3

Scales of the Air Pollution Problem

Ambient air pollution exists at all scales, from extremely local to global.[1] This chapter considers five different scales: local; urban; regional; continental; and global. The spheres of influence of the air pollutants themselves range from molecular (e.g. gases and nanoparticles) to planetary (e.g. diffusion of greenhouse gases throughout the troposphere). The local scale is up to about 5 km of the earth's surface. The urban scale extends to the order of 50 km. The regional scale is from 50 to 500 km. Continental scales are from 500 to several 1000 km. Of course, the global scale extends worldwide.

I. LOCAL

Local air pollution problems are usually characterized by one or several large emitters or a large number of relatively small emitters. The lower the release height of a source, the larger the potential impact for a given release. Carbon monoxide emitted from motor vehicles, which leads to high concentrations near roadways is an example. Any ground-level source, such as evaporation of volatile organic compounds from a waste treatment pond, will produce the highest concentrations near the source, with concentrations

[1] At an even smaller scale are *microenvironmental* (e.g. indoor air in a home, office, or garage) and *personal* (i.e. at the individual's breathing zone).

generally diminishing with distance. This phenomenon is known as a concentration gradient.

Large sources that emit high above the ground through stacks, such as power plants or industrial sources, can also cause local problems, especially under unstable meteorological conditions that cause portions of the plume to reach the ground in high concentrations.

There are many releases of pollutants from relatively short stacks or vents on the top of one- or two-story buildings. Under most conditions such releases are caught within the turbulent downwash downwind of the building. This allows high concentrations to be brought to the ground surface. Many different pollutants can be released in this manner, including compounds and mixtures that can cause odors. The modeling of the transport and dispersion of pollutants on this scale is discussed in Chapter 22.

Usually, the effects of accidental releases are confined to the local scale.

II. URBAN

Air pollution problems in urban areas generally are of two types. One is the release of primary pollutants (those released directly from sources). The other is the formation of secondary pollutants (those that are formed through chemical reactions of the primary pollutants).

Air pollution problems can be caused by individual sources on the urban scale as well as the local scale. For pollutants that are relatively nonreactive, such as carbon monoxide and particulate matter,[2] or relatively slowly reactive, such as sulfur dioxide, the contributions from individual sources combine to yield high concentrations. Since a major source of carbon monoxide is motor vehicles, "hot spots" of high concentration can occur especially near multilane intersections. The emissions are especially high from idling vehicles. The hot spots are exacerbated if high buildings surround the intersection, since the volume of air in which the pollution is contained is severely restricted. The combination of these factors results in high concentrations.

Tropospheric ozone is the dominant urban problem resulting from the formation of secondary pollutants. Many large metropolitan areas experience the formation of ozone from photochemical reactions of oxides of nitrogen and various species of hydrocarbons. These reactions are catalyzed by the ultraviolet light in sunlight and are therefore called photochemical reactions. Many metropolitan areas are in nonattainment for ozone; that is, they are not meeting the air quality standards. The Clean Air Act Amendments (CAAA) of 1990 recognize this as a major problem and have classified the various metropolitan areas to be in nonattainment according to the severity of the problem for that

[2] It should be noted that particulate matter is highly variable in its composition. Most of the particle may be nonreactive, but aerosols often contain chemically reactive substances, especially those sorbed onto the particle surface.

area. The CAAA sets timetables for the various classifications for reaching attainment with the National Ambient Air Quality Standards (NAAQS). Oxides of nitrogen, principally nitric oxide (NO), but also nitrogen dioxide (NO_2) are emitted from automobiles and from combustion processes. Hydrocarbons are emitted from many different sources. The various species have widely varying reactivities. Determining the emissions of the these chemical species from myriad sources as a basis for pollution control programs can be difficult, but methods continue to improve. These and other aspects of atmospheric chemistry are discussed in Chapter 7.

III. REGIONAL

At least three types of problems contribute to air pollution problems on the regional scale. The first is the blend of urban oxidant problems at the regional scale. Many major metropolitan are in close proximity to one another and continue to grow. Urban geographers refer to some of the larger urban aggregations as "megalopolises." As a result, the air from one metropolitan area, containing both secondary pollutants formed through reactions and primary pollutants, flows on to the adjacent metropolitan area. The pollutants from the second area are then added on top of the "background" from the first.

A second type of problem is the release of relatively slow-reacting primary air pollutants that undergo reactions and transformations during lengthy transport times. A common occurrence in environmental engineering is the direct relationship between time, spatial coverage, and chemical transformation. Thus, these protracted transport times result in transport distances over regional scales not only of the parent compounds but of numerous transformation byproducts. The gas, sulfur dioxide (SO_2), released primarily through combustion of fossil fuels (especially from coal and oil) is oxidized during long-distance transport to sulfur trioxide (SO_3):

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{3.1}$$

Although SO_2 is a gas, both gas phase and liquid phase oxidation of SO_2 occurs in the troposphere. The SO_3 in turn reacts with water vapor to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{3.2}$$

Sulfuric acid reacts with numerous compounds to form sulfates. These are fine (submicrometer) particulates.

Nitric oxide (NO) results from high-temperature combustion, both in stationary sources such as power plants or industrial plants in the production of process heat and in internal combustion engines in vehicles. The NO is oxidized in the atmosphere, usually rather slowly, or more rapidly if there is ozone present, to nitrogen dioxide (NO_2). NO_2 also reacts further with other constituents, forming nitrates, which is also in fine particulate form.

The sulfates and nitrates existing in the atmosphere as fine particulates, generally in the size range less than 1 μm, can be removed from the atmosphere by several processes. "Rain out" occurs when the particles serve as condensation nuclei that lead to the formation of clouds. The particles are then precipitated if the droplets grow to sufficient size to fall as raindrops. Another mechanism, known as "washout," also involves rain, but the particles in air are captured by raindrops falling through the air. Both mechanisms contribute to "acid rain," which results in the sulfate and nitrate particles reaching lakes and streams, and increasing their acidity. As such, acid rain is both a regional and continental problem (see discussion in the next section).

A third type of regional problem is visibility, which may be reduced by specific plumes or by the regional levels of particulate matter that produce various intensities of haze. The fine sulfate and nitrate particulates just discussed are largely responsible for reduction of visibility (see Chapter 14). This problem is of concern in locations of natural beauty, where it is desirable to keep scenic vistas as free of obstructions to the view as possible. Regional haze is a type of visibility impairment that is caused by the emissions of air pollutants from numerous sources across a broad region. The CAAA provides special protections for such areas; the most restrictive denoted as mandatory Federal Class I areas that cover 156 national parks and wilderness areas. On July 1, 1999, EPA published regulations to address regional haze in these areas. Decreased visibility can also impair safety, especially in aviation.

IV. CONTINENTAL

In a relatively small continental area such as Europe, there is little difference between what would be considered regional scale and continental scale. However, on larger continents there would be a substantial difference. Perhaps of greatest concern on the continental scale is that the air pollution policies of a nation are likely to create impacts on neighboring nations. Acid rain in Scandinavia has been considered to have had impacts from Great Britain and Western Europe. Japan has considered that part of their air pollution problem, especially in the western part of the country, has origins in China and Korea. For decades, Canada and the United States have cooperated in studying and addressing the North American acid rain problem.

A. The Science of Acid Rain

Acid rain is a regional air pollution concern, affecting surface waters in large parts of North America and Europe. We hear the term frequently, but what is it? Some correctly point out that in fact most of the rain falling in North America has been acidic since even before industrialization. The main source of natural acidity is carbon dioxide (CO_2) gas that is dissolved into water droplets in the atmosphere and the resulting carbonic acid (H_2CO_3) is ionized, lowering the water's pH. Given the mean partial pressure of CO_2 in the air is 3.0×10^{-4} atm, it is possible to calculate the pH of water in equilibrium with the air at 25°C, and the concentration of all species present in this solution. We can also assume that the mean concentration of CO_2 in the troposphere is 350 ppm, but this concentration is rising by some estimates at a rate of 1 ppm per year. The concentration of the water droplet's CO_2 in water in equilibrium with air is obtained from the partial pressure of Henry's law constant[3]:

$$p_{CO_2} = K_H[CO_2]_{aq} \tag{3.3}$$

The change from carbon dioxide in the atmosphere to carbonate ions in water droplets follows a sequence of equilibrium reactions:

$$CO_{2(g)} \xleftrightarrow{K_H} CO_{2(aq)} \xleftrightarrow{K_r} H_2CO_{3(aq)} \xleftrightarrow{K_{a1}} HCO^-_{3(aq)} \xleftrightarrow{K_{a2}} CO^{2-}_{3(aq)} \tag{3.4}$$

The Henry's law constant is a function of a substance's solubility and vapor pressure.

A more precise term for acid rain is acid deposition, which comes in two forms: wet and dry. Wet deposition refers to acidic rain, fog, and snow. The dry deposition fraction consists of acidic gases or particulates. The severity of ecological effects stemming from acid deposition depends on many factors, especially the strength of the acids and the buffering capacity of the soils. Note that this involves every species in the carbonate equilibrium reactions of Eq. 3.4 (see Fig. 3.1). The processes that release carbonates increase the buffering capacity of natural soils, which moderates the effects of acid rain. Thus, carbonate-rich soils like those in the Central North America are able to withstand even elevated acid deposition compared to the thin soil areas, such as those in the Canadian Shield, the New York Finger Lakes region, and much of Scandinavia.

The concentration of carbon dioxide (CO_2) is constant, since the CO_2 in solution is in equilibrium with the air that has a constant partial pressure of CO_2. And the two reactions and ionization constants for carbonic acid are:

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad K_{a1} = 4.3 \times 10^{-7} \tag{3.5}$$

and;

$$HCO_3^- + H_2O \leftrightarrow CO_3^{-2} + H_3O^+ \quad K_{a2} = 4.7 \times 10^{-11} \tag{3.6}$$

[3] For a complete explanation of the Henry's law constant, including how it is calculated and example problems (see Chapter 6).

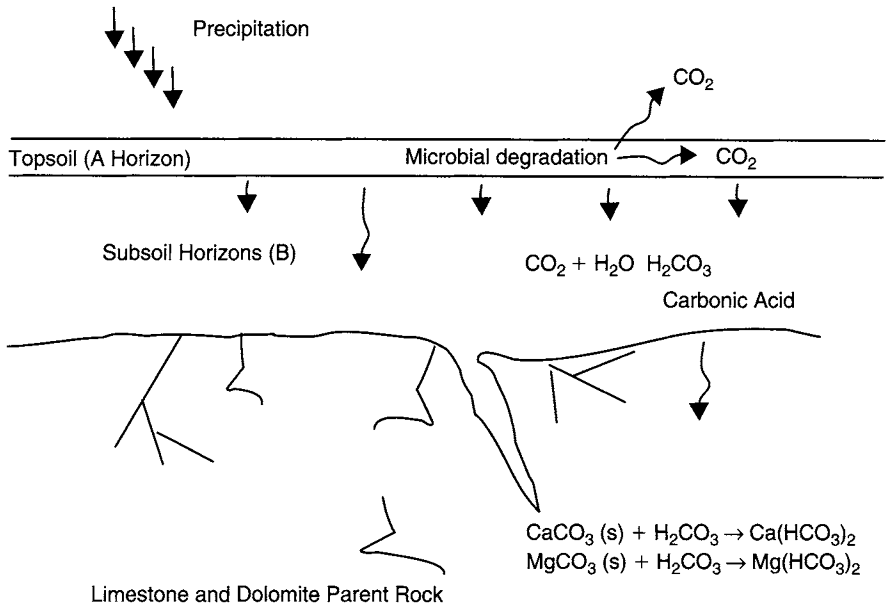

Fig. 3.1. Biogeochemistry of carbon equilibrium. The processes that release carbonates are responsible for much of the buffering capacity of natural soils against the effects of acid rain.

K_{a1} is four orders of magnitude greater than K_{a2}, so the second reaction can be ignored for environmental acid rain considerations. The solubility of gases in liquids can be described quantitatively by Henry's law, so for CO_2 in the atmosphere at 25°C, we can apply the Henry's law constant and the partial pressure to find the equilibrium. The K_H for $CO_2 = 3.4 \times 10^{-2} \mathrm{mol\,L^{-1}\,atm^{-1}}$. We can find the partial pressure of CO_2 by calculating the fraction of CO_2 in the atmosphere. Since the mean concentration of CO_2 in the earth's troposphere is 350 ppm by volume in the atmosphere, the fraction of CO_2 must be 350 divided by 1 000 000 or 0.000350 atm.

Thus, the carbon dioxide and carbonic acid molar concentration can now be found:

$$[CO_2] = [H_2CO_3] = 3.4 \times 10^{-2} \mathrm{mol\,L^{-1}\,atm^{-1}} \times 0.000350\,\mathrm{atm} = 1.2 \times 10^{-5}\,\mathrm{M}$$

At equilibrium, $[H_3O^+] = [HCO^-]$.

Taking this and our carbon dioxide molar concentration, gives us:

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[HCO_3^-][H_3O^+]}{CO_2} = \frac{[H_3O^+]^2}{1.2 \times 10^{-5}}$$

$$[H_3O^+]^2 = 5.2 \times 10^{-12}$$

$$[H_3O^+] = 2.6 \times 10^{-6}\,\mathrm{M}$$

Since pH, by definition is the negative log of the hydronium ion, $[H_3O^-]$, concentration (that is, $pH = -\log_{10} [H_3O^+] \approx -\log_{10}[H^+]$), then we calculate the pH. Thus, the droplet pH is about 5.6.

In the next section we are concerned with global air pollution. A big concern is possible warming of the troposphere. However, in addition to the radiant effect of carbon dioxide, what will happen to the acidity of precipitation with increasing concentrations of the gas? For example, if the concentration of CO_2 in the atmosphere increases to 400 ppm, what will happen to the pH of "natural rain"?

The new molar concentration would be $3.4 \times 10^{-2} \text{mol L}^{-1} \text{atm}^{-1} \times 0.000400 \text{atm} = 1.4 \times 10^{-5}$M, so $4.3 \times 10^{-7} = [H_3O^+]^2/1.4 \times 10^{-5}$ and $[H_3O^+]^2 = 6.0 \times 10^{-12}$ and $[H_3O^+] = 3.0 \times 10^{-6}$M. So, the droplet pH would be about 5.5. This means that the incremental increase in atmospheric carbon dioxide can be expected contribute to greater acidity in natural rainfall. But, how is it then that some rain can have a pH of 2 or even lower?

Much of the pH reduction occurs as the result of interactions with a few specific air contaminants. For example, sulfur oxides produced in the burning of fossil fuels (especially coal) is a major contributor to low pH in rain. In fact, CO_2 is not the principal concern of acid rain. Other processes have led to dramatic increases in droplet acidity, especially sulfuric and nitric acid formation from the ionization of the oxides of sulfur and nitrogen, which further decreases this pH level to those harmful to aquatic organisms. Acid precipitation can result from the emissions of plumes of strong acids, such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) in the forms of acid mists, but most commonly the pH drop is the result of secondary reactions of the acid gases SO_2 and NO_2:

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow \text{several intermediate reactions} \rightarrow \{2H^+ + SO_4^{2-}\}_{aq} \tag{3.7}$$

$$2NO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow \text{several intermediate reactions} \rightarrow \{2H^+ + NO_3^-\}_{aq} \tag{3.8}$$

In its simplest terms, SO_2 is emitted from the combustion of fuels containing sulfur, the reaction being

$$S + O_2 \xrightarrow{\text{heat}} SO_2 \tag{3.9}$$

The sulfur dioxide is then photochemically oxidized:

$$SO_2 + O \xrightarrow{\text{sunlight}} SO_3 \tag{3.10}$$

The sulfur trioxide is reduced to form sulfuric acid, which is ionized in water:

$$SO_3 + H_2 \rightarrow H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \tag{3.11}$$

Sulfur oxides do not literally produce sulfuric acid in the clouds, but the concept is the same.[4] The precipitation from air containing high concentrations of sulfur oxides is poorly buffered and its pH readily drops.

Nitrogen oxides, emitted mostly from automobile exhaust, but also from any other high-temperature combustion, contribute to the acid mix in the atmosphere. The chemical reactions that apparently occur with nitrogen are:

$$N_2 + O_2 \rightarrow 2NO \tag{3.12}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3.13}$$

$$NO_2 + O_3 + H_2O \rightarrow 2HNO_3 + O_2 \rightarrow 2H^+ + 2NO_3^- + O_2 \tag{3.14}$$

Thus, the principal acid is nitric acid, HNO_3.

Hundreds of lakes in North America and Scandinavia have become so acidic that they no longer can support fish life. In a recent study of Norwegian lakes, more than 70% of the lakes having a pH of less than 4.5 contained no fish, and nearly all lakes with a pH of 5.5 and above contained fish. The low pH not only affects fish directly, but also contributes to the release of potentially toxic metals such as aluminum, thus magnifying the problem.

In North America, acid rain has already decimated the populations of numerous fish and many plants in 50% of the high mountain lakes in the Adirondacks. The pH in certain lakes has reached such levels of acidity as to replace the trout and native plants with acid-tolerant rough fish species and mats of algae.

The deposition of atmospheric acid on freshwater aquatic systems prompted the EPA to suggest a limit from 10 to 20 kg SO_4^{2-} per hectare per year. Putting this limit into the context of existing emissions, the state of Ohio alone has total annual emissions are 2.4×10^6 metric tons of gaseous sulfur dioxide (SO_2) per year. If all of this is converted to SO_4^{2-} and is deposited on the State of Ohio, the total would be 360 kg per hectare per year.[5] Similar calculations for the sulfur emissions for northeastern United States indicate that the rate of sulfur emission is 4 to 5 times greater than the rate of deposition. What happens to all of the excess sulfur? Certainly, as the reactions above indicate, much of it is oxidized into acidic chemical species. Canada and the United States have been discussing this for over a decade. Likewise, much of the problem in Scandinavia can be traced to the use of tall stacks in Great Britain and the lowland countries of continental Europe. British industries for some years simply built increasingly tall stacks as a method of air pollution control, reducing the immediate ground-level concentration, but emitting the

[4] Actually many acid–base systems in the environment are in equilibrium condition among acids, bases, ionic, and other chemical species. For example, in natural waters, carbonic acid which is responsible for most natural acidity in surface waters is indicated as $H_2CO_3^*$. The asterisk indicates that the actual acid is only part of the equilibrium, which also consists of CO_2 dissolved in the water, CO_2 dissolved in the air, and ionic forms, especially carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-).

[5] US Environmental Protection Agency, Washington, DC.

same pollutants into the higher atmosphere. The air quality in the United Kingdom improved, but at the expense of acid rain at other parts of Europe. One of the difficulties in dealing with acid rain and global climate change is that they in essence are asking society to cut back on combustion. And, to many, combustion is tantamount to progress and development.

V. GLOBAL

The release of radioactivity from the accident at Chernobyl would be considered primarily a regional or continental problem. However, higher than usual levels of radioactivity were detected in the Pacific Northwest part of the United States soon after the accident. Likewise, persistent organic pollutants, such as polychlorinated biphenyls (PCBs) have been observed in Arctic mammals, thousands of miles from their sources. These observations demonstrate the effects of long-range transport.

A particularly noteworthy air pollution problem of a global nature is the release of chlorofluorocarbons used as propellants in spray cans and in air conditioners, and their effect on the ozone layer high in the atmosphere (see Chapter 15).

Some knowledge of the exchange processes between the stratosphere and the troposphere and between the Northern and Southern Hemispheres was learned in the late 1950s and early 1960s as a result of the injection of radioactive debris into the stratosphere from atomic bomb tests in the Pacific. The debris was injected primarily into the Northern Hemisphere in the stratosphere. The stratosphere is usually quite stable and resists vertical air exchange between layers. It was found that the exchange processes in the stratosphere between the Northern and Southern Hemispheres is quite slow. However, radioactivity did show up in the Southern Hemisphere within 3 years of the onset of the tests, although the levels remained much lower than those in the Northern Hemisphere. Similarly, the exchange processes between the troposphere into the stratosphere are quite slow. The main transfer from the troposphere into the stratosphere is injection through the tops of thunderstorms that occasionally penetrate the tropopause, the boundary between the troposphere and the stratosphere. Some transfer of stratospheric air downward also occurs through occasional gaps in the tropopause. Since the ozone layer is considerably above the troposphere, the transfer of chlorofluorocarbons upward to the ozone layer is expected to take place very slowly. Thus, there was a lag from the first release of these gases until an effect was seen. Similarly, with the cessation of use of these materials worldwide, there has been a commensurate lag between in restoration of the ozone layer (see Chapter 15).

Another global problem is climate change that is generated by excessive amounts of radiant gases (commonly known as greenhouse gases), especially methane (CH_4) and CO_2, which is not normally considered an air pollutant. But a portion of this radiation is intercepted by the carbon dioxide in the air and is reradiated both upward and downward. That which is radiated downward keeps the ground from cooling rapidly. As the carbon dioxide concentration continues to increase, the earth's temperature is expected to increase.

A natural air pollution problem that can cause global effects is injection into the atmosphere of fine particulate debris by volcanoes. The addition of this particulate matter has caused some spectacular sunsets throughout the earth. If sufficient material is released, it can change the radiation balance. Blocking of the incoming solar radiation will reduce the normal degree of daytime warming of the earth's surface. A "mini-ice age" was caused in the mid-1800s, when a volcanic mountain in the Pacific erupted. The summer of that year was much cooler than usual and snow occurred in July in New England.

Global phenomena like climate can be sensitive to the effects of air pollutants. Like most environmental systems climate varies in its response to different pollutants. In fact, some pollutants lead to cooling whereas others lead to heating of the troposphere. Currently, the major concern of much of the scientific community is with warming. For example, the International Panel of Climate Change (IPCC) reports that between 1970 and 2004, global greenhouse gas emissions increased by 70%. Models vary in predicting how this increase will affect mean global temperatures and other climatic variables, but many scientists and policy makers fear that delays in curbing the trend could lead to a substantial environmental and societal catastrophe.

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QUESTIONS

1. What situation of emission has the potential to produce the greatest local problem?
2. What are the two types of air pollution problems found in urban areas?
3. What are the two primary gaseous pollutants that transform to fine-particle form during long-range transport?
4. In addition to the secondary pollutants discussed in this chapter, identify two more. How do these byproducts different from the parent chemical species?
5. If the concentration of CO_2 in the atmosphere increases to 500 ppm, what will happen to the pH of rain? Where might the biggest effects from such an increase be felt?
6. What are major concerns on the continental scale? What are some ways to ameliorate them?
7. What are two global issues and how might they best be addressed?