titanium, phosphorus, potassium, and sodium. Elemental carbon (soot, carbon black) is a significant fly ash constituent.

Asbestos

Asbestos is the name given to a group of fibrous silicate minerals, typically those of the serpentine group, for which the approximate formula is $Mg_3P(Si_2O_5)(OH)_4$. The tensile strength, flexibility, and nonflammability of asbestos have led to many uses in the past including structural materials, brake linings, insulation, and pipe manufacture.

Asbestos is of concern as an air pollutant because, when inhaled, it can cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs). Therefore, uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

Toxic Metals

Some of the metals found predominantly as particulate matter in polluted atmospheres are known to be hazardous to human health. All of these except beryllium are so-called “heavy metals.” Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second. Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

Atmospheric mercury is of concern because of its toxicity, volatility, and mobility. Some atmospheric mercury is associated with particulate matter. Much of the mercury entering the atmosphere does so as volatile elemental mercury from coal combustion and volcanoes. Volatile organomercury compounds, such as dimethylmercury, $(CH_3)_2Hg$, and monomethylmercury salts, such as $(CH_3)HgBr$, are also encountered in the atmosphere.

With the reduction of leaded fuels, atmospheric lead is of less concern than it used to be. However, during the decades that leaded gasoline containing tetraethyllead was the predominant automotive fuel, particulate lead halides were emitted in large quantities. Lead halides are emitted from engines burning leaded gasoline through the action of dichlorethane and dibromoethane added as halogenated scavengers to form volatile lead chloride, lead bromide, and lead chlorobromide, thereby preventing the accumulation of lead oxides inside engines.

Beryllium is used for the formulation of specialty alloys employed in electrical equipment, electronic instrumentation, space gear, and nuclear reactor components, so that distribution of beryllium is by no means comparable to that of other toxic metals such as lead or mercury. However, because of its “high tech” applications, consumption of beryllium may increase in the future. Because of its high toxicity, beryllium has the lowest allowable limit in the atmosphere of all the elements. One of the main results resulting from the recognition of beryllium toxicity hazards was the elimination of this element from phosphors (coatings that produce visible light from ultraviolet light) in fluorescent lamps.

Radioactive Particles

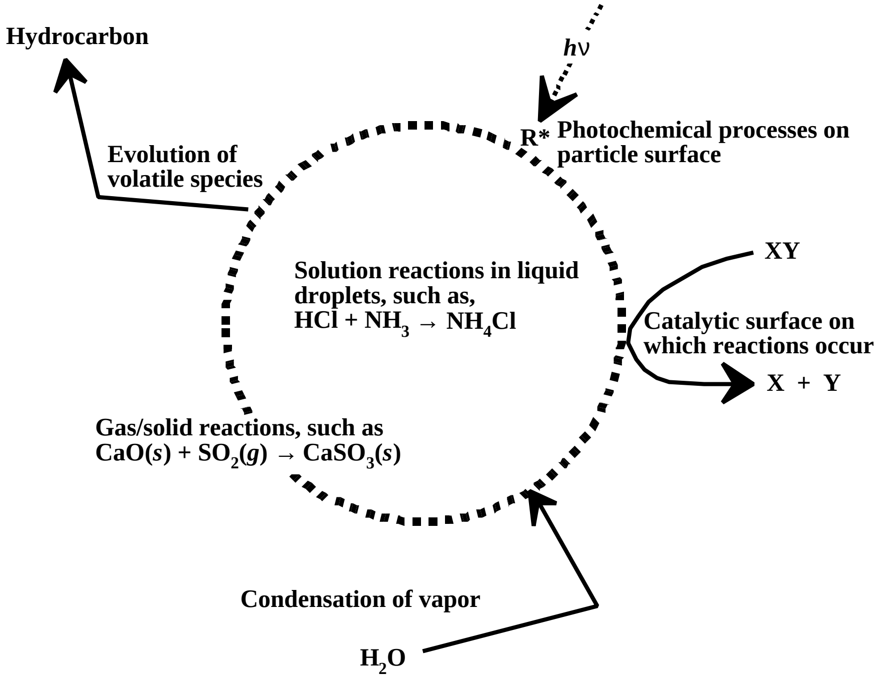
A significant natural source of radionuclides in the atmosphere is **radon**, a noble gas product of radium decay. Radon may enter the atmosphere as either of two isotopes, ^{222}Rn (half-life 3.8 days) and ^{220}Rn (half-life 54.5 seconds). Both are alpha emitters in decay chains that terminate with stable isotopes of lead. The initial decay products, ^{218}Po and ^{216}Po, are nongaseous and adhere readily to atmospheric particulate matter. Therefore, some of the radioactivity detected in these particles is of natural origin. Furthermore, cosmic rays act on nuclei in the atmosphere, reacting to produce other radionuclides, including ^{7}Be, ^{10}Be, ^{14}C, ^{39}Cl, ^{3}H, ^{22}Na, ^{32}P, and ^{33}P.

The combustion of fossil fuels introduces radioactivity into the atmosphere in the form of radionuclides contained in fly ash. Large coal-fired power plants lacking ash-control equipment can introduce up to several hundred milliCuries of radionuclides into the atmosphere each year, far more than either an equivalent nuclear or oil-fired power plant.

The above-ground detonation of nuclear weapons, which hopefully will not ever occur again, can add large amounts of radioactive particulate matter to the atmosphere. Among the radioisotopes that can be detected in rainfall falling after atmospheric nuclear weapon detonation are ^{91}Y, ^{141}Ce, ^{144}Ce, ^{147}Nd, ^{147}Pm, ^{149}Pm, ^{151}Sm, ^{153}Sm, ^{155}Eu, ^{156}Eu, ^{89}Sr, ^{90}Sr, ^{115m}Cd, ^{129m}Te, ^{131}I, ^{132}Te, and ^{140}Ba. (Note that "^{m}" denotes a metastable state that decays by gamma-ray emission to an isotope of the same element.)

15.4 EFFECTS OF PARTICLES

Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility. Particles provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena. Some chemical and physical aspects of atmospheric particles are illustrated in Figure 15.2.



Hydrocarbon
hν
Evolution of volatile species
R*
Photochemical processes on particle surface
XY
Solution reactions in liquid droplets, such as, $HCl + NH_3 \rightarrow NH_4Cl$
Catalytic surface on which reactions occur
X + Y
Gas/solid reactions, such as $CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$
Condensation of vapor
H_2O

Figure 15.2 Aspects of particle reactions and effects in the atmosphere.

The most visible influence that aerosol particles have upon air quality results from optical effects. Particles smaller than about 0.1 µm in diameter scatter light much like molecules, that is, Rayleigh scattering. Generally, such particles have an insignificant effect upon visibility in the atmosphere. The light-scattering and intercepting properties of particles larger than 1 µm are approximately proportional to the particle's cross-sectional area. Particles of 0.1 µm–1 µm cause interference phenomena because they are about the same dimensions as the wavelengths of visible light, so their light-scattering properties are especially significant.

Atmospheric particles inhaled through the respiratory tract may damage health. Relatively large particles are mostly retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them. The respiratory system possesses mechanisms for the expulsion of inhaled particles. In the ciliated region of the respiratory system, particles are carried as far as the entrance to the gastrointestinal tract by a flow of mucus. Macrophages in the nonciliated pulmonary regions carry particles to the ciliated region.

The respiratory system may be damaged directly by particulate matter that enters the blood system or lymph system through the lungs. In addition, soluble components of the particulate matter may be transported to organs some distance from the lungs and have a detrimental effect on these organs. Particles cleared from the respiratory tract are largely swallowed into the gastrointestinal tract.

A strong correlation has been found between increases in the daily mortality rate and acute episodes of air pollution. In such cases, high levels of particulate matter are accompanied by elevated concentrations of SO_2 and other pollutants, so that any conclusions must be drawn with caution.

15.5 CONTROL OF PARTICULATE EMISSIONS

The removal of particulate matter from gas streams is the most widely practiced means of air pollution control. A number of devices that differ widely in effectiveness, complexity, and cost have been developed for this purpose. The selection of a particle removal system for a gaseous waste stream depends upon the particle loading, nature of particles (size distribution), and type of gas scrubbing system used.

Particle Removal by Sedimentation and Inertia

The simplest means of particulate matter removal is **sedimentation**, a phenomenon that occurs continuously in nature. Gravitational settling chambers can be employed for the removal of particles from gas streams by simply settling under the influence of gravity. These chambers take up large amounts of space and have low collection efficiencies, particularly for small particles.

Gravitational settling of particles is enhanced by increased particle size, which occurs spontaneously by coagulation. Thus, over time, the size of particles increases and the number of particles decreases in a mass of air that contains particles. Brownian motion of particles less than about 0.1 µm in size is primarily responsible for their contact, enabling coagulation to occur. Particles greater than about 0.3 µm in radius do not diffuse appreciably and serve primarily as receptors of smaller particles.

Inertial mechanisms used for particle removal depend upon the fact that the radius of the path of a particle in a rapidly moving, curving air stream is larger than the path of the stream as a whole. Therefore, when a gas stream is spun by vanes, a fan, or a tangential gas inlet, the particulate matter may be collected on a separator wall because the particles are forced outward by centrifugal force. Devices utilizing this mode of operation are called **dry centrifugal collectors**.

Particle filtration

Fabric filters, as their name implies, consist of fabrics that allow the passage of gas but retain particulate matter. These are used to collect dust in bags contained in structures called *baghouses*. Periodically, the fabric composing the filter is shaken to remove the particles and to reduce back-pressure to acceptable levels. Typically, the bag is in a tubular configuration, as shown in Figure 15.3. Numerous other configurations are possible. Collected particulate matter is removed from bags by mechanical agitation, blowing air on the fabric, or rapid expansion and contraction of the bags.

Although simple, baghouses are generally effective in removing particles from exhaust gas. Particles as small as 0.01 µm in diameter are removed, and removal efficiency is relatively high for particles down to 0.5 µm in diameter.

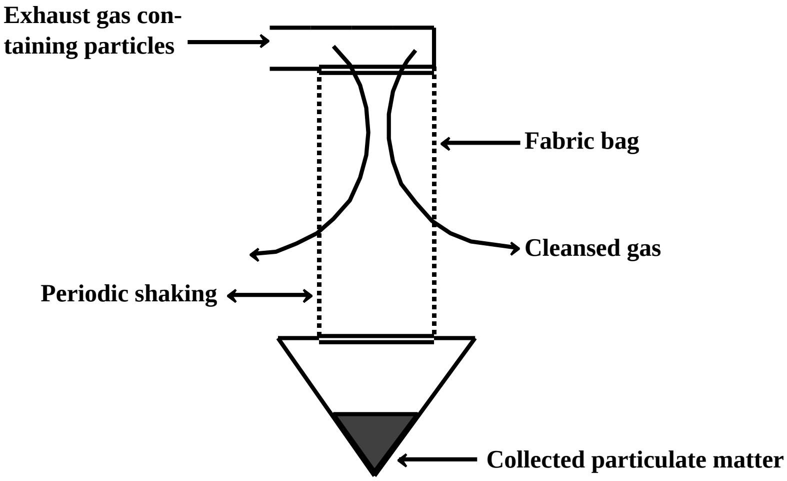

Exhaust gas containing particles
Fabric bag
Cleansed gas
Periodic shaking
Collected particulate matter

Figure 15.3 Baghouse collection of particulate emissions.

Scrubbers

A venturi scrubber passes gas through a converging section, throat, and diverging section as shown in Figure 15.4. Injection of the scrubbing liquid at right angles to incoming gas breaks the liquid into very small droplets, which are ideal for scavenging particles from the gas stream. In the reduced-pressure (expanding) region of the venturi, some condensation can occur, adding to the scrubbing efficiency. In addition to removing particles, venturis can serve as quenchers to cool exhaust gas and as scrubbers for pollutant gases.

Electrostatic Removal

Aerosol particles may acquire electrical charges. In an electric field, such particles are subjected to a force, F (dynes) given by

$$F = eq \qquad (15.5.1)$$

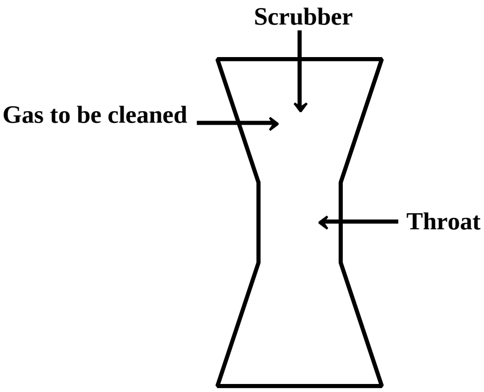

Scrubber
Gas to be cleaned
Throat

Figure 15.4 Venturi scrubber.

where E is the voltage gradient (statvolt/cm) and q is the electrostatic charge charge on the particle (in esu). This phenomenon has been widely used in highly efficient **electrostatic precipitators**, as shown in Figure 15.5. The particles acquire a charge when the gas stream is passed through a high-voltage, direct-current corona. Because of the charge, the particles are attracted to a grounded surface, from which they may be later removed. Ozone may be produced by the corona discharge. Similar devices used as household dust collectors may produce toxic oxone if not operated properly.

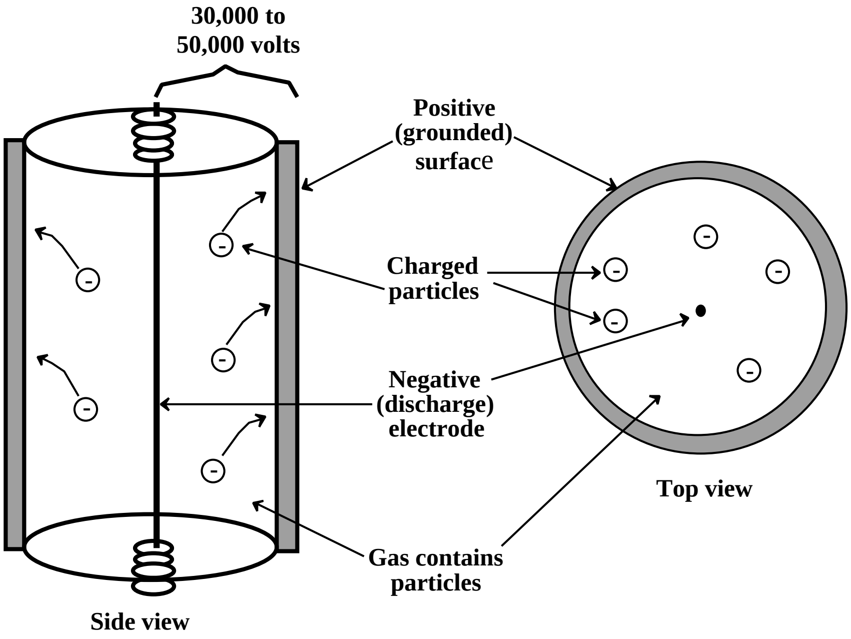

30,000 to
50,000 volts
Positive
(grounded)
surface
Charged
particles
Negative
(discharge)
electrode
Gas contains
particles
Side view
Top view

Figure 15.5 Schematic diagram of an electrostatic precipitator.

15.6 CARBON OXIDES

Carbon Monoxide

Carbon monoxide, CO, causes problems in cases of locally high concentrations. The toxicity of carbon monoxide is discussed in Chapter 23. The overall atmospheric concentration of carbon monoxide is about 0.1 ppm. Much of this CO is present as an intermediate in the oxidation of methane by hydroxyl radical. Because of carbon monoxide emissions from internal combustion engines, highest levels of this toxic gas tend to occur in congested urban areas at times when the maximum number of people are exposed, such as during rush hours. At such times, carbon monoxide levels in the atmosphere have become as high as 50–100 ppm. Automotive air pollution control devices have reduced these levels significantly during the last 25 years.

Control of Carbon Monoxide Emissions

Since the internal combustion engine is the primary source of localized pollutant carbon monoxide emissions, control measures have been concentrated on the automobile. Carbon monoxide emissions may be lowered by employing a leaner air-fuel mixture, that is, one in which the weight ratio of air to fuel is relatively high. At air-fuel(weight:weight) ratios exceeding approximately 16:1, an internal combustion engine emits virtually no carbon monoxide. Modern automobiles use catalytic exhaust reactors and precise computerized control of engine operation to cut down on carbon monoxide emissions.

Fate of Atmospheric CO

The residence time of carbon monoxide in the atmosphere is of the order of 4 months. It is generally agreed that carbon monoxide is removed from the atmosphere by reaction with hydroxyl radical, $HO^{\bullet}$:

$$CO + HO^{\bullet} \rightarrow CO_2 + H \tag{15.6.1}$$

The reaction produces hydroperoxyl radical as a product:

$$O_2 + H + M \rightarrow HOO^{\bullet} + M \text{ (M is an energy-absorbing third body, usually a molecule of } O_2 \text{ or } N_2\text{)} \tag{15.6.2}$$

$HO^{\bullet}$ is regenerated from $HOO^{\bullet}$ by the following reactions:

$$HOO^{\bullet} + NO \rightarrow HO^{\bullet} + NO_2 \tag{15.6.3}$$

$$HOO^{\bullet} + HOO^{\bullet} \rightarrow H_2O_2 \tag{15.6.4}$$

The latter reaction is followed by photochemical dissociation of H_2O_2 to regenerate $HO^{\bullet}$:

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \tag{15.6.5}$$

Methane is also involved through the atmospheric CO-$HO^{\bullet}$-CH_4 cycle.

Soil microorganisms act to remove CO from the atmosphere. Therefore, soil is a sink for carbon monoxide.

Carbon Dioxide and Global Warming

Carbon dioxide and other infrared-absorbing trace gases in the atmosphere contribute to global warming—the "greenhouse effect"—by allowing incoming solar radiant energy to penetrate to the Earth's surface while reabsorbing infrared radiation emanating from it. Levels of these "greenhouse gases" have increased at a rapid rate during recent decades and are continuing to do so. Concern over this phenomenon has intensified since about 1980. This is because the 1990s have been the warmest 10-year period recorded since accurate temperature records have been kept. Prior to that time the 1980s were the warmest decade on record. In March 2000 the U.S. National Climatic Data Center announced that the 1999-2000 winter in the 48 contiguous United States was the warmest on record, with an average winter temperature of 3.6˚C. The two preceding winters had also set records of 3.2˚C for the 1998-1999 winter and 3.1˚C for the 1997-1998 winter. During the 1999-2000 winter both the first freeze and first snowfall came later than ever in colder regions of the 48 states, including New England and the Northern Plains. Numerous places across the northern tier of states set high temperature records during February 2000. The spring of 2000 was the warmest ever recorded in the United States. Figure 15.6 shows trends in global temperature over the last century.

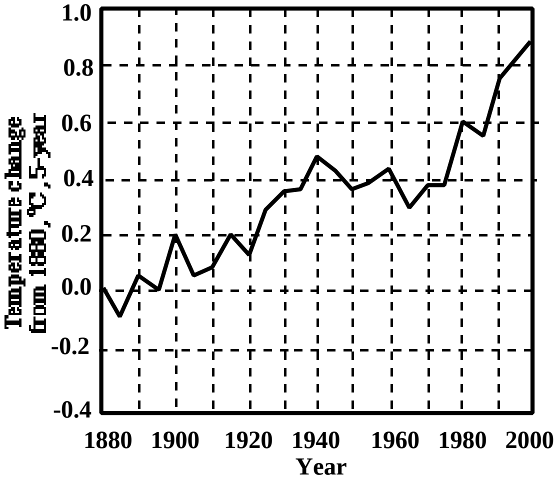


Figure 15.6 Trends in global temperature over the last century.

There are many uncertainties surrounding the issue of greenhouse warming. However, it is known that CO_2 and other greenhouse gases, such as CH_4, absorb infrared radiation by which Earth loses heat. The levels of these gases have increased markedly since about 1850, as nations have become industrialized and as forest lands and grasslands have been converted to agriculture. Chlorofluorocarbons, which also are greenhouse gases, were not even introduced into the atmosphere until the 1930s. Although trends in levels of these gases are well known, their effects on global temperature and climate are much less certain. The phenomenon has been the subject of much computer modeling. Most models predict global warming of 1.5–5˚C, about as much again as has occurred since the last ice age. Such warming would have profound effects on rainfall, plant growth, and sea levels, which might rise as much as 0.5–1.5 meters.

Carbon dioxide is the gas most commonly thought of as a greenhouse gas; it is responsible for about half of the atmospheric heat retained by trace gases. It is produced primarily by burning of fossil fuels and deforestation accompanied by burning and biodegradation of biomass. On a molecule-for-molecule basis, methane, CH_4, is 20–30 times more effective in trapping heat than is CO_2. Other trace gases that contribute are chlorofluorocarbons and N_2O.

Analyses of gases trapped in polar ice samples indicate that pre-industrial levels of CO_2 and CH_4 in the atmosphere were approximately 260 parts per million and 0.70 ppm, respectively. Over the last 300 years, these levels have increased to current values of around 360 ppm, and l.8 ppm, respectively; most of the increase by far has taken place at an accelerating pace over the last 100 years. (A note of interest is the observation based upon analyses of gases trapped in ice cores that the atmospheric level of CO_2 at the peak of the last ice age about 18,000 years past was 25 percent *below* preindustrial levels.) About half of the increase in carbon dioxide in the last 300 years can be attributed to deforestation, which still accounts for approximately 20 % of the annual increase in this gas. Carbon dioxide is increasing by about 1 ppm per year. Methane is going up at a rate of almost 0.02 ppm/year. The comparatively very rapid increase in methane levels is attributed to a number of factors resulting from human activities. Among these are direct leakage of natural gas, byproduct emissions from coal mining and petroleum recovery, and release from the burning of savannas and tropical forests. Biogenic sources resulting from human activities produce large amounts of atmospheric methane. These include methane from bacteria degrading organic matter, such as municipal refuse in landfills; methane evolved from anaerobic biodegradation of organic matter in rice paddies; and methane emitted as the result of bacterial action in the digestive tracts of ruminant animals.

The steady increase in global carbon dioxide levels is shown in Figure 15.7, which also shows a seasonal cycle in carbon dioxide levels in the northern hemisphere. Maximum values occur in April and minimum values in late September or October. These oscillations are due to the “photosynthetic pulse,” influenced most strongly by forests in middle latitudes. Forests have a much greater influence than other vegetation because trees carry out more photosynthesis. Furthermore, forests store enough fixed but readily oxidizable carbon in the form of wood and humus to have a marked influence on atmospheric CO_2 content. Thus, during the summer months, forest trees carry out enough photosynthesis to reduce the atmospheric carbon dioxide content markedly. During the winter, metabolism of biota, such as bacterial decay of humus, releases a significant amount of CO_2. Therefore, the current worldwide destruction of forests and conversion of forest lands to agricultural uses contributes substantially to a greater overall increase in atmospheric CO_2 levels.

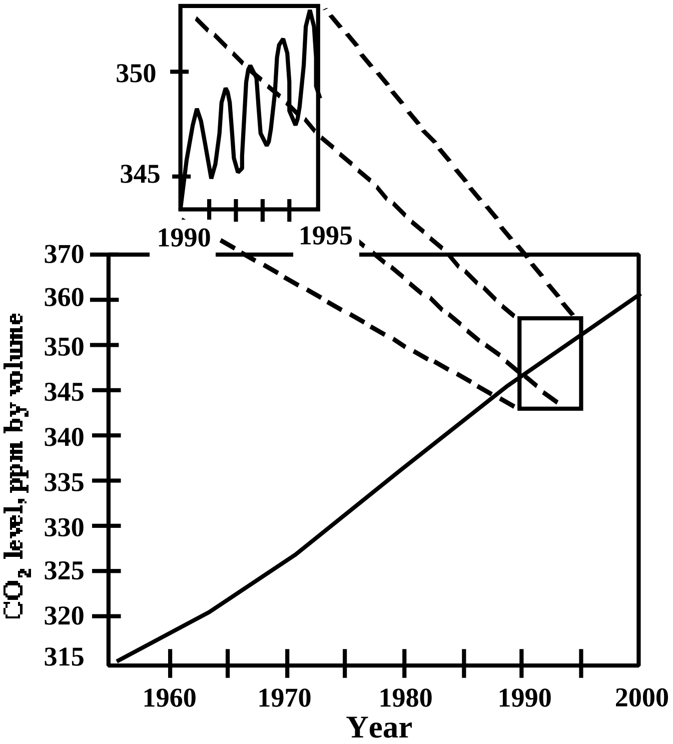


Figure 15.7 Increases in atmospheric CO_2 levels in recent years. The inset illustrates seasonal variations in the Northern Hemisphere.

Both positive and negative feedback mechanisms may be involved in determining the rates at which carbon dioxide and methane build up in the atmosphere. Laboratory studies indicate that increased CO_2 levels in the atmosphere cause accelerated uptake of this gas by plants undergoing photosynthesis, which tends to slow buildup of atmospheric CO_2. Given adequate rainfall, plants living in a warmer climate that would result from the greenhouse effect would grow faster and take up more CO_2. This could be an especially significant effect of forests, which have a high CO_2-fixing ability. However, the projected rate of increase in carbon dioxide levels is so rapid that forests would lag behind in their ability to fix additional CO_2. Similarly, higher atmospheric CO_2 concentrations will result in accelerated sorption of the gas by oceans. The amount of dissolved CO_2 in the oceans is about 60 times the amount of CO_2 gas in the atmosphere. However, the times for transfer of carbon dioxide from the atmosphere to the top layers of the ocean are of the order of years. Because of low mixing rates, the times for transfer of carbon dioxide from the upper approximately 100-meter layer of the oceans to ocean depths is much longer, of the order of decades. Therefore, like the uptake of CO_2 by forests, increased absorption by oceans will lag behind the emissions of CO_2. Severe drought conditions resulting from climatic warming could cut down substantially on CO_2 uptake by plants. Warmer conditions would accelerate release of both CO_2 and CH_4 by microbial degradation of organic matter. (It is important to realize that about twice as much carbon is held in soil in dead organic matter— necrocarbon—potentially degradable to CO_2 and CH_4 as is present in the atmosphere.) Global warming might speed up the rates at which biodegradation adds these gases to the atmosphere.

Carbon dioxide levels will continue to increase at a rate dependent upon future levels of CO_2 production and the fraction of that production that remains in the atmosphere. Given plausible projections of CO_2 production and a reasonable estimate that half of that amount will remain in the atmosphere, projections can be made that indicate that sometime during the middle part of the next century the concentration of this gas will reach 600 ppm in the atmosphere. This is well over twice the levels estimated for pre-industrial times. Much less certain are the effects that this change will have on climate. It is virtually impossible for the elaborate computer models used to estimate these effects to accurately take account of all variables, such as the degree and nature of cloud cover. Clouds both reflect incoming light radiation and absorb outgoing infrared radiation, with the former effect tending to predominate. The magnitudes of these effects depend upon the degree of cloud cover, brightness, altitude, and thickness. In the case of clouds, too, feedback phenomena occur; for example, warming induces formation of more clouds, which reflect more incoming energy. Most computer models predict global warming of at least 3.0˚C and as much as 5.5˚C occurring over a period of just a few decades. These estimates are sobering because they correspond to the approximate temperature increase since the last ice age 18,000 years past, which took place at a much slower pace of only about 1 or 2˚C per 1,000 years.

Drought is one of the most serious problems that could arise from major climatic change resulting from greenhouse warming. Typically, a 3-degree warming would be accompanied by a 10 % decrease in precipitation. Water shortages would be aggravated, not just from decreased rainfall, but from increased evaporation, as well. Increased evaporation results in decreased runoff, thereby reducing water available for agricultural, municipal, and industrial use. Water shortages, in turn, lead to increased demand for irrigation and to the production of lower quality, higher salinity runoff water and wastewater. In the U. S., such a problem would be especially intense in the Colorado River basin, which supplies much of the water used in the rapidly growing U.S. Southwest.

A variety of other problems, some of them unforeseen as of now, could result from global warming. An example is the effect of warming on plant and animal pests — insects, weeds, diseases, and rodents. Many of these would certainly thrive much better under warmer conditions.

Interestingly, another air pollutant, acid-rain-forming sulfur dioxide (see Section 15.7), may have a counteracting effect on greenhouse gases. This is because sulfur dioxide is oxidized in the atmosphere to sulfuric acid, forming a light-reflecting haze. Furthermore, the sulfuric acid and resulting sulfates act as condensation nuclei (Section 14.5) that increases the extent, density, and brightness of light-reflecting cloud cover.

Chemically and photochemically, carbon dioxide is a comparatively insignificant species because of its relatively low concentrations and low photochemical reactivity. The one significant photochemical reaction that carbon dioxide undergoes, and a major source of CO at higher altitudes, is the photodissociation of CO_2 by energetic solar ultraviolet radiation in the stratosphere:

$$CO_2 + h\nu \rightarrow CO + O \qquad (15.6.6)$$

15.7 SULFUR DIOXIDE SOURCES AND THE SULFUR CYCLE

Figure 15.8 shows the main aspects of the global sulfur cycle. This cycle involves primarily H_2S, $(CH_3)_2S$, SO_2, SO_3, and sulfates. There are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. Approximately 100 million metric tons of sulfur per year enter the global atmosphere through anthropogenic activities, primarily as SO_2 from the combustion of coal and residual fuel oil. The greatest uncertainties in the cycle have to do with nonanthropogenic sulfur, which enters the atmosphere largely as SO_2 and H_2S from volcanoes, and as $(CH_3)_2S$ and H_2S from the biological decay of organic matter and reduction of sulfate. The single largest source of natural sulfur discharged to the atmosphere is now believed to be biogenic dimethyl sulfide, $(CH_3)_2S$, from marine sources. Any H_2S that does get into the atmosphere is converted rapidly to SO_2 by the following overall process:

$$H_2S + {}^3\!/_2O_2 \rightarrow SO_2 + H_2O \qquad (15.7.1)$$

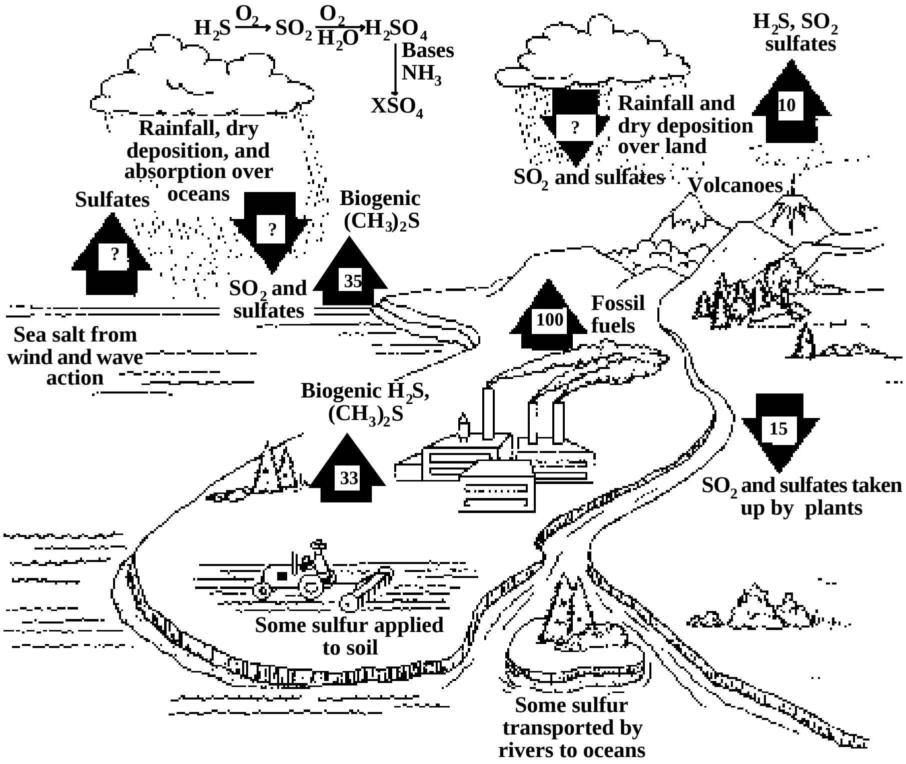

$H_2S \xrightarrow{O_2} SO_2 \xrightarrow[H_2O]{O_2} H_2SO_4$
Bases
NH_3
XSO_4
H_2S, SO_2
sulfates
Rainfall, dry deposition, and absorption over oceans
?
Rainfall and dry deposition over land
?
10
SO_2 and sulfates
Volcanoes
Sulfates
?
Biogenic $(CH_3)_2S$
35
SO_2 and sulfates
100
Fossil fuels
Sea salt from wind and wave action
Biogenic H_2S, $(CH_3)_2S$
33
15
SO_2 and sulfates taken up by plants
Some sulfur applied to soil
Some sulfur transported by rivers to oceans

Figure 15.8 The global atmospheric sulfur cycle. Fluxes of sulfur represented by the arrows are in millions of metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year.

The initial reaction is hydrogen ion abstraction by hydroxyl radical, followed by two other reactions to give SO_2:

$$H_2S + HO\bullet \rightarrow HS\bullet + H_2O \tag{15.7.2}$$

$$HS\bullet + O_2 \rightarrow HO\bullet + SO \tag{15.7.3}$$

$$SO + O_2 \rightarrow SO_2 + O \tag{15.7.4}$$

The primary source of anthropogenic sulfur dioxide is coal, from which sulfur must be removed at great expense to keep sulfur dioxide emissions at acceptable levels. Approximately half of the sulfur in coal is in some form of pyrite, FeS_2, and the other half is organic sulfur. The production of sulfur dioxide by the combustion of pyrite is given by the following reaction:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \tag{15.7.5}$$

Sulfur Dioxide Reactions in the Atmosphere

Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, can influence the atmospheric chemical reactions of sulfur dioxide. Like many other gaseous pollutants, sulfur dioxide undergoes chemical reactions resulting in the formation of particulate matter. Whatever the processes involved, much of the sulfur dioxide in the atmosphere ultimately is oxidized to sulfuric acid and sulfate salts, particularly ammonium sulfate and ammonium hydrogen sulfate.

Effects of Atmospheric Sulfur Dioxide

Atmospheric sulfur dioxide's primary health effect is upon the respiratory tract, producing irritation and increasing airway resistance, especially to people with respiratory weaknesses and sensitized asthmatics. Increased effort to breathe and stimulated mucus secretion may occur with sulfur dioxide inhalation in air.

Acute exposure to high levels of atmospheric sulfur dioxide kills leaf tissue (leaf necrosis). The edges of the leaves and the areas between the leaf veins are particularly damaged. Chronic exposure of plants to sulfur dioxide causes chlorosis, a bleaching or yellowing of green leaves. Sulfur dioxide in the atmosphere is converted to sulfuric acid, so that in areas with high levels of sulfur dioxide pollution, plants may be damaged by sulfuric acid aerosols. Such damage appears as small spots where sulfuric acid droplets have impinged on leaves.

Sulfur Dioxide Removal

A number of processes are being used to remove sulfur and sulfur oxides from fuel before combustion and from stack gas after combustion. Most of these efforts concentrate on coal, since it is the major source of sulfur oxides pollution. Physical separation techniques can be used to remove discrete particles of pyritic sulfur from coal. Chemical methods can also be employed for removal of sulfur from coal. Fluidized bed combustion of coal promises to eliminate SO_2 emissions at the point of combustion. The process consists of burning granular coal in a bed of finely divided limestone or dolomite maintained in a fluid-like condition by air injection. Heat calcines the limestone,

$$CaCO_3 \rightarrow CaO + CO_2 \tag{15.7.6}$$

and the lime produced absorbs SO_2:

$$CaO + SO_2 \ (+ \tfrac{1}{2}O_2) \rightarrow CaSO_3 \ (CaSO_4) \tag{15.7.7}$$

Many processes have been proposed or studied for the removal of sulfur dioxide from stack gas. Table 15.2 summarizes major stack gas scrubbing systems. These include throwaway and recovery systems as well as wet and dry systems.

Current practice with lime and limestone scrubber systems often injects slurry into the scrubber loop beyond the boilers. These scrubbers can remove well over 90% of both SO_2 and fly ash when operating properly. In addition to corrosion and scaling problems, disposal of lime sludge poses formidable obstacles. The quantity of this sludge may be appreciated by considering that approximately 1 ton of limestone is required for each 5 tons of coal.

Recovery systems in which sulfur dioxide or elemental sulfur are removed from the spent sorbing material, which is recycled, are much more desirable from an environmental viewpoint than are throwaway systems. Many kinds of recovery processes have been investigated, including those that involve scrubbing with magnesium oxide slurry, sodium sulfite solution, ammonia solution, or sodium citrate solution.

Sulfur dioxide trapped in a stack-gas-scrubbing process can be converted to hydrogen sulfide by reaction with synthesis gas (H_2, CO, CH_4),

$$SO_2 + (H_2, CO, CH_4) \rightleftarrows H_2S + CO_2 \tag{15.7.8}$$

The Claus reaction is then employed to produce elemental sulfur:

$$2H_2S + SO_2 \rightleftarrows 2H_2O + 3S \tag{15.7.9}$$

15.8 NITROGEN OXIDES IN THE ATMOSPHERE

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Microbially generated nitrous oxide is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its levels decrease rapidly with altitude in the stratosphere due to the photochemical reaction

$$N_2O + h\nu \rightarrow N_2 + O \tag{15.8.1}$$

and some reaction with singlet atomic oxygen:

$$N_2O + O \rightarrow N_2 + O_2 \tag{15.8.2}$$

$$N_2O + O \rightarrow NO + NO \tag{15.8.3}$$

Table 15.2 Major Stack Gas Scrubbing Systems[1]

Process	Reaction	Significant advantages or disadvantages
Lime slurry scrubbing[2]	$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$	Up to 200 kg of lime are needed per metric ton of coal, producing huge quantities of wastes
Limestone slurry scrubbing[2]	$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2(g)$	Lower pH than lime slurry, not so efficient
Magnesium oxide scrubbing	$Mg(OH)_2(slurry) + SO_2 \rightarrow MgSO_3 + H_2O$	The sorbent can be regenerated, which can be done off site, if desired.
Sodium-base scrubbing	$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$ $2NaHSO_3 + \text{heat} \rightarrow Na_2SO_3 + H_2O + SO_2$ (regeneration)	No major technological limitations. Relatively high annual costs.
Double alkali[2]	$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ $Ca(OH)_2 + Na_2SO_3 \rightarrow CaSO_3(s) + 2NaOH$ (regeneration of NaOH)	Allows for regeneration of expensive sodium alkali solution with inexpensive lime.

[1] For details regarding these and more-advanced processes see (1) Satriana, M., *New Developments in Flue Gas Desulfurization Technology*, Noyes Data Corp., Park Ridge, NJ, 1982, and (2) Lunt, R., Arthur D. Little, and J.D. Cunic, *Profiles in Flue Gas Desulfurization*, American Institute of Chemical Engineers, New York, NY, 2000.

[2] These processes have also been adapted to produce a gypsum product by oxidation of $CaSO_3$ in the spent scrubber medium:

$$CaSO_3 + {}^1/_2O_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O(s)$$

Gypsum has some commercial value, such as in the manufacture of plasterboard, and makes a relatively settleable waste product.

These reactions are significant in terms of depletion of the ozone layer. Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O, could contribute to ozone layer depletion.

Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NO_x, these gases enter the atmosphere from natural sources, such as lightning and biological processes, and from pollutant sources. The latter are much more significant because of regionally high NO_2 concentrations, which can cause severe air quality deterioration. Practically all anthropogenic NO_2 enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources. The contribution of automobiles to nitric oxide production in the U.S. has become somewhat lower in the last decade as newer automobiles with nitrogen oxide pollution controls have become more common.

Most NO_2 entering the atmosphere from pollution sources does so as NO generated from internal combustion engines. At the very high temperatures in an automobile combustion chamber, the following reaction occurs:

$$N_2 + O_2 \rightarrow 2NO \qquad (15.8.4)$$

High temperatures favor both a high equilibrium concentration and a rapid rate of formation of NO. Rapid cooling of the exhaust gas from combustion "freezes" NO at a relatively high concentration because equilibrium is not maintained. Thus, by its very nature, the combustion process both in the internal combustion engine and in furnaces produces high levels of NO in the combustion products.

Atmospheric Reactions of NO_x

Atmospheric chemical reactions convert NO_x to nitric acid, inorganic nitrate salts, organic nitrates, and peroxyacetyl nitrate (see Chapter 16). The principal reactive nitrogen oxide species in the troposphere are NO, NO_2, and HNO_3. These species cycle among each other, as shown in Figure 15.9. Although NO is the primary form in which NO_x is released to the atmosphere, the conversion of NO to NO_2 is relatively rapid in the troposphere.

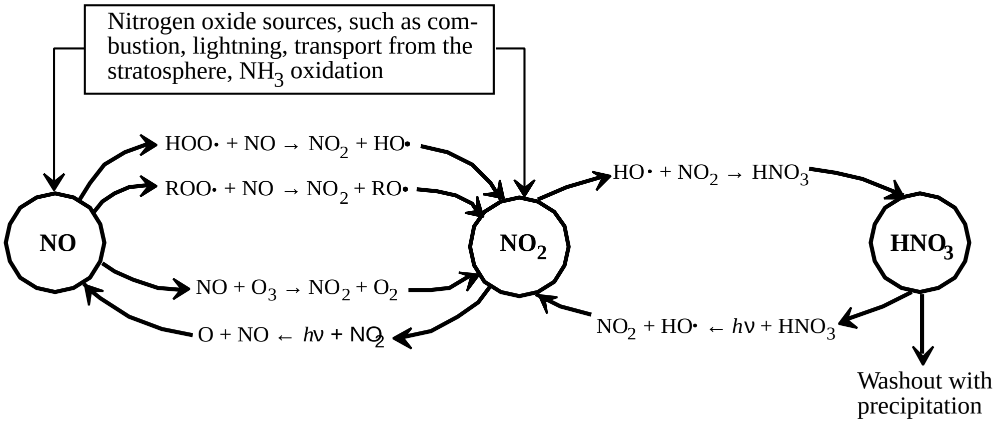

Nitrogen oxide sources, such as combustion, lightning, transport from the stratosphere, NH_3 oxidation
$HOO\cdot + NO \rightarrow NO_2 + HO\cdot$
$ROO\cdot + NO \rightarrow NO_2 + RO\cdot$
$HO\cdot + NO_2 \rightarrow HNO_3$
NO
NO_2
HNO_3
$NO + O_3 \rightarrow NO_2 + O_2$
$O + NO \leftarrow h\nu + NO_2$
$NO_2 + HO\cdot \leftarrow h\nu + HNO_3$
Washout with precipitation

Figure 15.9 Principal reactions among NO, NO_2, and HNO_3 in the atmosphere. ROO• represents an organic peroxyl radical, such as the methylperoxyl radical, $CH_3OO\cdot$.

Nitrogen dioxide is a very reactive and significant species in the atmosphere. It absorbs light throughout the ultraviolet and visible spectrum penetrating the troposphere. At wavelengths below 398 nm, photodissociation to oxygen atoms occurs,

$$NO_2 + h\nu \rightarrow NO + O \qquad (15.8.5)$$

giving rise to several significant inorganic reactions, in addition to a host of atmospheric reactions involving organic species. The reactivity of NO_2 to photodissociation is shown clearly by the fact that in direct sunlight the half-life of NO_2 is much shorter than that of any other atmospheric component (only 1 or 2 minutes).

Harmful Effects of Nitrogen Oxides

Nitric oxide, NO, is biochemically less active and less toxic than NO_2. Acute exposure to NO_2 can be quite harmful to human health. For exposures ranging from several minutes to 1 hour, a level of 50–100 ppm of NO_2 causes inflammation of lung tissue for a period of 6–8 weeks, after which time the subject normally recovers. Exposure of the subject to 150–200 ppm of NO_2 causes *bronchiolitis fibrosa obliterans*, a condition fatal within 3–5 weeks after exposure. Death generally results within 2–10 days after exposure to 500 ppm or more of NO_2. "Silo-filler's disease," caused by NO_2 generated by the fermentation of ensilage containing nitrate, is a particularly striking example of nitrogen dioxide poisoning. Deaths have resulted from the inhalation of NO_2-containing gases from burning celluloid and nitrocellulose film and from spillage of NO_2 oxidant from missile rocket motors.

Although extensive damage to plants is observed in areas receiving heavy exposure to NO_2, most of this damage probably comes from secondary products of nitrogen oxides, such as PAN formed in smog (see Chapter 16). Exposure of plants to several parts per million of NO_2 in the laboratory causes leaf spotting and breakdown of plant tissue. Exposure to 10 ppm of NO causes a reversible decrease in the rate of photosynthesis.

Nitrogen oxides are known to cause fading of dyes used in some textiles. This has been observed in gas clothes dryers and is due to NO_x formed in the dryer flame. Much of the damage to materials caused by NO_x, stress-corrosion cracking of electrical apparatus, comes from secondary nitrates and nitric acid.

Control of Nitrogen Oxides

The level of NO_x emitted from stationary sources such as power plant furnaces generally falls within the range of 50–1000 ppm. NO production is favored both kinetically and thermodynamically by high temperatures and by high excess oxygen concentrations. These factors must be considered in reducing NO emissions from stationary sources. Reduction of flame temperature to prevent NO formation is accomplished by adding recirculated exhaust gas, cool air, or inert gases.

Low-excess-air firing is effective in reducing NO_x emissions during the combustion of fossil fuels. As the term implies, low-excess-air firing uses the minimum amount of excess air required for oxidation of the fuel, so that less oxygen is available for the reaction

$$N_2 + O_2 \rightarrow 2NO_2 \qquad (15.8.6)$$

in the high temperature region of the flame. Incomplete fuel burnout, with the emission of hydrocarbons, soot, and CO, is an obvious problem with low-excess-air firing. This may be overcome by a two-stage combustion process. In the first stage, fuel is fired at a relatively high temperature with a substoichiometric amount of air, and NO formation is limited by the absence of excess oxygen. In the second stage, fuel burnout is completed at a relatively low temperature in excess air; the low temperature prevents formation of NO.

Removal of NO_X from stack gas presents some formidable problems. Possible approaches to NO_X removal are catalytic decomposition of nitrogen oxides, catalytic reduction of nitrogen oxides, and sorption of NO_X by liquids or solids.

Ammonia in the Atmosphere

Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes. Among the various sources of atmospheric ammonia are microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems. High concentrations of ammonia gas in the atmosphere are generally indicative of accidental release of the gas.

Ammonia is removed from the atmosphere by its affinity for water and by its action as a base. It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres. Ammonia reacts with these acidic aerosols to form ammonium salts:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \tag{15.8.7}$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_3 \tag{15.8.8}$$

Ammonium salts are among the more corrosive salts in atmospheric aerosols.

15.9. ACID RAIN

As discussed in this chapter, much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, respectively. These, combined with hydrochloric acid arising from hydrogen chloride emissions, cause acidic precipitation that is now a major pollution problem in some areas.

Precipitation made acidic by the presence of acids stronger than $CO_2(aq)$ is commonly called **acid rain**; the term applies to all kinds of acidic aqueous precipitation, including fog, dew, snow, and sleet. In a more general sense, **acid deposition** refers to the deposition on the earth's surface of aqueous acids, acid gases (such as SO_2), and acidic salts (such as NH_4HSO_4). According to this definition, deposition in solution form is *acid precipitation*, and deposition of dry gases and compounds is *dry deposition*. Although carbon dioxide is present at higher levels in the atmosphere, sulfur dioxide, SO_2, contributes more to the acidity of precipitation for two reasons. The first of these is that sulfur dioxide is significantly more soluble in water than is carbon dioxide, as indicated by its Henry's law constant (Section 5.3) of 1.2 $\text{mol} \times L^{-1} \times \text{atm}^{-1}$ compared to 3.38×10^{-2} $\text{mol} \times L^{-1} \times \text{atm}^{-1}$ for CO_2. Secondly, the value of K_{a1} for $SO_2(aq)$,

$$SO_2(aq) + H_2O \leftarrow\rightarrow H^+ + HSO_3^- \tag{15.9.1}$$

$$K_{a1} = \frac{[H^+][HSO_3^-]}{[SO_2]} = 1.7 \times 10^{-2} \tag{15.9.2}$$

is more than four orders of magnitude higher than the value of 4.45×10^{-7} for CO_2.

Although acid rain can originate from the direct emission of strong acids, such as HCl gas or sulfuric acid mist, most of it is a secondary air pollutant produced by the atmospheric oxidation of acid-forming gases such as the following:

$$SO_2 + {}^1\!/_2O_2 + H_2O \xrightarrow[\text{ing of several steps}]{\text{Overall reaction consist-}} \{2H^+ + SO_4^{2-}\}(aq) \qquad (15.9.3)$$

$$2NO_2 + {}^1\!/_2O_2 + H_2O \xrightarrow[\text{ing of several steps}]{\text{Overall reaction consist-}} 2\{H^+ + NO_3^-\}(aq) \qquad (15.9.4)$$

Chemical reactions such as these play a dominant role in determining the nature, transport, and fate of acid precipitation. As the result of such reactions, the chemical properties (acidity, ability to react with other substances) and physical properties (volatility, solubility) of acidic atmospheric pollutants are altered drastically. For example, even the small fraction of NO that does dissolve in water does not react significantly. However, its ultimate oxidation product, HNO_3, though volatile, is highly water-soluble, strongly acidic, and very reactive with other materials. Therefore, it tends to be removed readily from the atmosphere and to do a great deal of harm to plants, corrodible materials, and other things that it contacts.

Although emissions from industrial operations and fossil fuel combustion are the major sources of acid-forming gases, acid rain has also been encountered in areas far from such sources. This is due in part to the fact that acid-forming gases are oxidized to acidic constituents and deposited over several days, during which time the air mass containing the gas may have moved as much as several thousand km. It is likely that the burning of biomass, such as is employed in “slash-and-burn” agriculture evolves the gases that lead to acid formation in more-remote areas. In arid regions, dry acid gases or acids sorbed to particles may be deposited with effects similar to those of acid rain deposition.

Acid rain spreads out over areas of several hundred to several thousand kilometers. This classifies it as a *regional* air pollution problem rather than a *local* air pollution problem for smog and a *global* one for ozone-destroying chlorofluorocarbons and greenhouse gases. Other examples of regional air pollution problems are those caused by soot, smoke, and fly ash from combustion sources and fires (forest fires). Nuclear fallout from weapons testing or from reactor fires (of which, fortunately, there has been only one major one to date—the one at Chernobyl in the former Soviet Union) can also be regarded as a regional phenomenon.

Acid precipitation shows a strong geographic dependence, as illustrated in Figure 15.10, representing the pH of precipitation in the continental U.S. The preponderance of acidic rainfall in the northeastern U.S., which also affects southeastern Canada, is obvious. Analyses of the movements of air masses have shown a correlation between acid precipitation and prior movement of an air mass over major sources of anthropogenic sulfur and nitrogen oxides emissions. This is particularly obvious in southern Scandinavia, which receives a heavy burden of air pollution from densely populated, heavily industrialized areas in Europe.

Acid rain has been observed for well over a century, with many of the older observations from Great Britain. The first manifestations of this phenomenon were elevated levels of SO_4^{2-} in precipitation collected in industrialized areas. More modern evidence was obtained from analyses of precipitation in Sweden in the 1950s, and of U.S. precipitation a decade or so later. A vast research effort on acid rain was conducted in North America by the National Acid Precipitation Assessment Program, which resulted from the U.S. Acid Precipitation Act of 1980.

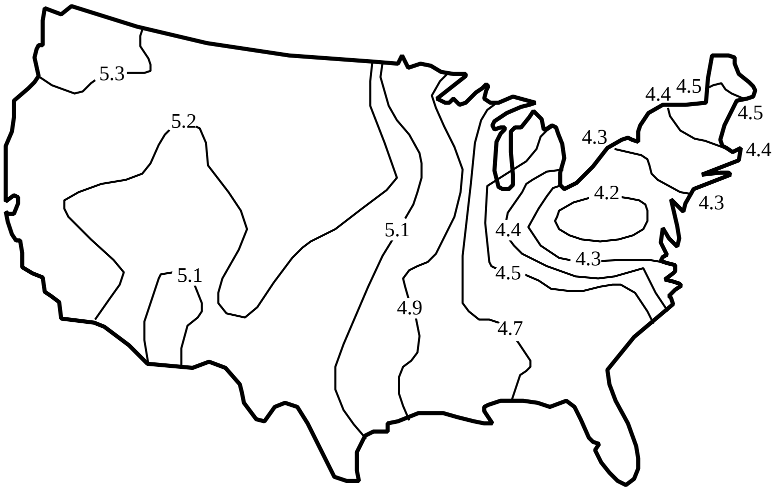


Figure 15.10 Isopleths of pH illustrating a hypothetical precipitation-pH pattern in the lower 48 continental United States. Actual values found may vary with the time of year and climatic conditions.

The longest-term experimental study of acid precipitation in the U.S. has been conducted at the U.S. Forest Service Hubbard Brook Experimental Forest in New Hampshire’s White Mountains. It is downwind from major U.S. urban and industrial centers and is, therefore, a prime candidate to receive acid precipitation. This is reflected by mean annual pH values ranging from 4.0 to 4.2 during the 1964–74 period. During this period, the annual hydrogen ion input ($[H^+]$ × volume) increased by 36%.

Table 15.3 shows typical major cations and anions in pH-4.25 precipitation. Although actual values encountered vary greatly with time and location of collection, this table does show some major features of ionic solutes in precipitation. The predominance of sulfate anion shows that sulfuric acid is the major contributor to acid precipitation. Nitric acid makes a smaller, but significant, contribution to the acid present. Hydrochloric acid ranks third.

It is useful to distinguish between primary sulfate species emitted directly by point sources and secondary sulfate species formed from gaseous sulfur compounds, primarily by the atmospheric oxidation of SO_2. A low primary-sulfate content indicates transport of the pollutant from some distance, whereas a high primary-sulfate content indicates local emissions (the high water solubility of sulfate species means that they do not move far from their sources before being removed with precipitation). This information can be useful in determining the effectiveness of SO_2 control in reducing atmospheric sulfate, including sulfuric acid. Primary and secondary sulfates can be measured using the oxygen-18 content of the sulfates, which is higher in sulfate emitted directly from a power plant than it is in sulfate formed by the oxidation of SO_2.

Table 15.3 Typical Values of Ion Concentrations in Acidic Precipitation

Cations		Anions	
Ion	Concentration equivalents/L × 10^6	Ion	Concentration equivalents/L × 10^6
H^+	56	SO_4^{2-}	51
NH_4^+	10	NO_3^-	20
Ca^{2+}	7	Cl^-	12
Na^+	5	Total	83
Mg^{2+}	3		
K^+	2		
Total	83		

Ample evidence exists of the damaging effects of acid rain. The major effects are the following:

- Direct phytotoxicity to plants from excessive acid concentrations. (Evidence of direct or indirect phytoxicity of acid rain is provided by the declining health of eastern U.S. and Scandinavian forests and especially by damage to Germany’s Black Forest.)
- Phytotoxicity from acid-forming gases, particularly SO_2 and NO_2, that accompany acid rain
- Indirect phytotoxicity, such as from Al^{3+} liberated from soil
- Destruction of sensitive forests
- Respiratory effects on humans and other animals
- Acidification of lake water with toxic effects to lake flora and fauna, especially fish fingerlings
- Corrosion of exposed structures, electrical relays, equipment, and ornamental materials. Because of the effect of hydrogen ion,

  $$2H^+ + CaCO_3(s) \rightarrow Ca^{2+} + CO_2(g) + H_2O$$

  limestone, $CaCO_3$, is especially susceptible to damage from acid rain
- Associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds. (As mentioned in Section 15.6, intensification of cloud cover and changes in the optical properties of cloud droplets—specifically, increased reflectance of light—resulting from acid sulfate in the atmosphere may even have a mitigating effect on greenhouse warming of the atmosphere.) A significant association exists between acidic sulfate in the atmosphere and haziness.

Forms of precipitation other than rainfall may contain excess acidity. Acidic fog can be especially damaging because it is very penetrating. In early December 1982, Los Angeles experienced a severe, 2-day episode of acid fog. This fog consisted of a heavy concentration of acidic mist particles at ground level that reduced visibility and were very irritating to breathe. The pH of the water in these particles was 1.7, much lower than ever before recorded for acid precipitation. Another source of precipitation heavy in the ammonium, sulfate, and nitrate ions associated with atmospheric acid is **acid rime**. Rime is frozen cloudwater that may condense on snowflakes or exposed surfaces. Rime constitutes up to 60% of the snowpack in some mountainous areas, and the deposition of acidic constituents with rime may be a significant vector for the transfer of acidic atmospheric constituents to Earth's surface in some cases.

15.10 FLUORINE, CHLORINE, AND THEIR GASEOUS COMPOUNDS

Fluorine, hydrogen fluoride, and other volatile fluorides are produced in the manufacture of aluminum, and hydrogen fluoride is a byproduct in the conversion of fluorapatite (rock phosphate) to phosphoric acid, superphosphate fertilizers, and other phosphorus products. Hydrogen fluoride gas is a dangerous substance that is so corrosive that it even reacts with glass. It is irritating to body tissues, and the respiratory tract is very sensitive to it. Brief exposure to HF vapors at the part-per-thousand level may be fatal. The acute toxicity of F_2 is even higher than that of HF. Chronic exposure to high levels of fluorides causes fluorosis. The symptoms of fluorosis include mottled teeth and pathological bone conditions that can be manifested by defective bone structure.

Plants are particularly susceptible to the effects of gaseous fluorides. Fluorides from the atmosphere appear to enter the leaf tissue through the stomata. Fluoride is a cumulative poison in plants, and exposure of sensitive plants to even very low levels of fluorides for prolonged periods results in damage. Characteristic symptoms of fluoride poisoning are chlorosis (fading of green color due to conditions other than the absence of light), edge burn, and tip burn. Conifers (such as pine trees) afflicted with fluoride poisoning may have reddish-brown necrotic needle tips.

Silicon tetrafluoride gas, SiF_4, a gaseous fluoride pollutant produced during some steel and metal smelting operations that employ CaF_2, fluorspar. Fluorspar reacts with silicon dioxide (sand), releasing SiF_4 gas:

$$2CaF_2 + 3SiO_2 \rightarrow 2CaSiO_3 + SiF_4 \qquad (15.10.1)$$

Another gaseous fluorine compound, sulfur hexafluoride, SF_6, occurs in the atmosphere at levels of about 0.3 parts per trillion. It is extremely unreactive with an atmospheric lifetime estimated at 3200 years, and is used as an atmospheric tracer. It does not absorb ultraviolet light in either the troposphere or stratosphere, and is probably destroyed above 60 km by reactions beginning with its capture of free electrons. Current atmospheric levels of SF_6 are significantly higher than the estimated background level of 0.04 ppt in 1953, when commercial production of it began. The compound is very useful in specialized applications including gas-insulated electrical equipment and inert blanketing/degassing of molten aluminum and magnesium. Increasing uses of sulfur hexafluoride are of concern because it is the most powerful greenhouse gas known, with a global warming potential (per molecule added to the atmosphere) about 23,900 times that of carbon dioxide.

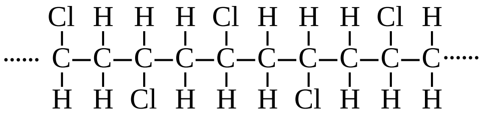
Chlorine and Hydrogen Chloride

Chlorine gas, Cl_2, does not occur as an air pollutant on a large scale but can be quite damaging on a local scale. Chlorine was the first poisonous gas deployed in World War I. It is widely used as a manufacturing chemical, in the plastics industry, for example, as well as for water treatment and as a bleach. Therefore, possibilities for its release exist in a number of locations. Chlorine is quite toxic and is a mucous-membrane irritant. It is very reactive and a powerful oxidizing agent. Chlorine dissolves in atmospheric water droplets, yielding hydrochloric acid and hypochlorous acid, an oxidizing agent:

$$H_2O + Cl_2 \rightarrow H^+ + Cl^- + HOCl \qquad (15.10.2)$$

Spills of chlorine gas have caused fatalities among exposed persons.

Hydrogen chloride, HCl, is emitted from a number of sources. Incineration of chlorinated plastics, such as polyvinylchloride, releases HCl from combustion.



$$\cdots\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdots$$

Polyvinylchloride

Some compounds released to the atmosphere as air pollutants hydrolyze to form HCl. Such incidents have occurred as the result of leaks of liquid silicon tetrachloride, $SiCl_4$. This compound reacts with water in the atmosphere to form a choking fog of hydrochloric acid droplets:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \qquad (15.10.3)$$

Other incidents have occurred when powdered aluminum chloride has been spilled. This compound also produces HCl gas when wet,

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \qquad (15.10.4)$$

generating fumes of hydrochloric acid.

15.11 HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE

Hydrogen sulfide is produced by microbial decay of sulfur compounds and microbial reduction of sulfate (see the discussion of microbial transformation of sulfur in Chapter 11, Section 11.13), from geothermal steam, from wood pulping, and from a number of miscellaneous natural and anthropogenic sources. Most atmospheric hydrogen sulfide is rapidly converted to SO_2 and to sulfates. The organic homologs of hydrogen sulfide, the mercaptans, enter the atmosphere from decaying organic matter and have particularly objectionable odors.

Hydrogen sulfide pollution from artificial sources is not as much of an overall air pollution problem as sulfur dioxide pollution. However, there have been several acute incidents of hydrogen sulfide emissions resulting in damage to human health and even fatalities. The most notorious such incident occurred in Poza Rica, Mexico, in 1950. Accidental release of hydrogen sulfide from a plant used for the recovery of sulfur from natural gas caused the reported deaths of 22 people and the hospitalization of over 300.

Hydrogen sulfide at levels well above ambient concentrations destroys immature plant tissue. This type of plant injury is readily distinguished from that due to other phytotoxins. More-sensitive species are killed by continuous exposure to around 3000 ppb H_2S, whereas other species exhibit reduced growth, leaf lesions, and defoliation.

Damage to certain kinds of materials is a very expensive effect of hydrogen sulfide pollution. Paints containing lead pigments, $2PbCO_3{\bullet}Pb(OH)_2$ (no longer used), were particularly susceptible to darkening by H_2S. A black layer of copper sulfide forms on copper metal exposed to H_2S. Eventually, this layer is replaced by a green coating of basic copper sulfate such as $CuSO_4{\bullet}3Cu(OH)_2$. The green “patina,” as it is called, is very resistant to further corrosion. Such layers of corrosion can seriously impair the function of copper contacts on electrical equipment. Hydrogen sulfide also forms a black sulfide coating on silver.

Carbonyl sulfide, COS, is now recognized as a component of the atmosphere at a tropospheric concentration of approximately 500 parts per trillion by volume, corresponding to a global burden of about 2.4 teragrams. It is, therefore, a significant sulfur species in the atmosphere.

Both COS and CS_2 are oxidized in the atmosphere by reactions initiated by the hydroxyl radical. The initial reactions are

$$HO\bullet + COS \rightarrow CO_2 + HS\bullet \tag{15.11.1}$$

$$HO\bullet + CS_2 \rightarrow COS + HS\bullet \tag{15.11.2}$$

The sulfur-containing products undergo further reactions to sulfur dioxide and, eventually, to sulfate species.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Atmospheric aerosols are [1]____
_______________________________________. Condensation aerosols are formed by
[2]____ and
dispersion aerosols are formed by [3]____
____. As applied to the formation of
atmospheric aerosols, the reaction $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ shows[4]______
____

____. In general, the proportions of elements in atmospheric particulate matter reflect[5]________________________ ___________________________. The two reactions $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ and $H_2SO_4 + 2NaCl(\text{particulate}) \rightarrow 2Na_2SO_4(\text{particulate}) + 2HCl$ show why particulate matter largely from ocean spray origin in a coastal area receiving sulfur dioxide pollution may show [6]_____________________________ __________________________. Insofar as origins of elements in particulate matter are concerned, soil erosion, rock dust, and coal combustion produce [7]_____ __________; incomplete combustion of carbonaceous fuels produces [8]____________; marine aerosols and incineration of organohalide polymer wastes produces [9]______ __________; and combustion of residual petroleum produces [10]________________. Mineral particulate matter in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel that can be collected in furnace flues is called [11]____________________. Three adverse respiratory health effects caused by inhalation of asbestos are [12]____________________________________ ___________________________. The toxic metal of greatest concern in the urban atmosphere is [13]___________ because it [14]________________________________ ___________________________. A significant natural source of radionuclides in the atmosphere is [15]________________,which initially decays to [16]________________. Another significant source of radioactivity in the atmosphere is [17]______________ _______________________ and a former source of atmospheric radioactivity was [18] _______________________________. Three effects of atmospheric particles are [19] ____. The most common health effects of atmospheric particles are on the [20]___________ ______________. Some of the most common ways to control particulate emissions are [21]____ ____. Carbon monoxide causes pollution problems in cases of [22]__________________________________. _______________. It is of most concern because of its [23]____________________. Automobiles are equipped with [24]_______________________________________ to cut down carbon monoxide emissions. It is generally agreed that carbon monoxide is removed from the atmosphere by [25]__________________________. The greatest pollution concern with carbon dioxide is its role as [26]_____________ ___________________. The two major sources of atmospheric carbon dioxide are [27]____. Most sulfates enter the atmosphere from [28]____________________________ and most sulfur dioxide from [29]_____________________________________. The fate of any H_2S that does get into the atmosphere is that it is [30]____. Sulfur dioxide’s primary health effect is upon the [31]__________________________. Chronic exposure of plants to sulfur dioxide causes [32]_____________. Sulfur dioxide can be removed from stack gas by [33]__________________ processes, of which the major types are [34]____ ____________________. The three oxides of nitrogen normally encountered in the atmosphere are [35]______________________________________. Nitric oxide (NO) and nitrogen dioxide (NO_2) are collectively designated [36]_____, most of which enters the atmosphere as [37]______________________. The most important photo-chemical reaction of NO_2, and one that can lead to photochemical smog formation is [38]

. Pulmonary exposure to 150–200 ppm of NO_2 causes [39]
, a condition fatal within 3–5 weeks after exposure. During the combustion of fossil fuels, [40]_________________
__________________________ is effective in reducing NO_x emissions. Sources of atmospheric ammonia are [41]____
____
____Much of the sulfur and nitrogen oxides entering the atmosphere are converted to [42]___________
___________________________, which, along with hydrochloric acid arising from hydrogen chloride emissions, cause [43]_____________________________. The major damaging effects of acid precipitation are [44]_________________________________
____
____
____
____
____
____.
Two specific gaseous fluorine-containing air pollutants are [45]_________________
_________________________. Though not directly toxic, the fluorine-containing air pollutants with the greatest potential for damage to the atmosphere are the [46]_____
____. Halons, which are related to chlorofluorocarbons, are compounds that contain [47]____________ and are used in [48]
. The concern with chlorofluoro-carbon air pollutants is [49]
. The first reaction in this harmful process is [50]________________________________,
the Cl atoms of which undergo the reaction [51]
with ozone. The most prominent instance of ozone layer destruction that has been documented in recent years is [52]_________________________. The highly damaging conse-quence of stratospheric ozone destruction is that it would allow [53]
_____________, which would result in [54]___________________________________
_________________________. Atmospheric chlorine dissolves in atmospheric water droplets, yielding [55]____.
Natural sources of hydrogen sulfide are [56]_________________________________
_______________________________________.

Answers to Chapter Summary

1. solid or liquid particles smaller than 100 µm in diameter
2. condensation of vapors or reactions of gases
3. grinding of solids, atomization of liquids, aerosol or dispersion of dusts
4. oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic sub-stance that accumulates atmospheric water to form small liquid droplets
5. relative abundances of elements in the parent material
6. anomalously high sulfate and corresponding low chloride content
7. Al, Fe, Ca, Si
8. C
9. Na, Cl
10. V

11. fly ash
12. asbestosis, mesothelioma, and bronchogenic carcinoma
13. lead
14. comes closest to being present at a toxic level
15. radon
16. ^{218}Po and ^{216}Po
17. the combustion of fossil fuels
18. the above-ground detonation of nuclear weapons
19. reduction and distortion of visibility, provision of active surfaces upon which heterogeneous atmospheric chemical reactions can occur, and nucleation bodies for the condensation of atmospheric water vapor
20. respiratory tract
21. sedimentation, inertial mechanisms, baghouses, scrubbers, electrostatic precipitators
22. concentrated localized pollution
23. toxicity
24. catalytic converters
25. reaction with hydroxyl radical
26. a greenhouse gas
27. burning of fossil fuels and deforestation
28. marine sources
29. scrubbing
30. converted rapidly to SO_2
31. respiratory tract
32. chlorosis
33. scrubbing
34. throwaway and recovery systems
35. nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2)
36. NO_x
37. NO
38. $NO_2 + h\nu \rightarrow NO + O$
39. *bronchiolitis fibrosa obliterans*
40. low excess air firing
41. microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems
42. sulfuric and nitric acids
43. acidic precipitation
44. direct phytotoxicity to plants from excessive acid concentrations; phytotoxicity from acid-forming gases; indirect phytotoxicity, such as from Al^{3+} liberated from acidified soil; destruction of sensitive forests, respiratory effects on humans and other animals; acidification of lake water with toxic effects to lake flora and fauna; corrosion to exposed structures, electrical relays, equipment, and ornamental materials; and associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds.
45. fluorine gas and hydrogen fluoride
46. chlorofluorocarbons (CFC)
47. bromine

48. fire extinguisher systems
49. their potential to destroy stratospheric ozone
50. $Cl_2CF_2 + h\nu \rightarrow Cl\cdot + ClCF_2\cdot$
51. $Cl + O_3 \rightarrow ClO + O_2$
52. the Antarctic ozone hole
53. penetration of high-energy ultraviolet radiation
54. adverse biological effects, such as increased skin cancer
55. hydrochloric acid and hypochlorous acid
56. microbial decay of sulfur compounds and microbial reduction of sulfate

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QUESTIONS AND PROBLEMS

1. A freight train that included a tank car containing anhydrous NH_3 and one containing concentrated HCl was wrecked, causing both of the tank cars to leak. In the region between the cars a white aerosol formed. What was it, and how was it produced?
2. What two vapor forms of mercury might be found in the atmosphere?
3. Analysis of particulate matter collected in the atmosphere near a seashore shows considerably more Na than Cl on a molar basis. What does this indicate?
4. What type of process results in the formation of very small aerosol particles?
5. Which size range encompasses most of the particulate matter mass in the atmosphere?
6. Why are aerosols in the 0.1–1 µm size range especially effective in scattering light?
7. Per unit mass, why are smaller particles more effective catalysts for atmospheric chemical reactions?
8. What is the rationale for classifying most acid rain as a secondary pollutant?
9. Distinguish among UV-A, UV-B, and UV-C radiation. Why does UV-B pose the greatest danger in the troposphere?
10. Why is it that “highest levels of carbon monoxide tend to occur in congested urban areas at times when the maximum number of people are exposed?”
11. Which unstable, reactive species is responsible for the removal of CO from the atmosphere?
12. Which of the following fluxes in the atmospheric sulfur cycle is smallest: (a) Sulfur species washed out in rainfall over land, (b) sulfates entering the atmosphere as “sea salt,” (c) sulfur species entering the atmosphere from volcanoes, (d) sulfur species entering the atmosphere from fossil fuels, (e) hydrogen sulfide entering the atmosphere from biological processes in coastal areas and on land.
13. Of the following agents, the one that would not favor conversion of sulfur dioxide to sulfate species in the atmosphere is: (a) Ammonia, (b) water, (c) contaminant reducing agents, (d) ions of transition metals such as manganese, (e) sunlight.
14. The air inside a garage was found to contain 10 ppm CO by volume at standard temperature and pressure (STP). What is the concentration of CO in mg/L and in ppm by mass?
15. Assume that an incorrectly adjusted lawn mower is operated in a garage such that the combustion reaction in the engine is

$$C_8H_{18} + {}^{17}/_{2}O_2 \rightarrow 8CO + 9H_2O$$

If the dimensions of the garage are 5 × 3 × 3 meters, how many grams of gasoline must be burned to raise the level of CO in the air to 1000 ppm by volume at STP?

16. A 12.0-L sample of waste air from a smelter process was collected at 25˚C and 1.00 atm pressure, and the sulfur dioxide was removed. After SO_2 removal, the volume of the air sample was 11.50 L. What was the percentage by weight of SO_2 in the original sample?

17. What is the oxidant in the Claus reaction?

18. How many metric tons of 5%–S coal would be needed to yield the H_2SO_4 required to produce a 3.00–cm rainfall of pH 2.00 over a 100 km^2 area?

19. In what major respect is NO_2 a more significant species than SO_2 in terms of participation in atmospheric chemical reactions?

20. Match the effect on the right with its most likely source or cause from the left, below:

    A. Sunlight and autos
    B. Burning of all types of fossil fuels
    C. Chlorofluorocarbons
    D. Burning of coal, especially

    1. Global warming
    2. Increased acidity in the atmosphere
    3. Pollutant oxidants in the lower troposphere
    4. Destruction of stratospheric ozone

21. Of the following, the most likely to be formed by pyrosynthesis is

    A. Sulfate particles
    B. Ammonium particles
    C. Sulfuric acid mist
    D. PAHs
    E. Ozone in smog

22. Of the following, the true statement related to carbon monoxide in the atmosphere is

    A. It is strictly a pollutant with none coming from natural sources.
    B. It is an intermediate in reactions by which methane is removed by normal atmospheric processes.
    C. It is increasing in the atmosphere at a rate of approximately 1 ppm per year.
    D. Although produced by a reaction with hydroxyl radical it does not react with HO•.
    E. Most harmful levels of CO are produced as secondary pollutants.

23. Of the following, the **untrue** statement regarding the fate of sulfur dioxide in the atmosphere is

    A. It reacts to form particulate matter.
    B. It is largely oxidized by reactions occurring inside water aerosol droplets.
    C. Although acidic, it can react to form an even more acidic species.
    D. The presence of hydrocarbons and nitrogen oxides generally accelerates sulfur dioxide oxidation.
    E. It is produced as a stable species during smog-forming conditions.

24. Assume that the wet limestone process requires 1 metric ton of $CaCO_3$ to remove 90% of the sulfur from 4 metric tons of coal containing 2% S. Assume that the sulfur product is $CaSO_4$. Calculate the percentage of the limestone converted to calcium sulfate.

25. Of the following, the statement that is **untrue** is

    A. Acid rain is denoted by any precipitation with a pH less than neutral (7.00).
    B. Acid may be deposited as acidic salts and acid gases, in addition to liquid acid rain
    C. Acid rain is a regional air pollution problem as distinguished from local or global problems.
    D. Carbon dioxide makes rainfall slightly acidic
    E. Acid rain is often associated with elevated levels of sulfate ion, SO_4^{2-}.