1 Effects And Sources of Air Pollutants

1-1 Introduction

Air pollution is woven throughout the fabric of our modern life. A by-product of the manner in which we build our cities, air pollution is waste remaining from the ways we produce our goods, transport ourselves and our goods, and generate the energy to heat and light the places where we live, pay, and work. A major cause of air pollution is combustion; yet combustion is essential to life as we know it. When perfect or theoretical combustion occurs, the hydrogen and carbon in the fuel combine with oxygen from the air to produce heat, light, carbon dioxide, and water vapor. However, impurities in the fuels, poor fuel-to-air ratio, or too high or too low combustion temperatures cause the formation of such side products as carbon monoxide, sulfur oxides, nitrogen oxides, fly ash, and unburned hydrocarbons—all air pollutants.

Air pollution is not a recent phenomenon. King Edward I of England tried to clear the smoky sky over London in 1375 by banning the use of “sea coal.” The British Parliament ordered the torturing and hanging of a person who sold and burned the outlawed coal. Under Richard II (1377–1399) and later under Henry V (1413–1422), England took steps to regulate and restrict the use of coal [1]. One of the earliest recorded publications dealing with air pollution is a pamphlet published in 1601 by royal command of Charles II: “Fumifugium; or the Inconvenience of the Air and Smoke of London Dissipated, together with Some Remedies Humbly Proposed,” written by John Evelyn, one of the founding members of the Royal Society [1].

The use of coal in the generation of energy was a major factor in the Industrial Revolution, which formed the basis of our current technological society. Unfortunately, intimately associated with the benefits of our technological society are the
fouling and degrading of our environment. One of the earliest legal attempts to control air pollution in the United States appears to be a 1886 ordinance making illegal the “smoke of visible vapor” as exhaust from steam automobiles.

Such natural processes as forest fires, decaying vegetation, dust storms, and volcanic eruptions are always polluted the air. As recently as 1991, Mount Pinatubo in the Philippines erupted, killing 200 people and emitting particulates and sulfur dioxide 35 miles high into the atmosphere, creating worldwide weather and climatic influences. Although the total global production of many gases and particulate matter is considered as pollutants in much greater from anthropogenic sources, global distribution and dispersion of these pollutants result in lower average concentrations than those from natural sources. By precipitation, oxidation, and absorption, the oceans and the soil, the atmosphere can cleanse itself of most known pollutants given sufficient time [2, 3]. Yet data collected in the last 20 years suggest that concentrations of gases such as carbon dioxide and chlorofluorocarbons (CFCs) are increasing, with potential consequences such as global warming and increased intensity of ultraviolet radiation due to depletion of the ozone layer in the stratosphere. In addition, anthropogenic-generated pollutants are usually concentrated in the more populated, urbanized regions of the world. In the United States alone, more than 150 million metric tons of gaseous, solid, and liquid waste products are discharged into the atmosphere in 1994. Currently the rate at which pollutants are discharged into the atmosphere in highly populated regions at times exceeds the local cleansing rate of the atmosphere.

1-2 Air Pollution Episodes

Although limited evidence of air pollution was experienced as early as 1272, it was documented as a major problem only in relatively recent years (i.e., the late 19th and the 20th centuries) considering the history of humankind. During a fog in London as far back as 1873, 208 expected deaths from lung-related illnesses were reported. In December 1930, a heavily industrialized section of the Meuse Valley, in Belgium, experienced a severe three-day fog during which hundreds of people became ill and 60 died—more than 10 times the normal number. During a thick nine-day fog in January 1983, 592 people in Manchester and the Salford area of England died—again a large increase in the death rate. In 1948, in Donora, Pennsylvania, a small mill town dominated by steel and chemical plants, a four-day fog made 20% of the city’s 14,000 inhabitants sick. Twenty persons died. Ten years later, Donora residents who had been acutely ill during that episode were found to have a higher rate of sickness and to die at an earlier age than the average for all the townspeople. It was not until a great fog blanketed London in 1952 that the sinister potential of air pollution became fully apparent. That fog lasted from December 5 to December 8, and 10 days later it was learned that the total number of deaths in Greater London during that period exceeded the average by 4,000. The statistics indicated that almost all those who died unexpectedly had records of bronchitis, emphysema, or heart trouble, and that people in the last category were most vulnerable. In January 1960, 1000 extra deaths in London were blamed on an extended fog. In that year, Parliament passed a Clean Air Act and Britain embarked on a program to decrease the burning of soft coal [4]. We have since recognized that these “fogs” were also air pollution episodes that contained pollutants that consisted in creating a dense haze or fog-like condition. The combination of smoke and fog characteristic of many of these historic episodes has been referred to as “smog.” In situations where hydrosolubles, nitrogen oxides, and sunlight are present, these episodes are worsened by the formation of photochemical smog.

The smog conditions of Los Angeles, New York City, Chicago, Mexico City, and other large urban areas around the world are widely publicized in today’s press. Although similar episodes have not been reported in the United States in the last 30 years, there are a substantial number of areas that have unacceptable air quality during certain periods of the year. In 1985, in the United States, there were a number of cities, counties, or metropolitan areas in violation of national air quality standards for specific air pollutants. These locations include 77 areas for ozone, 36 for carbon monoxide, 82 for particulate matter, 43 for sulfur dioxide, 11 for lead, and 40 for nitrogen dioxide [5]. Concentrations of ozone in the South Coast basin of California (Los Angeles area) exceeded the ozone standard 145 days in 1985, with concentrations as high as 0.25 parts per million by volume (ppmv) compared to the air quality standard of 0.12 ppm. On the positive side, the number of exceedances in that area has progressively decreased to 83 times in 1994 with a high of 0.26 ppm. (See http://www.epa.gov/smaq/pogf for current air quality information on the South Coast Air Quality District.)

The misuse of air resources is evident throughout the world. Urban air pollution is an increasing problem in Latin America and the Caribbean due primarily to the rapid expansion in the size and industrialization of the urban population. Areas like São Paulo, Brazil, Santiago, Chile, and Mexico City, Mexico frequently exceed their air quality standards. In these areas, the World Health Organization (WHO) guidelines for particulate matter (60 to 90 μg/m³ annual arithmetic mean) were exceeded with concentrations that were up to six times the standard during the period of 1983–1987 [6]. Similarly, concentrations of particulate matter in Amman, Jordan, have been found to be 2–3 times WHO guidelines [7]. During 1991, concentrations of ozone in Mexico City exceeded the Mexican standard (0.11 ppm) on 307 days. In March 1992, the ozone concentration in Mexico City reached 0.17 ppm, nearly four times the standard [8].

The continued development of synthetic chemicals has also resulted in more emphasis worldwide on the safe handling of toxic materials that lead to the off-gases from processes during manufacturing or during accidental releases. A recent accidental release was the Bhopal, India, accident in which methyl isocyanate vapor was released killing more than 2000 people.

1-3 General Nature of Air Pollution Problems

Only a finite amount of air, land, and water resources exist and, as population increases, the portion available for each person decreases. From the beginning of time until 1900, the population of the world increased to 1.7 billion. In 1974 world population reached 3.7 billion, and grow to the awesome figure of 5.6 billion in
1983 with an estimated annual growth rate of 1.6 percent. The population of the United States has followed a similar trend. In addition, technological advances in the field of agriculture have greatly reduced the number of jobs in rural areas. As in other developed countries, today two-thirds of the population lives in urban areas comprising about 1 percent of the land. Suburban growth and superhighways have made it possible for more people to travel greater distances and thus to converge faster on our cities. Hence, an increasing population combined with a high standard of living has led to a drastically intensified output and concentration of air pollutants in localized areas.

For developed or developing countries, there appears to be a close relationship between the gross domestic product (GDP) per capita and energy consumption per capita [9]. This is illustrated by recent data for selected countries, shown in Table 1–1 [9, 10]. The values represent 1989–1991 estimates. These data indicate that the quantity of goods and services enjoyed by a citizen is closely related to the quantity of energy consumed (directly or indirectly) by that citizen. In other words, the availability and use of energy is a requisite for a high standard of living. Historically, this increase in energy consumption has also increased the emission of pollutants into the environment. Our ability to maintain a sustainable environment for the future clearly depends on the success of our efforts worldwide to reduce the energy requirements needed to produce the products we have come to enjoy and to find new and improved means of reducing or eliminating the emission of pollutants from our sources of energy.

In the past, industry, agriculture, and individual polluters have found it more economical to discharge waste products into the atmosphere than to exercise waste control. In general, the organization or activity causing the pollution did not suffer the consequences of the pollution; likewise, those who benefited from a reduction in air pollution resulting from the installation of control equipment did not directly bear the cost of the equipment. Since the 1960s in the United States, as the public has become increasingly concerned with environmental problems, air has come to be regarded as a resource within the public domain. As a result, air pollution is considered a public problem, a concern not only of those who discharge the pollution, but also of those who may suffer as a result. Many other countries have experienced a similar transition in philosophy.

The rational control of air pollution rests on four basic assumptions [12].

1. Air is in the public domain. Such an assumption is necessary if air pollution is to be treated as a public problem, of concern not only to those who discharge the pollution but also to those who may suffer as a result.

2. Air pollution is an inevitable concomitant of modern life. There is a conflict between our economic and biological concerns; in the past, this conflict was recognized only after air pollution disasters. An ongoing systematic development of policies and programs to conserve the atmosphere for its most fundamental biological function is essential.

3. Scientific knowledge has been and must continue to be applied to the shaping of public policy. While current information about the sources and effects of air pollution is extensive, it is far from complete. A great deal of work is still left to be done to develop effective control strategies, including pollution prevention and minimization and the continued improvement and application of control devices and technologies. Nevertheless, sufficient information is available to make substantial further reductions in air pollution emissions.

4. Methods of decreasing air pollution must not increase pollution in other sectors of the environment. Control techniques for reducing pollution from air, water, or land often result in a transfer of the pollutant or a secondary pollutant to another medium. For example, the removal of sulfur dioxide from the flue gas of a coal-burning power plant by wet scrubbers produces a large quantity of liquid or sludge which must then be disposed of. In a similar manner, the stripping of organic compounds from contaminated groundwater may result in emission of toxic organic compounds into the air. Such methods may not be true solutions to pollution and are becoming increasingly scrutinized to ensure that pollution is not simply transferred to a different medium, but rather destroyed or converted to a less polluting form.

### TABLE 1-1 Comparison of Energy Consumption by Country

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zaire</td>
<td>180</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>China</td>
<td>370</td>
<td>36</td>
<td>14</td>
</tr>
<tr>
<td>India</td>
<td>380</td>
<td>9</td>
<td>42</td>
</tr>
<tr>
<td>Chile</td>
<td>2,500</td>
<td>54</td>
<td>75</td>
</tr>
<tr>
<td>Russia</td>
<td>5,220</td>
<td>191</td>
<td>17</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>5,800</td>
<td>168</td>
<td>35</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>18,500</td>
<td>159</td>
<td>114</td>
</tr>
<tr>
<td>France</td>
<td>18,500</td>
<td>194</td>
<td>176</td>
</tr>
<tr>
<td>Canada</td>
<td>19,600</td>
<td>281</td>
<td>69</td>
</tr>
<tr>
<td>United States</td>
<td>19,500</td>
<td>273</td>
<td>71</td>
</tr>
<tr>
<td>Japan</td>
<td>29,774</td>
<td>111</td>
<td>268</td>
</tr>
</tbody>
</table>

*Based on estimates from 1969–91.

### 1-4 Definition and General Listing of Air Pollutants

Many definitions of air pollution have been proposed. Here is one definition: "Air pollution may be defined as the presence in the outdoor and/or indoor atmosphere of one or more contaminants or combinations thereof in such quantities and of such duration as may be or may tend to be injurious to human, plant, or animal life, or property or which unreasonably interferes with the comfortable enjoyment of life or property or the conduct of business." In a similar vein, the laws of the state of Wisconsin define air pollution as "...the presence in the atmosphere of one or more contaminants in such quantities and of such duration as is or tends to be injurious to human health or welfare, animal or plant life, or property, or would unreasonably interfere with the enjoyment of life or property." Every state
and country has a similar definition. The Wisconsin law further defines contaminants as "... dust, fumes, mist, liquid, smoke, other particulate matter, vapor, gas, odorous substances, or any combination thereof that shall not include uncombined water vapor."

In the context of the current regulatory environment in the United States, air pollution exists in four broad categories:

1. **Ambient Air Pollution.** This refers to air pollution in the outdoor environment and involves a complex array of sources and pollutants, meteorological transport of the pollutants to a receptor, and a wide range of social, economic, and health effects. The regulatory authority lies within the U.S. Environmental Protection Agency (EPA).

2. **Indoor Air Pollution.** This refers to air pollution in the indoor environment in which people live and sleep. Regulatory responsibility has been a subject of much debate. The U.S. EPA has played an increasingly active role in studying and issuing guidelines, particularly in the areas of radon and passive cigarette smoke. There are, as yet, no federal regulations regarding indoor air pollution.

3. **Occupational (Industrial Hygiene) Air Pollution.** This type of air pollution is associated with exposure to a large range of pollutants (particles, mists, acid vapors, and organic and inorganic gases) in the workplace. The regulatory standards associated with the workplace are under the Occupational Safety and Health Administration (OSHA) and are generally developed by the American Conference of Governmental and Industrial Hygienists (ACGIH) and the National Institute of Occupational Safety and Health (NIOSH).

4. **Personal Exposure.** This final category refers to exposure to dust, fumes, gases, or mists to which an individual exposes oneself. Examples include cigarette/cigar smoking, sniffing of glue, and many other practices which can cause damage to the human body.

Although the primary focus of this text is on ambient air pollution and its control, the recent emphasis on toxic air pollutants has and continues to utilize the vast experience gained in the occupational area. The OSHA standards have provided the basis for many of the ambient air quality guidelines for toxic air pollutants that have been developed by various states. In a similar manner, an understanding of the control technologies used by industrial sources of air pollution has been used to improve the quality of indoor air.

One method of defining an air pollutant is to first specify the composition of "clean" or "normal" dry atmospheric air and then classify all other materials or increased amounts of those materials present in the composition of atmospheric air, as pollutants if their presence results in damage to human beings, plants, animals, or materials. Table 1-2 lists the chemical composition of dry atmospheric air typically found in rural areas or over the ocean far from land masses. Atmospheric air also contains from 1 to 3 percent by volume water vapor and traces of sulfur dioxide, formaldehyde, iodine, sodium chloride, ammonia, carbon monoxide, methane, and dust and pollen.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Volume (Percent)</th>
<th>Concentration (ppm*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>78.084 ± 0.006</td>
<td>780.840</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20.946 ± 0.002</td>
<td>209.460</td>
</tr>
<tr>
<td>Argon</td>
<td>0.934 ± 0.001</td>
<td>9.340</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.037 ± 0.004</td>
<td>3.70</td>
</tr>
<tr>
<td>Neon</td>
<td>1.80</td>
<td>18.0</td>
</tr>
<tr>
<td>Helium</td>
<td>5.20</td>
<td>52.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.25</td>
<td>12.5</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.50</td>
<td>5.0</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.08</td>
<td>0.8</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>0.02</td>
<td>0.2</td>
</tr>
<tr>
<td>Ozon</td>
<td>0.01 - 0.04</td>
<td></td>
</tr>
</tbody>
</table>

*ppm is an abbreviation of parts per million by volume.


Historically, neither carbon dioxide nor uncombined water vapor was considered to be a pollutant. This condition could change in the future since the discharge of either substance into the atmosphere in increased quantities may result in a significant change in the global atmospheric temperature. Likewise, certain odors now considered nuisances rather than pollutants may eventually be designated pollutants.

It is common practice to express the concentration of a gaseous pollutant present in the air as parts per million (ppm) on a volumetric basis. Thus,

\[
\text{1 volume of gaseous pollutant} = 1 \text{ ppm}
\]

\[
\frac{10^6 \text{ volumes (pollutant + air)}}{10^6 \text{ volume}} = 1 \text{ ppm}
\]

or

\[
0.001 \text{ percent by volume} = 1 \text{ ppm}
\]

The concentration of a pollutant on a mass basis is commonly expressed as micrograms of pollutant per cubic meter of air. Symbolically,

\[
\text{micrograms} = \frac{\mu g}{m^3}
\]

\[
\text{cubic meter}
\]

At 25°C and 101.3 kPa (1 atm) pressure the relationship between parts per million and micrograms per cubic meter is found from

\[
\frac{m_{\text{ppm}}}{V_{\text{air}}} = \frac{\mu g}{V_{\text{air}}} = \frac{m_{\text{ppm}}}{R_p T}
\]

where the pollutant gas is assumed to behave as an ideal gas, and \(M_{\text{ppm}}\) is the molecular weight of the pollutant. If \(P\) is taken as 1 atm, \(T\) as 238 K, and \(R\) as 0.08205 atm m³/kg mol K, then the equation reduces to

\[
\frac{m_{\text{ppm}}}{V_{\text{air}}} = \frac{m_{\text{ppm}}}{V_{\text{air}}} = \frac{M_{\text{ppm}}}{V_{\text{air}}} = 24.8
\]
where the mass of pollutant per unit volume is now expressed as kg/m³. Finally, by multiplying the right side by $10^6$ to convert the mass to micrograms, and by dividing by $10^3$ so that $V_p/V_{at}$ can be expressed as parts per million, then the basic relation between the concentration in μg/m³ and ppm at 1 atm and 25°C is

$$C(\mu g/m^3) = \frac{ppm \times \text{molecular weight} \times (10^5)}{24.5} \quad (1-1)$$

For conditions of 1 atm and 0°C (273 K) the constant in the denominator becomes 22.4. The concentration (mass/volume) at other conditions can be determined by multiplying the constant by the appropriate ratio of temperatures and pressures according to the ideal gas law. Sometimes concentrations are also expressed in parts per billion (ppb), parts per hundred million (pphm) or parts per trillion (ppt). The concentration in ppm, ppb, pphm, ppt, or volume per volume remains constant at all temperatures and pressures as long as all of the gases (pollutant + air + any other gases present) remain in the gaseous state and behave as an ideal gas.

The following examples illustrate the calculations required for converting from one system of units to another.

**EXAMPLE 1-1**

The exhaust gas from an automobile contains 1.5 percent by volume of carbon monoxide. What is the concentration of CO in milligrams per cubic meter (mg/m³) at 25°C and 1 atm pressure? What is the concentration in μg/m³ in the exhaust pipe if it is at 200°C and 1.1 atm of pressure?

**Solution**

The conversion of data from percent by volume to parts per million is made by noting that

1 percent by volume = 1 percent by moles = $10^6$ ppm

Hence 1.5 percent by volume in 15,000 ppm of CO. In addition, the molar mass (molecular weight) of CO is 28.0 g/mole. Substitution of these data into Equation (1-1) yields

$$C(\mu g/m^3) = \frac{15,000 \times (28.0) \times (10^5)}{24.5} = 17.1 \times 10^6$$

There are $10^6$ micrograms (μg) in 1 milligram (mg). Therefore, the concentration of CO in the desired units at 25°C is

CO concentration = $17.1 \times 10^6 \times \mu g/m^3 \times 10^3 (\mu g/mg) = 17.1 \times 10^9$ mg/m³

The concentration in μg/m³ of the CO in the exhaust pipe at 200°C and 1.1 atm is calculated as follows:

The constant, 22.4, at 0°C (273 K) and 1 atm becomes

22.41 \left(\frac{P_{298K}}{P_{273K}}\right) \left(\frac{V_{at}}{V_{298K}}\right) = 22.41 \left(\frac{473K}{273K}\right) (1.1 atm) = 36.3

$$C(\mu g/m^3) = \frac{15,000 \times (28.0) \times (10^5)}{36.3} = 11.9 \times 10^6$$

The CO concentration will be lowered by dispersion when the exhaust gas enters the atmosphere. In contrast to the above values, the national ambient air quality standard (based on a 8-hr measurement) is only 10 mg/m³.

**EXAMPLE 1-2**

The average daily concentration of sulfur dioxide is observed to be 415 μg/m³ at 25°C and 1 atm. What is the concentration of SO₂ in parts per million?

**Solution**

The molecular weight of sulfur dioxide is 64.0 g/mole. Substitution into Equation (1-1) gives

$$C(\mu g/m^3) = \frac{415 \times (64.0) \times (10^5)}{24.5}$$

Solving for the concentration of SO₂ in parts per million, we find that

$$ppm = \frac{415(24.5)}{64.0 \times 10^5} = 0.163$$

This concentration is greater than the national ambient air quality standard of 0.14 ppm (based on a 24-hr average) presented in Table 2-1.

**EXAMPLE 1-3**

The ozone concentration is observed to be 118 μg/m³ at an urban monitoring station. Does this value exceed the concentration found in standard dry air as listed in Table 1-2?

**Solution**

The molecular weight of ozone (O₃) is 48.0 g/mole. Substituting the appropriate values into Equation (1-1) and solving for the concentration in parts per million, we find that

$$ppm = \frac{118(24.5)}{48(10^5)} = 0.060$$

The concentration of ozone in standard dry air as given in Table 1-2 ranges from 0.01 to 0.04 ppm. Thus the value of 118 μg/m³, which corresponds to 0.060 ppm or 60 ppb, exceeds the tabulated value. The value is less than the national ambient air quality standard of 0.05 ppm (8-hr average).

**EXAMPLE 1-4**

The maximum concentration of dust in the atmosphere during a 24-hr period was found to be 0.00010 gram per dry standard cubic foot (gr/dscf). What is the equivalent concentration in micrograms per cubic meter?
Solution
From Appendix B it is found that 1 gr/ft$^3$ equals 2.29 g/m$^3$. Hence,

$$\text{concentration} = \frac{0.000190 \text{ gr/m}^3 \times \left(\frac{2.29 \text{ g/m}^3}{1 \text{ gr/ft}^3}\right)}{1 \text{ ft}^3} \times \frac{1}{8} \times \frac{1}{10^6 \mu g}$$

$$= 298 \mu g/m^3$$

This value is relatively high when compared to typical ambient concentrations of 50 to 100 μg/m$^3$. Typical uncontrolled emissions of particles from industrial processes are 1–3 gr/ft$^3$ while outlet emissions from high efficiency control devices are in the range of 0.001–0.06 gr/ft$^3$.

A general classification of ambient air pollutants is as follows:

1. Particulate matter
2. Sulfur-containing compounds
3. Organic compounds
4. Nitrogen-containing compounds
5. Carbon monoxide
6. Halogen compounds
7. Radiotoxic compounds
8. Photochemical oxidants
9. Other inorganic compounds

Particulate matter is further divided into subclasses which include fine particles (less than 2.5 μm in diameter), coarse particles (above 2.5 μm in diameter), fumes (0.001–1 μm in diameter), and mists (0.1–100 μm in diameter). Fumes are particles formed by condensation, sublimation, or thermal reaction; and sometimes are designated as smoke. Mists are comprised of liquid particles formed by condensation and are fairly large in diameter compared to fumes or smoke. As a larger class, fumes, smoke, mist, and fog are called aerosols.

Figure 1-1 illustrates the distribution of the surface area of atmospheric aerosols and shows the sources, the primary processes involved in introducing mass into each size range, the primary atmospheric removal mechanisms, and the distinction between fine and coarse particles is of fundamental importance. Fine and coarse particles generally originate from different sources or different activities within the same source. In addition, they are removed from the atmosphere by different mechanisms, require different control techniques, and have different chemical composition and different optical properties.

Items in the above list can be grouped into two broad classifications: primary and secondary pollutants. Primary pollutants are those emitted directly from sources, while secondary ones are those formed in the atmosphere by chemical reactions between primary pollutants and chemical species normally found in the atmosphere (i.e., the accumulation range in Figure 1-1). Table 1-3 lists examples of primary gaseous pollutants and some of the secondary pollutants (both gases and particles) that are formed in the atmosphere. Note that carbon dioxide has been placed in parentheses in the table, since CO$_2$ normally is not considered a pollutant. However, the increase in CO$_2$ concentration worldwide is the basis for concern regarding its effect on global warming.

![Diagram of atmospheric aerosol surface area distribution showing principle sources, main sources for each range, and growth and renewal mechanisms.](image)

**TABLE 1-3** General Classification of Gaseous Air Pollutants

<table>
<thead>
<tr>
<th>Class</th>
<th>Primary Pollutants</th>
<th>Secondary Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur-containing compounds</td>
<td>SO$_2$, H$_2$S</td>
<td>SO$_2$, H$_2$SO$_4$, HNO$_3$, DMSO, SO$_3$, HNO$_3$</td>
</tr>
<tr>
<td>Organic compounds</td>
<td>H$_2$C compounds</td>
<td>Ketones, aldehydes, C$_2$ acids, organic aerosols</td>
</tr>
<tr>
<td>Nitrogen-containing compounds</td>
<td>NO, NH$_3$</td>
<td>NO, NO$_2$, NNO$_3$, HNO, NO$_2$</td>
</tr>
<tr>
<td>Oxides of carbon</td>
<td>CO (CO$_2$)</td>
<td>(None)</td>
</tr>
<tr>
<td>Halogen compounds</td>
<td>HCl, HF</td>
<td>(None)</td>
</tr>
<tr>
<td>Photochemical oxidants</td>
<td></td>
<td>O$_3$, NO$_2$, H$_2$O$_2$, peroxyacetyl nitrate</td>
</tr>
</tbody>
</table>

*DMSO and HNO$_3$ are sulfate and nitrate compounds, respectively.
The following sections present information on a number of specific pollutants in more detail, including the physical and chemical behaviour of the pollutants and the effects of these pollutants. It is beyond the scope of this text to present a comprehensive list of pollutants and their effects. Thus the discussion has been restricted, in general, to pollutants that relate directly to or for which national ambient air quality standards have been established: particulate matter, carbon monoxide, sulfur oxides, oxides of nitrogen, hydrocarbons, photochemical oxidants, and lead. An additional 180 hazardous air pollutants are in the process of being regulated under the Clean Air Act Amendments of 1990 and are discussed in more detail in Chapter 2.

1-5 Particulate Matter

Particulate matter is a term employed to describe dispersed airborne solid and liquid particles larger than single molecules (molecules are approximately 0.0002 μm in diameter) but smaller than 600 μm (1 μm = 1 micrometer = 10^-6 cm). Particles in this size range have a lifetime in suspension varying from a few seconds to several months. Particles less than 0.1 μm in diameter undergo random Brownian motions resulting from collision with individual molecules. Particles between 0.1 and 2 μm in diameter have settling velocities in still air which, while finite, are small compared with wind velocities. These particles tend to be removed by rainout and washout as shown in Figure 1-1. Particles larger than 2 μm have significant but small settling velocities. Particles above approximately 20 μm in diameter have larger settling velocities and are removed from the air by gravity and other inertial processes. Equations for settling velocities and inertial separation will be presented later in the text. Since Brownian motion increases for smaller particle sizes and inertial forces increase for larger particle sizes, some particulate control devices exhibit a minimum collection efficiency between 0.65 and 1.0 μm. These include devices such as electrostatic precipitators and fabric filter baghouses.

1-5 A The Measurement of Particulate Matter

The earliest measurements of particulate matter were based on the property that large particles settle. The measurement was made by placing an open-mouthed "dust fall" collector (bucket) with known area in the ambient environment for a specified time (typically one month or longer). The amount of dust fall or settleable particulate matter was then determined by filtering the insoluble dust fall or by evaporation of the filtrate to determine the total (soluble + insoluble) dust fall. The dust fall rate was reported in mass/area-time (i.e., tons/m²-year or kg/m²-day). The acid precipitation sampler shown in Figure 1-2a is a modern version of the dust fall sampler. It contains two dust fall collectors—one for collection of dry deposition, the other for deposition during rainfall. A heated sensor is used to detect the presence of rain and triggers a switch which causes the canopy to move from one collector to the other.

The most common measurement of particulate matter during the 1970s and 1980s in the United States was the high-volume sampler which measured total suspended particulate matter (TSP). The sampler, shown in Figure 1-2b, operates with a flowrate of 1.1.1 m³/min (40-60 cubic feet per minute) for a period of 24 hours. The flow passes through a high-efficiency filter where the particulate matter is collected. The mass of particulate matter collected in 24 hours divided by the total volume sampled provides the measure of the total suspended particulate matter (TSP), and is reported in μg/m³. The high-volume sampler was the basis for the 24-hour TSP air quality standard discussed in Chapter 2.
canopy over the filter prevents settleable particulate matter from reaching the filter. The typical size range of particles reaching the filter is less than 25-50 μm (aerodynamic diameter). Research in the late 1960s and 1970s on the effects of particulate matter on human health concluded that the particle size is cut-off of the high-volume sampler was significantly larger than that of the human respiratory system. As a result, the air quality standard and the associated particulate sampler were modified to have a cut diameter of 10 μm. The standard, referred to as the PM₁₀ standard, has a 24-hour maximum value of 150 μg/m³ [17] as compared to 250 μg/m³ for the TSP standard. One example configuration of the PM₁₀ sampler is shown in Figure 1-1c in which the high-volume sampler's canopy is replaced with a PM₁₀ inlet which effectively prevents particles with aerodynamic diameters greater than 10 μm from reaching the filter [18].

Although the PM₁₀ standard is based on a 24-hour average concentration, analyzers are now available that allow the continuous measurement of PM₁₀ concentrations. One such instrument utilizes a filter tape on which the PM₁₀ particles are collected. See Figure 1-1d. A low level of beta radiation is emitted from a radionuclide source and passes through the particles deposited on the tape. As the mass of particles increases, the beta radiation penetrating the filter and reaching the detector on the opposite side of the tape decreases. The change in penetration of the radiation is directly proportional to the change in mass of particles deposited, in essence creating a radiometric microbalance.

The particle size cut-off for the above samplers is referred to as an aerodynamic particle size cut-off and is related to the fact that particle removal in the respiratory tract is dominated by gravitational and inertial forces. Both of these are affected by the particle size, dₚ, and particle density, ρₚ. The aerodynamic diameter of a particle is defined as the diameter of a sphere of unit density (ρₚ = 1 g/cm³) that has the same terminal gravitational settling velocity in still air as the actual particle in question. The aerodynamic particle size can be approximated as follows:

\[ d_{\text{aero}} = d_{\text{p}} \times \left( \frac{K_{C_2} \rho_{\text{p}}}{K_{C_1}} \right)^{1/2} \]

The term K₁ is referred to as the Cunningham Correction Factor and will be discussed in detail in Chapter 5. Since it approaches 1.0 for particles greater than about 1 μm, the ratio of K₂ of the particle diameter d₂ and K₁ of the particle diameter d₁ is approximately 1. In addition, since by definition, d₂ has a particle density ρ₂ of 1 g/cm³, the above definition is often reported as simply

\[ d_{\text{aero}} = d_{\text{p}} \times (\rho_{\text{p}})^{1/2} \]

where the units on ρ are in g/cm³. This equation can be used to estimate the approximate aerodynamic diameter of particles whose physical size is greater than about 1 μm with less than a 10 percent error.

Particles with the same aerodynamic particle size tend to behave the same way under a gravitational or inertial force. For example, a particle with a physical size of 10 μm and a particle density of 1 g/cm³ has the same aerodynamic particle size as a 5 μm particle with a density of 4 g/cm³.

\[ d_{\text{aero}} = 10 \mu m \times (1) ^{1/2} = 10 \mu m \]

\[ d_{\text{aero}} = 5 \mu m \times (4) ^{1/2} = 10 \mu m \]

'Related, the 5 μm particle with a density of 4 g/cm³ behaves aerodynamically as if it were a 10 μm particle with "unit density."

The importance of utilizing the aerodynamic particle size and establishing the PM₁₀ type sampler is illustrated in Figure 1-3. The graph provides a comparison of the deposition of particles in the alveolar region of the lungs by mouth and nose breathing [13]. For mouth breathers, the particle size below which particles begin to penetrate into and deposits in the lungs is approximately 10 μm (aerodynamic size). Particles greater than 10 μm either do not enter the breathing passages or are removed in the upper respiratory tract by inertial impaction and gravitational separation. The deposition in the lungs increases up to a value of approximately 50 percent at 2.5 μm. Deposition begins to decrease as the particle size decreases below about 2.5 μm since inertial impaction continues to decrease. The minimum deposition at approximately 0.2 to 0.4 μm is similar to the minimum efficiency discussed earlier regarding high efficiency air pollution control devices. The lack of efficient collection mechanisms in this range also exists in the human body. Thus, these particles are breathed in but, fortunately, only a small fraction is deposited, resulting in the majority being expelled as one exhales. Below 0.2 μm the deposition begins to increase again due to the increased effect of Brownian diffusion of the particles. Figure 1-3 also shows the deposition in the lungs for nasal breathing (only 20-25 percent compared to 50 percent for mouth breathing), clearly showing the importance of the nasal tract.
passages in removing particles. The similarities between the human nasal passages and air pollution control devices are such that both require an understanding of the same collection mechanisms.

1-5-B Visibility and Related Atmospheric Characteristics

One of the most common effects of air pollution is the reduction in visibility resulting from the absorption and scattering of light by airborne liquid and solid materials. Visibility is principally affected by fine particles that are formed in the atmosphere from gas-phase reactions. Although the molecules are not directly visible, carbon dioxide, water vapor, and ozone in increased concentrations change the absorption and transmission characteristics of the atmosphere. Much effort has been expended in recent years to relate the concentration of airborne pollutants to the optical characteristics of various plumes in the atmosphere. Reduction in visibility is not only aesthetically unacceptable; it may also have strong psychological effects. In addition, a safety hazard may be created in the event of extreme reductions in visibility.

Scattering and Absorption of Light

The Glossary of Meteorology [16] gives the following definition of visibility:

In United States weather observing practice, the greatest distance in a given direction at which it is just possible to see and identify with the unaided eye (a) in the daytime, a prominent dark object against the sky or horizon, and (b) at night, a known, preferably distant, moderately intense light source. After visibility has been determined around the entire horizon circle, they are resolved into a single average value of prevailing visibility for reporting purposes. Visibility is dependent upon both the ability of the eye to distinguish an object because it is in contrast with the background, and the transmissivity of light through the atmosphere. Changes in contrast with viewing distance occur because (a) additional light is introduced into the eye path or (b) light is lost from the line of sight because of the atmosphere. In both cases this contrast between the object and the background approaches zero. When the eye can no longer distinguish a difference between the object and the background, the object is said to be beyond the limit of visibility. The aforementioned reduction in contrast is due to the absorption and scattering of light by particles in the atmosphere.

If air molecules were the only factor in the attenuation of light, a visibility of more than 150 m could be calculated based on the Rayleigh scattering theory. Smoke and haze have been reported to reduce airport visibility to less than 3 m and sometimes to nearly 1 m [20]. According to Blachin [21], dust particles in a concentration of 2000 cm$^{-3}$ can obscure a mountain at 50 m, while a concentration of 100,000 cm$^{-3}$ can reduce visibility to 1 m. A concentration of NO$_2$ of 8 to 10 ppm would probably reduce visibility to about 1 m. Thus, light attenuation by other than Rayleigh scattering must occur. Because of its absorption characteristics, NO$_2$ causes the sky to appear brownish in color in addition to reducing visibility. A concentration of 0.1 ppm NO$_2$ would probably not be noticeable, whereas 1.0 ppm could be detected by the eye.

Consider an object illuminated by a light beam of intensity $I_0$, a distance $d$ from an observer. Let the light passing through an incremental distance $dx$ be reduced by absorption and scattering by an amount $df$ which is proportional to the intensity $I$. Middleton [22] has shown that

$$ df = -c_a dx $$

where $c_a$ is the overall extinction coefficient (with units of length$^{-1}$) and the negative sign indicates that the intensity is reduced along the light path by the atmosphere. Integration over the path length from 0 to $d$ gives (for constant $c_a$)

$$ I = I_0 e^{-c_a d} $$

where $I$ is the intensity at distance $d$, and $I_0$ is the original intensity at $x = 0$. This is illustrated in Figure 1-4.

The extinction coefficient includes the effects of both scattering and absorption by gas molecules and aerosols. It is often desirable to separate the effects of scattering and absorption, in which case the overall extinction coefficient in Equation (1-3) is written as

$$ c_a = c_{scatt} + c_{abs} $$

where $c_{scatt}$, and $c_{abs}$ refer to scattering and absorption of light by gas molecules, while $c_{scatt}$ and $c_{abs}$ refer to scattering and absorption of light by particles. These are defined further in the following paragraphs.

Thus the fractional transmittance, $I/I_0$, of a light is a function of both the path length $d$ and the interception qualities of the particles and gases. The value of the overall extinction coefficient is a function of the wavelength of the incident light, the concentration of air molecules and absorbing gases that are present, particle size and shape, and the optical properties of the particles. In addition, $I/I_0$ is a strong function of the scattering angle, that is, the angle between the direction of the light and the line of sight of the observer.

The attenuation of light in the atmosphere by scattering is due to Rayleigh scattering by air molecules ($c_{scatt}$) as shown in Figure 1-5 and by particles of a size comparable to the wavelength of the incident light ($c_{abs}$) [23]. In addition, Figure 1-6 illustrates that certain molecules such as NO$_2$ absorb light thus adding

![FIGURE 1-4 Loss of intensity through path length, d](image-url)
Based on Equation (1-5), it is possible to calculate the limit of visibility (or visual range) if \( \sigma_{\text{ext}} \) is known. If no particles or gaseous pollutants are present, the extinction is due only to the Rayleigh scattering by air molecules. Rayleigh scattering is a function of the wavelength of light as shown in Figure 1-5 and varies from approximately 0.006 km\(^{-1}\) at 0.03 \( \mu \text{m} \) (red light) to as high as 0.03 km\(^{-1}\) at 0.45 \( \mu \text{m} \) (blue light) at sea level. At 0.45 \( \mu \text{m} \) and sea level, \( L_o \) is estimated to be approximately

\[
L_o = \frac{3.9}{0.05 \text{ km}^{-1}} = 130 \text{ km}
\]

or 81 miles, and represents the approximate maximum value of the limit of visibility with no particles or gaseous pollutants present. For green light (0.5 \( \mu \text{m} \)), \( L_o \) would be nearly 160 to 210 miles at sea level due to the decrease in the Rayleigh extinction coefficient as the wavelength increases. Obviously, as one looks skyward, the limit of visibility increases dramatically due to the rapid decrease in the concentration of air molecules, allowing one to distinguish between the sun, moon, and stars. When aerosols are present, the \( L_o \) may be reduced drastically.

Mie (in Middleton [22]) developed the following expression for the extinction coefficient due to particle scattering:

\[
\sigma_{\text{ext,part}} = N K r^2
\]

where \( N \) is the number of particles of radius \( r \) per unit volume, and \( K \) is the scattering area ratio, or the ratio of area of wave front acted upon by the particle to the area of the particle.

Values of \( K \) for selected particles may be found in the literature [24, 25]. When the particulate matter in the light path is not homogeneous, the value of \( \sigma_{\text{ext,part}} \) is the sum of the individual values of \( \sigma_{\text{ext,part}} \) for the various groups of particles. Thus, for forward scattering,

\[
\sigma_{\text{ext,forward}} = \sum_{i=1}^{n} N_i K_i r_i^2
\]

For spheres that do not absorb but scatter light, Van de Hulst [25] presents a curve relating \( K \) to the term \( 4 \pi r \) \( m - 1 / 3 \), where \( m \) is the refractive index of the particles, \( r \) is the particle radius, and \( A \) is the wavelength of the incident light.

Figure 1-6 is a reproduction of the data of Van de Hulst.

If it is further assumed that attenuation is due to scattering by particles only and that the particulate matter is in the form of spheres of the same size and uniformly distributed, an approximation equation for the limit of visibility can be formulated by combining Equations (1-5) and (1-6). As a result,

\[
L_o = \frac{5.2 \rho_p r}{\sigma_{\text{ext}}}
\]

where \( C \) is the particulate concentration (mass/volume) in the direction of sight, \( \rho_p \) is the particle density, and \( r \) is the particle radius. Note that \( C = (4/3) \pi r^3 \rho_p N \) for \( N \) spheres or particles of radius, \( r \). A consistent set of units must be used. This expression indicates that the limit of visibility is inversely proportional to the scattering coefficient and the concentration of particles in the atmosphere, and in
direct proportion to the diameter and specific gravity of the particles. The greatest range in possible values occurs with the variables \( C \) and \( \nu \) The visibility is greatly affected by concentrations greater than 100 \( \mu g/m^2 \) and by particles in the 0.1 to 1.0 \( \mu m \) size. Unfortunately, as discussed previously, many particulate removal devices are least effective in this same size range. The particles released to the atmosphere may be small in percent of the overall weight originally in the stack gas before cleaning, but their size is very effective in reducing visibility. An empirical relation [26] between the visual range and the concentration is

\[
L_v = \frac{1.2 \times 10^4}{C} \quad (1-9)
\]

where \( C \) is in micrograms per cubic meter and \( L_v \) is in kilometers. Data indicate that the actual value of \( L_v \) may be a factor of 2 larger or smaller than that calculated from the above expression. However, as a rule of thumb, the product of the limit of visibility and concentration in the units expressed for Equation (1-9) is around 1000. Equation (1-9) is an estimate based on typical atmospheric particulate conditions, while Equation (1-8) is the visibility for a given particle size or an appropriate mean particle size. Both equations may be in considerable error when the relative humidity exceeds 30 percent. Above this value, particles tend to develop into fog droplets as a result of their hygroscopic tendencies under high relative humidity conditions. Other empirical relations for scattering coefficients or visibility limits appear in the literature [27].

**EXAMPLE 1-5**

Consider nonabsorbing particles of 1.0 \( \mu m \) diameter with a refractive index of 1.33 suspended in air and exposed to daytime radiation. The density of the particles is taken to be 1.6 \( g/cm^3 \). The wavelength of visible light can be taken to be 0.48 \( \mu m \).

(a) What is the concentration of particles in micrograms per cubic meter which results in a limit of visibility of 1.5 \( km \) (1 mile)?

(b) What is the concentration of suspended particles if the effective diameter is 0.6 \( \mu m \) and the visibility is 8.05 \( km \) (5.0 miles)?

**Solution**

(a) The value of the scattering ratio, \( K' \), can be estimated from Figure 1-6 as follows:

\[
\frac{4\pi \tau_{lm} - 1}{\lambda} = \frac{4(3.14)(0.5 \mu m)(0.33)}{0.48 \mu m} = 4.3
\]

From Figure 1-6, \( K = 3.2 \) for \( \tau = 1.33 \). The concentration can then be estimated from Equation (1-8). Substitution of the above values yields

\[
C = \frac{5.2 \rho \nu}{K L_v}
\]

\[
C = \frac{5.2(1.5 \frac{g}{cm^3})(10^6 cm^3/m^3)(0.5 \times 10^{-4} m)}{3.2 \times 1610 m} = 2.5 \times 10^{-4} g/m^3
\]

or 250 \( \mu g/m^3 \).

(b) The solution in this case is attained in the same fashion as above.

\[
\frac{4\pi \tau_{lm} - 1}{\lambda} = \frac{4(3.14)(0.25 \mu m)(0.33)}{0.48 \mu m} = 2.2
\]

which gives a value of \( K = 1.0 \). The concentration is

\[
C = \frac{5.2(1.5 \frac{g}{cm^3})(10^6 cm^3/m^3)(0.25 \times 10^{-4} m)}{1.0 \times 10^6 m} = 2.5 \times 10^{-4} g/m^3
\]

FIGURE 1-6 Approximate value of the scattering ratio, \( K \), for nonabsorbing spheres. [26]
EXAMPLE 1-6 Nitrogen dioxide absorbs visible light as illustrated in Figure 1-6.

(a) Determine the limit of visibility in the ambient air at sea level at a wavelength of 0.46 μm, if the NO₂ concentration is 0.03 ppm and there are no particles.

(b) What color would the sky appear under this condition?

Solution

(a) For a wavelength of 0.46 μm (blue light) with no particles present, the extinction coefficient, \( \sigma_{\text{ext}} \), would only be due to Rayleigh scattering and NO₂ absorption. Thus,

\[ \sigma_{\text{ext}} = \sigma_{\text{Rayleigh}} + \sigma_{\text{abs, NO₂}} \]

For air, Figure 1-5 shows that \( \sigma_{\text{Rayleigh}} = 0.025 \text{ km}^{-1} \). The extinction coefficient for 0.1 ppm of NO₂ is 0.16 km⁻¹. Since the extinction coefficient is proportional to concentration, then

\[ \sigma_{\text{abs, NO₂}} = 0.16 \text{ km}^{-1} \times \left( \frac{0.03 \text{ ppm}}{0.1 \text{ ppm}} \right) = 0.048 \text{ km}^{-1} \]

Therefore,

\[ L_{\text{c}} = \frac{4.9}{0.025 + 0.048} = 55.7 \text{ km} \]

or approximately 34.6 miles. The visibility reduction from the presence of the NO₂ is nearly twice that of the Rayleigh scattering.

(b) Looking at Figure 1-5, it is apparent that the blue light is absorbed much more strongly than green or red in descending order. As a result, any light passing through the environment will tend to take on a brownish red hue due to the greater loss of the blue, slight loss of green, and the preferential passing of the yellow and red light. This same phenomenon is responsible for the reddish hue taken on by large power plant plumes which are observed downwind from the plants under certain lighting conditions.

Plume Opacity

The principles of light extinction by absorption and scattering due to particles form the basis for a number of continuous emission monitoring systems (CEMS) which are used to monitor the emission of pollutants (both point sources and fugitive emissions) and to determine whether they are meeting emission standards. These standards are referred to as opacity standards. Opacity is defined as the percent of the light that is prevented from passing through a plume or fugitive emission. Since \( I/I_{o} \) is the fraction of light transmitted through a plume as illustrated in Figure 1-7, then

\[ \text{Opacity} \% = \left(1 - \frac{I}{I_{o}}\right) \times 100\% \quad (1-10) \]

Here, \( I/I_{o} \) can be determined from Equation (1-3) where the path length, \( d \), is the stack diameter. In general, the opacity monitor is mounted on the exit stack of a process and monitors the loss of light between a light source and a photo-detector.

Figure 1-7 Illustration of opacity monitor.

In single pass systems, the source and detector are located on opposite sides of the stack. In double pass systems, the source and detector are located on the same side of the stack with a reflector on the opposite side. The double pass system provides more sensitivity in that the path length, \( d \), is twice as long as a single pass system, providing for a greater reduction in intensity of the light source. For sources without an opacity monitor, the opacity may be monitored by a person who is a certified, visible emissions reader. In this case, the person has actually been trained to observe and report the opacity of the stack [28].

1-5-C Effects of Atmospheric Particulate Matter on Materials, Vegetation, and Animals

Atmospheric particles can be chemically inert or chemically active themselves; they may be inert but absorb chemically active substances from the atmosphere, or they may combine to form chemically active species. Depending upon its chemical composition and physical state, particulate matter causes wide damage to materials. Particles will soil painted surfaces, clothing, and curtains merely by settling on them.

More important, particulate matter can cause direct chemical damage either by intrinsic corrosiveness or by the action of corrosive chemicals absorbed or adsorbed, by inert particles emitted into the atmosphere. Metals ordinarily can resist corrosion in dry air alone or even in clean moist air. However, hygroscopic particles commonly found in the atmosphere can corrode metal surfaces with no other pollutants present. Examples of the corrosion of metallic surfaces exposed to industrial atmospheres are well documented [29] and will not be listed here. The damage caused by particulate matter on materials is enhanced when sulfur dioxide is present due to the acidic nature which is created when the sulfur dioxide absorbs onto the surface of the particulate matter [30].

Little is known of the effects of particulate matter in general on vegetation. A few studies have reported that combinations of particulate matter and other pollutants such as sulfur dioxide may increase foliar uptake of the sulfur dioxide,
increase foliar injury by heavy metals, and/or reduce plant growth and yield [30]. Coarse particles, such as dust, may be deposited directly onto leaf surfaces, reducing gas exchange, increasing the leaf surface temperature, and reducing photosynthesis. This can result in chlorosis (yellowing of leaves due to inability to develop chlorophyll), reduced growth, and leaf necrosis (or dying of portions of the leaf). Particles containing fluorides appear to cause some plant damage, and magnesium oxide falling on agricultural soils has resulted in poor plant growth. An animal’s health may suffer when the animal feeds on plants covered by toxic particulate matter. Such toxic compounds may be absorbed into the plant tissues or may remain as a surface contaminant of the plants. Fluorosis in animals has been attributed to their ingestion of vegetation covered with a fluoride-containing particulate matter [30]. Cattle and sheep that have ingested vegetation on which arsenic-containing particles have settled have been victims of arsenic poisoning [29].

1-5-D Effects of Atmospheric Particulate Matter on Human Health

Particulate matter alone or in combination with other pollutants constitutes a very serious health hazard. The pollutants enter the human body mainly via the respiratory system. Damage to the respiratory organs may follow directly, since it has been estimated that between 30 and 80 percent of the particles between 0.01 and 2.5 μm which are breathed will penetrate into the lungs where they are deposited as shown in Figure 1-3 [13].

Particulate matter may exert a toxic effect in one or more of the following three ways [25]:

1. The particle may be intrinsically toxic because of its inherent chemical and/or physical characteristics.
2. The particle may interfere with one or more of the mechanisms which normally clear the respiratory tract.
3. The particle may act as a carrier of an absorbed toxic substance in the case of liquid particles or adsorbed toxic substances in the case of solid particles.

It is extremely difficult to obtain a direct relationship between exposure to various concentrations of particulate matter and the resulting effects upon human health. The length of time of exposure is important. In some cases it has been observed that exposure to particulate matter in combination with other pollutants such as SO₂ produces more severe health deterioration than does exposure to each pollutant separately [30]. It is also difficult to reproduce in the laboratory the exact conditions that prevail in the ambient atmosphere.

To date, we have had to rely upon the statistical analysis of such data as increases in hospital admissions, clinic admissions, absences from work and school, mortality, and the limited data pertaining to the measured concentrations of atmospheric pollutants that prevailed during the subject time periods. Such data do indicate a relationship between increases in particulate concentrations and increases in the number of clinic and hospital visits for upper respiratory infections, cardiac diseases, bronchitis, asthma, pneumonia, and emphysema.

Deaths of elderly persons affected with respiratory diseases and cardiac conditions also show an increase during periods when the concentration of particulate matter is unusually high for several days. Evidence indicates that some of the particulate matter in the atmosphere is carcinogenic in nature [29], especially when combined with cigarette smoking.

As discussed in Section 1-5-A, the continuing development of the understanding of the effects of particulate matter on human health has resulted in basic changes in the way that particulate matter is measured. This progression began with an original air quality standard based on Total Suspended Particulate matter (TSP) and the high-volume sampler in 1970, to replacement of that standard with a PM₁₀ standard in 1987. In 1997, as a result of the findings reported in the most recent published Air Quality Criteria for Particulate Matter (EPA-450/6-95/001A; April 1995) the U.S. EPA promulgated new standards which address particulate matter with aerodynamic sizes of less than or equal to 2.5 μm (now referred to as the fine particle fraction). The range of particles that lie between PM₁₀ and PM₂.₅ is now referred to as the coarse fraction. For this reason, the historically reported effects of particulate matter as a function of dosage are very much dependent on the type of measurement which was made (i.e., TSP, PM₁₀, PM₂.₅, and PM₁₅).

The findings of epidemiological studies in recent years have been reported in terms of the relative risk associated with exposure to particulate matter indicators such as TSP, PM₁₀, etc. The relative risk RR is often reported as the increase above the baseline mortality or morbidity associated with a specific increase in the particulate matter concentration using one of the above specific indicators. For example, a relative risk RR of 1.06 in mortality for a 50 μg/m³ increase in PM₁₀ would imply that there is a 5 percent increase in the mortality rate associated with a 50 μg/m³ increase in PM₁₀. The 1999 air quality criteria document for particulate matter reported that the RR for total nonaccidental mortality associated with a 50 μg/m³ increase in 24-hour average PM₁₀ ranged from 1.015 to 1.085 (i.e., 1.5 to 8.5 percent increase in mortality). Higher risks were reported for the elderly and those with preexisting respiratory conditions. In the Harvard Six-Cities study, it was reported that the increased risk to daily mortality increased by about 0.8 percent for each 10 μg/m³ increase of PM₁₀ based on two day mean concentrations [61]. For fine particles (PM₂.₅), the Six-Cities study showed a statistically significant relationship with relative risks ranging from 1.02 to 1.06 per 25 μg/m³ increase in PM₂.₅ and a 1.5 percent increase in daily mortality for each 25 μg/m³. The relative risk associated with chronic, long-term exposure to particulate matter shows even higher mortality risk, however, long-term studies are more complicated in that concentrations of particulate matter have historically been higher in previous years. Thus the exposure may not have been constant and the relative risk contains more uncertainty.

Table 1-4 illustrates typical effects as related to the concentrations of particulate matter that have been reported in the air quality criteria documents which have been published since 1970, showing the progression of understanding up to and including data from the most recent 1996 document. The original TSP standard, the current PM₁₀ standards and the new (1997) PM₂.₅ standards are included.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Measurement Time</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>60–180 µg/m³</td>
<td>Annual geometric mean with SO₂ and moisture</td>
<td>Acceleration of erosion of steel and iron pipes</td>
</tr>
<tr>
<td>75 µg/m³</td>
<td>Annual geometric mean</td>
<td>Original NAQOS (TSP)</td>
</tr>
<tr>
<td>150 µg/m³</td>
<td>Relative humidity less than 70 percent</td>
<td>Visibility reduced to 5 m</td>
</tr>
<tr>
<td>100–150 µg/m³</td>
<td>With radiation levels of</td>
<td>Direct sunlight reduced one third increased death rate of persons over 50 may occur</td>
</tr>
<tr>
<td>80–100 µg/m³</td>
<td>30 µg/cm²/month</td>
<td>Over 50 may occur</td>
</tr>
<tr>
<td>100–150 µg/m³</td>
<td>With SO₂ &gt; 120 µg/m³</td>
<td>Direct sunlight reduced one third increased death rate of persons over 50 may occur</td>
</tr>
<tr>
<td>200 µg/m³</td>
<td>24-hr average and SO₂ &gt; 250 µg/m³</td>
<td>Illness of industrial workers may cause an increase in absence from work</td>
</tr>
<tr>
<td>500 µg/m³</td>
<td>24-hr maximum</td>
<td>Original NAQOS (TSP)</td>
</tr>
<tr>
<td>750 µg/m³</td>
<td>24-hr average and SO₂ &gt; 715 µg/m³</td>
<td>Acute bronchitis patients are likely to suffer acute worsening of symptoms</td>
</tr>
<tr>
<td>Air Quality based on PM₁₀</td>
<td>Current NAQOS (PM₁₀)</td>
<td>Excessive number of deaths and considerable increase in illness may occur</td>
</tr>
<tr>
<td>50 µg/m³</td>
<td>Annual arithmetic mean</td>
<td>Current NAQOS (PM₁₀)</td>
</tr>
<tr>
<td>10 µg/m³ increase</td>
<td>24-hr average</td>
<td>Relative risk is 1.08 to 1.09 for increased mortality</td>
</tr>
<tr>
<td>50 µg/m³ increase</td>
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</tr>
<tr>
<td>150 µg/m³</td>
<td>24-hr maximum</td>
<td>Current NAQOS (PM₁₀)</td>
</tr>
<tr>
<td>Air Quality Criteria based on PM₂.₅</td>
<td>Promulgated NAQOS (PM₂.₅, July 1997)</td>
<td>Current NAQOS (PM₂.₅)</td>
</tr>
<tr>
<td>15 µg/m³</td>
<td>Annual arithmetic mean</td>
<td>Promulgated NAQOS (PM₂.₅, July 1997)</td>
</tr>
<tr>
<td>25 µg/m³ increase</td>
<td>24-hr average</td>
<td>Relative risk is 1.02 to 1.06 for increased mortality</td>
</tr>
<tr>
<td>65 µg/m³</td>
<td>24-hr maximum</td>
<td>Promulgated NAQOS (PM₂.₅, July 1997)</td>
</tr>
</tbody>
</table>

Sources: Adapted from data presented in National Air Pollution Control Administration, Air Quality Criteria for Particulate Matter, APHA, Washington, D.C., 1988, and Air Quality Criteria for Particulate Matter, EPA450/00779-001/01/98, No. 1, April 1996, U.S. EPA.

in the table for comparison, listed: TSP air quality criteria are included in the table to provide perspective on the progression of understanding of health effects. The PM₁₀ and recently promulgated PM₂.₅ standards represent values above which the concentrations are currently considered to be detrimental to human health.

---

1-6 Carbon Monoxide

Carbon monoxide is a colorless and odorless gas. It is very stable and has a lifetime of 2 to 4 months in the atmosphere. It is a trace constituent of the troposphere and is produced by both natural processes and from anthropogenic sources. Data on global trends of CO indicated a 1 to 2 percent annual increase over the last several decades with a global background concentration in the range of 50 to 120 ppb [31]. Average background concentrations vary seasonally with higher concentrations in winter and lower levels in the summer months. Based on information summarized in Table 1-9, approximately 70 percent of anthropogenic CO emissions in the U.S. during the period of 1970 to 1980 were from highway vehicles. The percentage was decreased to 58 percent by 1991 primarily due to installation of emission control systems on newer vehicles. While CO emissions from individual vehicles have been lowered, the emissions reduction has been partially offset by the increase in the number of vehicle miles traveled. Soil fungi [28] may remove a significant amount of the quantity released, and it is generally assumed that CO is oxidized to CO₂ in the atmosphere, although the rate is quite slow. Carbon monoxide has also been found to be a minor participant in photochemical reactions leading to ozone formation.

1-6-A Effects of Carbon Monoxide on Materials and Plants

Carbon monoxide appears to have no detrimental effects on material surfaces. The results of numerous experiments have not shown CO to produce any harmful effects on the higher plant life at concentrations below 100 ppm during exposures for one to three weeks [32]. Ambient concentrations of CO rarely reach this level even for short periods of time.

1-6-B Effects of Carbon Monoxide on Health

There are many studies that show that high concentrations of carbon monoxide can cause physiological and pathological changes and ultimately death. Carbon monoxide is a poisonous inhalant that deprives the body tissues of necessary oxygen. Carbon monoxide has long been known to cause death when exposure to a high concentration (> 750 ppm) is encountered. The combination of carbon monoxide with hemoglobin leads to carboxyhemoglobin, COHb; the combination of oxygen and hemoglobin leads to oxyhemoglobin, O₂Hb. Hemoglobin has an affinity for CO that is approximately 240 times its affinity for oxygen [31]. That is, the partial pressure of CO required to saturate hemoglobin fully is only 1/240 of the partial pressure of oxygen required for complete saturation with oxygen. Exposure to a mixture of both gases leads to equilibrium concentrations of COHb and O₂Hb given by

\[
\frac{[\text{COHb}]}{[\text{O}_2\text{Hb}]} = M \frac{P_{\text{CO}}}{P_{\text{O}_2}}
\]

\[\text{(1-11)}\]
where \( P_{CO} \) and \( P_{O_2} \) represent the partial pressures of CO and O\(_2\) in the inhaled gas, and \( M \) is a constant equal to 240 for human blood. Thus, the quantity of COHb in the blood is a function of the concentration of CO in the air breathed. Fortunately the formation of COHb in the bloodstream is a reversible process. When exposure is discontinued, the CO that combined with the hemoglobin is released, and the blood is cleared of half its carbon monoxide in healthy subjects in 2 to 6 hr [31]. A blood level of 0.4 percent COHb is maintained by the CO produced within the body, independent of external sources.

**EXAMPLE 1-7** Make a rough estimate of the saturation value of COHb in the blood if the CO content in the air breathed is 190 ppm.

**Solution**

In order to apply Equation (1–11), we assume an \( M \)-value of 240. In addition, we assume that the oxygen content of the gas within the lungs is the same as in ambient air, that is, 21 percent or 210,000 ppm. Employing these values we find that

\[
\text{COHb} = \frac{M \cdot P_{CO}}{P_{O_2}} = \frac{240 \times 100}{210,000} = 0.11
\]

Since the ratio of CO to \( O_2 \) in the blood is found to be 0.11:1, the saturation value for carbon monoxide is roughly 10 percent (i.e., 0.11 out of a total of 1 plus 0.11). This is somewhat low since the oxygen content of incoming air is diluted by the gases which remain in the lungs.

Figure 1-8 relates the percent hemoglobin tied up as COHb as a function of CO concentration in the environment and the exposure time. On the basis of Figure 1-8, for example, exposures of 2 hours in duration at concentrations of 40 ppm result in 2 percent COHb, whereas a concentration of 100 ppm results in approximately 5 percent COHb in healthy male subjects engaged in sedentary activity [32].

The direct effect of COHb is to reduce the oxygen-carrying capacity of the blood. However, a secondary effect is also present. COHb interferes with the release of the oxygen carried by the remaining hemoglobin. This effect further reduces the oxygen-delivery capacity. Some cases of exposure for 8 hr or more to concentrations of 10 to 15 ppm have caused impaired time-interval discrimination. This concentration range is common during the day along downtown streets and particularly inside the vehicles in rush-hour traffic [31]. As indicated by Figure 1-10, such exposure would lead to a COHb concentration in the bloodstream of roughly 2.5 percent. Evidence indicates that exposure for 8 hr or more to concentrations of 50 ppm (85 mg/m\(^3\)) causes impaired performance on certain psychomotor tests. Such an exposure will produce an equilibrium value of 5 percent COHb in the blood. Exposure to higher concentrations has produced evidence of physiologic stress in patients with heart disease. Evidence has also been presented that ambient 24-hr maximum CO concentrations of 10 to 15 ppm in the Los Angeles basin were associated with excess mortality [32]. (The vast majority of this CO was due to emissions from gasoline engines.) In 1991-94, the maximum 8-hr concentrations of CO in the Los Angeles area were 1.5 to 2 times the 8-hr standard of 9 ppm.

A value of 67 mg/m\(^3\) (80 ppm) is considered an upper limit of safety in occupational environments for healthy persons for an 8-hr exposure. At 100 ppm, most people experience dizziness, headache, and lassitude. In terms of CO exposure, it should also be noted that cigarette smoke contains 400 to 450 ppm CO. The percent of COHb in blood of cigarette smokers increases as the number of cigarettes smoked per day increases. Blood samples from 23,000 blood donors in U.S. cities, suburbs, and rural areas revealed high concentrations of COHb. Forty-five percent of nonsmokers had blood containing 1.5 percent COHb. The blood of most smokers averaged above 5 percent COHb. Nonsmokers in Chicago averaged 2 percent COHb. One-pack-a-day smokers averaged 6.3 percent, and two-pack-a-day smokers averaged 7.7 percent [34]. Relating either ambient air CO concentration or percent of COHb in the blood to health effects is much more difficult than relating ambient CO concentration to the percent COHb.
There is disagreement as to whether CO is a threshold pollutant. Some experts believe that even small concentrations of CO produce some undesirable effects. Most American scientists believe that carbon monoxide is not a cumulative poison [32]. Chronic poisoning does not occur as a result of long-term exposure to relatively low concentrations. Persons particularly susceptible (those already affected with a disease that involves the oxygen capacity of the blood, such as anemia or cardiorespiratory disease) may be affected by CO levels existing on city streets. Exposure to low concentrations of CO (10 to 50 ppm) can impair a person's ability to estimate time intervals and affect visual acuity with regard to brightness threshold. There is some evidence that such effects on a person driving a car increase the chances of having an accident as one's abilities deteriorate [35].

Table 1-5 lists the health effects attributed to certain CO levels in the environment and COHb levels in the blood [31]. Generally speaking, the COHb level should be less than 2 percent except under extenuating circumstances for short time periods. In light of these health effects the Environmental Protection Agency's (EPA) air quality standards for CO are: 10 mg/m³ (9 ppb) for an 8-hr averaging period; 40 mg/m³ (38 ppb) for a 1-hr averaging period. In comparison to the primary national ambient air quality standards listed above, the "significant harm" level defined by EPA is 50 ppm for an 8-hr average, 75 ppm for a 4-hr average and 125 ppm for a 1-hr average. This is roughly equal to 5 to 10 percent carboxyhemoglobin level and can cause significant health effects. By plotting the 1-hr air quality standard of 36 ppm and the eight-hour standard of 9 ppm on Figure 1-8, it is apparent that the standard is intended to minimize the COHb to less than approximately 2 percent.

TABLE 1-5  Health Effects of Carbon Monoxide and COHb

<table>
<thead>
<tr>
<th>Environmental Condition</th>
<th>Carbon Monoxide Effects</th>
<th>COHb Level (Percent)</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 ppm 6-hr exposure</td>
<td>Ambient air quality standard</td>
<td>&lt; 1</td>
<td>No apparent effect</td>
</tr>
<tr>
<td>50 ppm 6-hr exposure</td>
<td>Structural changes in heart and brain of animals</td>
<td>1-2</td>
<td>Some evidence of effect on behavioral performance</td>
</tr>
<tr>
<td>50 ppm 50-min exposure</td>
<td>Changes in relative brightness threshold and visual acuity</td>
<td>2.5-5</td>
<td>Reduced exercise performance in healthy individuals</td>
</tr>
<tr>
<td>50 ppm 8- to 12-hr exposure time</td>
<td>Impaired performance on psychomotor tests</td>
<td>5-10</td>
<td>Reduced exercise duration due to increased chest pain (angina) in individuals with ischemic heart disease</td>
</tr>
<tr>
<td></td>
<td>Carboxyhemoglobin</td>
<td>10</td>
<td>Effects on visual perception, audition, motor performance, vigilance, and other measures of neurobehavioral performance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>Neurological symptoms including headaches, dizziness, weakness, nausea, confusion, and leading to unconsciousness and death with continued exposure to high levels</td>
</tr>
</tbody>
</table>

1-7  Sulfur OXides

Sulfur dioxide and sulfur trioxide are the dominant gaseous oxides of sulfur present in the atmosphere. Sulfur dioxide is a non-flammable, non-explosive, colorless gas that causes a taste sensation at concentrations from 0.3 to 1.0 ppm in air. At concentrations above 3.0 ppm the gas has a pungent, irritating odor. Sulfur dioxide is partly converted to sulfur trioxide or to sulfuric acid and its nitrate photolytic or catalytic processes in the atmosphere. Sulfur trioxide and moisture form sulfuric acid. The oxides of sulfur in combination with particulate matter and moisture produce the most damaging effects attributed to atmospheric air pollution. Unfortunately it has proven difficult to isolate the effects of sulfur dioxide. Brief discussion of the effects of sulfurous compounds will be presented in the following sections.

1-7-A  Effects of Sulfur Compounds on Visibility and Materials

As discussed in Section 1-5-A, fine particles in the atmosphere reduce the visual range by scattering and absorbing light. Since aerosols of sulfuric acid and other sulfates make up from 5 to 50 percent of the total suspended particulate matter in urban air, they contribute significantly to the reduction in visibility. Investigations [36] indicate that much atmospheric haze is caused by the formation of various aerosols resuluting from the photochemical reactions between SO₂, particulate matter, oxides of nitrogen, and hydrocarbons in the atmosphere. In laboratory measurements, mixtures of NO₂ and most common hydrocarbons form little or no aerosols when irradiated. However, considerable aerosol formation takes place when mixtures of olefin, NO₂, SO₂ are irradiated by sunlight. One of the major products of such complex photochemical reactions is light-scattering droplets of sulfuric acid mist.

Measurements indicate that a major fraction of the sulfate in urban air has an effective size of less than 2 μm, with the peak in the size distribution around 0.2 to 0.3 μm. Since the visible wavelength range of the electromagnetic spectrum is roughly from 0.4 to 0.8 μm, the presence of aerosols of this type can cause a pronounced reduction in visibility. Figure 1-9 shows the trend of the influence of SO₂ and relative humidity on the visual range [1]. Although not shown specifically, the combination of increasing SO₂ concentration and increasing relative humidity leads to increasing aerosol concentrations. This in turn is responsible for the decrease in visual range shown in the figure. The typical range of SO₂ concentrations in urban areas, 0.01 to 0.20 ppm, is shown by the crosshatched region in Figure 1-9. For SO₂ concentrations greater than 0.10 ppm, the limit of visibility becomes significant. Estimates show that a concentration of 0.10 ppm SO₂ with a relative humidity of 50 percent reduces the visibility to about 5 m [36], as shown in Figure 1-9. In 1993, the U.S. EPA reported that visibility reduction in the southwestern U.S. generally resulted from 20 to 40 percent natural causes and 60 to 80 percent anthropogenic-related sources of gases and particles. In the southeastern U.S. anthropogenic sources accounted for nearly 70 to 90 percent of the visibility reduction [57]. In the southeast in areas such as the Great Smoky Mountains National Park, the total extinction was estimated to be due to Rayleigh
However, at relative humidities greater than 70 percent the corrosion rate is greatly increased [38]. The American Society for the Testing of Materials (ASTM) has reported some long-range studies of atmospheric effects on the tensile strength of aluminum [39]. Exposure in rural areas led to a loss of 1 percent or less in tensile strength over 20 years, while industrial atmospheres led to a 14 to 17 percent loss in the same time period. The literature offers an extensive review of metal corrosion due to different atmospheric conditions through the early 1960s [40]. Sulfurous or sulfuric acids are capable of attacking a wide variety of building materials, including limestone, marble, roofing slate, and mortar. Fairly soluble sulfates are formed which can then leach away by rain. Textiles made of nylon, especially nylon hose, are also susceptible to pollutants in the atmosphere. Weakening is apparently caused by SO$_3$ or by sulfuric acid aerosol.

### 1-7-7 Effects on Human Health

Although sulfur dioxide and other oxides of sulfur have been studied intensely, many questions concerning the effects of sulfur dioxide upon health remain unanswered. Because sulfur oxides tend to occur in the same kinds of polluted atmosphere as particulate matter and high humidity, few epidemiologic studies have been able to differentiate adequately the effects of the individual pollutants.

Various animal species, including humans, respond to sulfur dioxide by bronchoconstriction, which may be assessed in terms of an increase in airway resistance [36]. Most individuals will show a response to SO$_2$ at concentrations of 5 ppm and above, and certain sensitive individuals show slight effects at 2 to 5 ppm. Sulfuric acid is a much more potent irritant than sulfur dioxide; therefore, most studies deal with combined sulfuric materials rather than with SO$_2$ alone. Analysis of numerous epidemiological studies clearly indicates an association between air pollution, as measured by the concentration of SO$_2$ accompanied by particulate matter and moisture, and health effects of varying severity [36]. This is especially true for short-term exposure. The association between long-term exposure and chronic disease morbidity and mortality is not so clear. Typical concentration data and associated health effects are presented in Table 1–6. As can be seen from these data, sulfur dioxide in combination with particulate matter and moisture is a potentially serious health hazard (see Table 1–4 also).

A comprehensive review of the physiological effects of SO$_2$ and SO$_3$ on humans and other animals was made in 1964 by Grenzwald [41]. That report indicates that sulfur dioxide acts as a pungent, suffocating, irritating gas in effect on the upper respiratory tract under moderate exposure. At concentrations below about 20 ppm, SO$_2$ produces only acute effects; to date, no chronic or cumulative effects on animals have been reported when exposure levels were moderate and exposure discontinuous. The results of other laboratory tests [1] tend to indicate that concentrations above 1 ppm of pure SO$_2$ are required before serious or even significant effects may be expected on the health of unimpaired individuals.

To illustrate the complexity of determining a satisfactory relationship between human health and the concentration of sulfur dioxide in the atmosphere, we cite the results of two studies. In a study relating the excess mortality in New York City...
### Effects of SO₂ at Various Concentrations

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 ppm, annual average</td>
<td>National Ambient Air Quality Standard chronic plant injury Accompanied by smoke at a concentration of 165 μg/m³, increased frequency of respiratory symptoms and lung disease may occur</td>
</tr>
<tr>
<td>0.037-0.092 ppm, annual mean</td>
<td>With low particulate level, increased hospital admission of older persons for respiratory diseases may occur, increased metal corrosion</td>
</tr>
<tr>
<td>0.11-0.19 ppm, 24-hr mean</td>
<td>With low particulate level, increased mortality may occur</td>
</tr>
<tr>
<td>0.14 ppm, 24-ppm mean</td>
<td>National Ambient Air Quality Standard</td>
</tr>
<tr>
<td>0.19 ppm, 24-ppm mean</td>
<td>With low particulate level, increased mortality may occur</td>
</tr>
<tr>
<td>0.25 ppm, 24-hr mean</td>
<td>Accompanied by smoke at a concentration of 750 μg/m³, increased daily death rate may occur (British data); a sharp rise in illness rates</td>
</tr>
<tr>
<td>0.5 ppm, 8 hr</td>
<td>Some trees show injury</td>
</tr>
<tr>
<td>0.52 ppm, 24-hr average</td>
<td>Accompained by particulate matter, increased mortality may occur</td>
</tr>
</tbody>
</table>


During the years 1963 to 1973, air pollution as indicated by SO₂ concentration and smoke level, H. Schimmel et al. [42] found that while SO₂ concentrations decreased from a high of 0.22 ppm to 0.03 ppm, mortality did not show a corresponding decrease. The smoke level remained approximately the same during the entire period. Schimmel et al. [42] also stated that studies conducted in England showed that mortality and morbidity have decreased with a rather sharp reduction in particulate matter, whereas the SO₂ levels have not changed very much. In a study of emergency room visits for asthma over a 4-month period, Goldstein and Block [43] found no relationship between daily visits to emergency rooms and daily levels of either smoke or SO₂ for residents of Harlem, in Brooklyn; however, they observed a strong correlation between daily visits for asthma and daily levels of SO₂ but not of smoke. Another study [44] reported evidence linking sulfur oxides and suspended particulate matter to acute respiratory diseases in children. Based on a 1972 survey of children in four New York communities, the study found that exposed children in the 1 to 12 age group experienced a 29 percent greater frequency of acute bronchitis than did children not similarly exposed. The significant increase could not be explained by other factors.

Although additional studies and more recent air quality criteria documents have been prepared, the U.S. EPA has concluded as recently as May 1990 that the existing health-based standards (established in 1970) for sulfur dioxide provide adequate nationwide protection from adverse health effects from acute and sustained, low-level exposure. However, it has been recognized that there are some localized areas (associated primarily with those that have not yet attained the air quality standards) where asthmatics may be repeatedly exposed to high SO₂ concentrations. To that end, a program was proposed in December 1986 to develop local intervention programs on a state-by-state basis. The intervention program is designed to establish a concern level of 0.06 ppm and an endangerment level of 2 ppm for 5-minute ambient concentration levels. In areas which exceed these levels, the proposed program would require corrective action to be taken.

#### 1.7-C Effects on Vegetation

Before discussing the effects of sulfur dioxide on vegetation, it is appropriate to make a few introductory comments. In general, damage to plants from air pollution usually occurs in the leaf structure, since the leaf contains the building mechanisms for the entire plant. A leaf typically may be divided into three regions. The epidermis forms a protective layer on the outside. The mesophyll is the center section of the leaf, and consists of two layers of cells called the palisade and the spongy parenchyma. In addition, a dense network of veins runs throughout the leaf from its base or stem. The veins provide the transport system for water and other chemicals as they are transferred to other portions of the plant. Of particular interest in air pollution studies are the openings through the epidermis into the mesophyll, called stomata. Gases and vapors pass in and out of the leaf structure through the stomata, each of which is surrounded by special guard cells that open or close the stomata. Among the most frequently encountered gases toxic to vegetation are sulfur dioxide, ozone, PAIN (peroxyacetyl nitrate), hydrogen fluoride, ethylene, hydrogen chloride, chlorine, hydrogen sulfide, and ammonia. Information on the injury to vegetation caused by gaseous air pollutants can be found in the federal air quality criteria publications. Another excellent source of information containing color photographs of damage to various vegetation can be found in the Air Pollution Atlas. While the reference is now out-of-print, it can still be found in many libraries.

The effect on leaves of excessive SO₂ in the atmosphere appears first as a cellular injury to the spongy parenchymal area in the mesophyll, followed by damage to the palisade region. On initial attack the leaf appears water-soaked. Upon drying, a bleached or very color appears in the affected areas. Apparently there is a threshold value below which the leaf is capable of consuming the gas without injury. One threshold value cited for sensitive plants is 0.3 ppm (765 μg/m³) sustained exposure for 8 hr. Concentrations of 0.3 to 0.5 ppm for several days lead to chronic injury to sensitive plants. The SO₂ enters the stomata directly and the plant cells in the mesophyll convert it to thiosulfate and then into sulfate. Apparently when excessive SO₂ is present the cells are unable to oxidize sulfate to sulfuric acid, and instead, disruption of the cell structure begins. Spinaches, lettuce, and other leafy vegetables are most sensitive, as are cotton and alfalfa. Pine needles are also affected, with either the needle tip or the whole needle becoming brown and brittle. A considerable amount of literature (over 40 articles in reference 22) deals with plant damage caused by sulfur compounds.

#### 1.7-D Acid Rain

Acid rain is a term commonly used to describe the wet and dry deposition of acidic substances from the atmosphere. These substances may be in the form of acid...
The acidity of water droplets is reported in terms of the pH where pH is the logarithm (base 10) of the molar concentration of hydrogen ions:

$$pH = -\log_\text{10}[H^+]$$

Pure water actually contains a hydrogen ion concentration that is approximately 10^-7 molar or pH = 7, sometimes referred to as neutral pH. However, water droplets formed by condensation in the atmosphere normally have a pH of approximately 5.6. This is due to the dissolution of atmospheric CO₂ into rainwater, which tends to lower the pH due to the formation of carbonic acid. By the early 1970s, however, individual pH values from 3 to 6 were measured in various parts of the world, with yearly averages between 4 and 5 [45]. Thus, hydrogen ion concentrations from 10 to 1000 times greater than expected from natural sources were discovered. Measurements in Guenter, Newfoundland, since 1976 indicate pH values of 4.0 to 4.5 on a yearly basis in that region [46]. Similar values are valid for the average pH of rainfall in the eastern half of the United States.

These low values are due in part to the transformation of SO₂ and NO₂ into acids when they are absorbed in cloud water and raindrops. For example, SO₂ can be absorbed from the gas phase into an aqueous droplet creating acidic conditions as follows [49]:

$$\text{SO}_2(g) \rightarrow \text{SO}_2(\text{aq})$$
$$\text{SO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{H}^+$$
$$\text{HSO}_3^- \rightarrow \text{SO}_3^{2-} + \text{H}^+$$

The relative proportions of various sulfite and sulfate ions are dependent on the detailed equilibrium chemistry within the aqueous phase. The presence of the SO₃²⁻ ion is generally believed to be the result of gas phase absorption of SO₂. However, the SO₃²⁻ is in a result of both aqueous phase oxidation of the SO₂⁻ ion as well as scavenging of preexisting sulfate particles by the water droplets. NO and NO₂ are also involved in atmospheric reactions which can lead to the formation of the NO₃⁻ ion and H⁺ in the aqueous phase (nitric acid). The kinetics of the HNO₃ formation are not as well understood as those for the formation of sulfuric acid. These acid aerosols, once formed, can be deposited in significant quantities, resulting in the phenomenon called acid rain.

The increasing presence of these acids is attributed to the increase in emissions of SO₂ and NOₓ that has occurred since the 1940s through the increased use of fossil fuels in industrialized nations. Data from the eastern United States indicate that roughly 60-70 percent of the acidity is due to sulfuric acid, and 30-40 percent is due to nitric acid [47]. While the concentrations of sulfates and nitrates formed in the atmosphere are frequently low, the deposition effect is cumulative.

Such pollutants travel in the lowest 2 km of the atmosphere, and are often carried hundreds of kilometers from their source. Their presence has been observed in a qualitative sense by the remarkable increase in summer haze in a number of regions of industrialized nations. Acid rain has affected areas in Switzerland, the southern part of the Scandinavian countries, Europe, and especially the northeastern half of North America. In the latter case, measurements indicate a severe problem in the Atlantic provinces of Canada and in the Adirondack Mountain region of the United States. Acid rain has also been found in the Midwest and southeastern parts of the United States. Even major urban areas on the West Coast are affected. The phenomenon has been under active study in Europe since the early 1950s. The problem exists in northern Europe since a major portion of the air pollution produced on the continent is transported in a north-easterly direction toward Scandinavia. Likewise, pollution produced in the central provinces of Canada and in the central and eastern states of the United States is carried in the summer and fall in a north-easterly direction.

Data taken at St. Margaret's Bay in eastern Canada indicate that upwards of 25 percent of the suspended particulate matter was in the form of sulfates [48]. Percentages as high as 70 percent have been measured elsewhere. Although the particulate concentration has been reduced in many industrialized nations due to effective control techniques on sources of particulate matter, the fraction of the remaining particulate matter which is in the form of an acid aerosol continues to increase since the removal of sulfur dioxide and nitric oxides has not paralleled that of particulate matter. Conditions in the atmosphere which favor aerosol sulfate formation include poor atmospheric dispersion and ample sunlight. Such conditions also are favorable to ozone formation.

There are several effects of acid rain that are of concern. First, there is an acidification of natural water sources. This can have a devastating effect on fish life. Trout and salmon are particularly sensitive to a low pH. Reproduction in many fish fails to occur at a pH less than 6.5. A decrease in plankton and bottom fauna is also observed as the pH is lowered, which reduces the food supply for fish. Second, a leaching of nutrients occurs in the soil. This denitrification can lead to a loss in productivity of crops and forests, or a change in the natural vegetation. Vegetation itself can be directly damaged, and an increase in corrosion of materials is observed. The severity of damage to soils and bodies of water is partially determined by the minerals in the soil in a given region. Those areas that contain rock such as calcium carbonate or similar minerals are buffered against the effects of acid rain. In such regions, lakes tend to maintain a pH closer to 6 or 8.

While isolated lakes may be neutralized to reduce the pH of the water, there is no way to quickly alter the acidity of a region once it has occurred. The long-term solution is the control of emissions at the source. Desulfurization of fossil fuels has been considered important in the past in order to prevent local air pollution. It has now become more apparent that SO₂ and NOₓ control are needed to prevent the long-range dispersion of pollutants as well. Thus emission control takes on an international scope, since emissions from one country are affecting the nature of rain in another country. The 1990 Clean Air Act Amendments to be discussed in Chapter 2 have addressed both pollutants with the intent of reducing levels of both pollutants significantly below the levels which existed in 1980 in the United States.
1-8 Effects of Hydrocarbons, Oxides of Nitrogen, Photochemical Oxidants

1-8-A Hydrocarbons

Although a national air quality standard was originally established in 1971 for non-methane hydrocarbons, it was withdrawn after extensive review in 1983. Hydrocarbons, in combination with the oxides of nitrogen in the presence of sunlight, form photochemical oxidants including ozone that do have adverse effects on human health and on plants. For that reason, however, it was felt that an ozone standard was more appropriate than a hydrocarbon standard.

Studies of the effects of ambient air concentrations of many of the gaseous hydrocarbons have not demonstrated direct adverse effects upon human health [43]. Studies of the carcinogenicity of certain classes of hydrocarbons do indicate that some cancers appear to be caused by exposure to aromatic hydrocarbons found in soots and tars. Identifiable airborne carcinogens include polynuclear aromatic hydrocarbons.

Gaseous hydrocarbons as a broad class also do not appear to cause any appreciable corrosive damage to materials. Of all the hydrocarbons, only ethylene has adverse effects on plants at known ambient concentrations. The principal effect of ethylene is to inhibit plant growth [48]. Concentrations of ethylene from 0.01 to 0.5 ppm have caused damage to sensitive plants including flower dropping and failure of the leaves to open properly. Injury to orchids and to cotton has been demonstrated.

While hydrocarbons as a general class of pollutants are not currently listed as criteria pollutants, a large number of specific hydrocarbon compounds are listed among the list of 189 hazardous air pollutants which are in the process of being regulated under the Title III Air Toxics provisions of the Clean Air Act Amendments of 1990. Hazardous air pollutants are discussed in more detail in Chapter 2.

1-8-B Oxides of Nitrogen

There are seven oxides of nitrogen that are present in the ambient air. These include nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O), NOx, N₂O₅, HNO₃, and NO₂. Nitric oxide and nitrogen dioxide are collectively referred to as NOₓ due to their interconvertibility in photochemical smog reactions. The term NOₓ is often used to represent the sum of the reactive oxides of nitrogen and all other compounds that are atmospheric products of NOₓ. NOₓ includes compounds such as nitric acid (HNO₃), nitrous acid (HNO₂), nitrate radical (NO₃), dinitrogen pentoxide (N₂O₅), and peroxycetyl nitrate (PAN). It excludes nitrous oxide (N₂O) and ammonia (NH₃). While these latter two are often sources of NOₓ in the atmosphere, they are not normally the reaction products of NOₓ reactions.

Of the oxides of nitrogen, NO is present in the highest concentrations in ambient air. Although NO is commonly present in the lower atmosphere (formed by biological action at the earth’s surface) it is not normally considered an air pollutant in the troposphere. However, it does participate in upper atmospheric reactions involving the ozone layer. Both NO (NO, NO₂) and NOₓ (i.e., HNO₃) have been shown to accelerate damage to materials in the ambient air: NO affects dyes and fabrics resulting in fading, and discoloration of archival and artistic materials and textile fibers, and loss of strength of textile fibers. As a result, NOₓ damage is a greater concern in the indoor environment than in the outdoor environment due to the presence of unvented combustion systems (gas stoves, etc.) that emit small concentrations of NOₓ. In addition, NOₓ in the ambient air can react with moisture to form nitric acid, which can cause considerable corrosion of metal surfaces.

Nitrogen dioxide also absorbs visible light and at a concentration of 0.55 ppm will cause appreciable reduction in visibility as discussed in Section 1-8-B. Nitrogen dioxide at a concentration of 0.55 ppm for a period of 10 to 12 hours has suppressed growth of such plants as pinto beans and tomatoes. Experiments with navel oranges show that yield is reduced by prolonged exposure to NOₓ at concentrations from 0.25 to 1 ppm.

Nitrogen dioxide acts as an acute irritant and in equal concentrations is more injurious than NO. However, at concentrations found in the atmosphere NOₓ is only potentially irritating and potentially related to chronic obstructive pulmonary disease (COPD). Table 1-7 summarizes the key health effects of exposure to NOₓ based on clinical and epidemiological studies [49].

In combination with unburned hydrocarbons, the oxides of nitrogen react in the presence of sunlight to form photochemical smog. The chemical reactions involved are discussed in Section 9-6. It is because of this chemical activity that the primary air quality standard for the oxides of nitrogen has been set at 100 µg/m³ (0.06 ppm) annual average. The components of photochemical smog which are the most damaging to plants and detrimental to human health are the photochemical oxidants, discussed in the following section.

1-8-C Photochemical Oxidants

Oxidizing agents such as ozone (O₃), peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBN), hydrogen peroxide (H₂O₂), and formic acid (HCOOH) and other trace substances which can oxidize potassium iodide are termed photochemical oxidants. Photochemical oxidants are products of atmospheric reactions involving volatile organic compounds (VOCs), NOₓ, the hydroxyl radical (OH), other radicals, and sunlight. As such, photochemical oxidants are generally secondary pollutants formed in the atmosphere from a complex set of reactions involving the atmospheric precursor pollutants and sunlight. Ozone and PAN are present in the highest concentrations, and the damaging effects of photochemical smog are generally related to the concentrations of these species. The aerosol formed during the chemical reactions that create photochemical smog cause a marked reduction in visibility and give the atmosphere a brownish cast.

Ozone attacks natural rubber and synthetic polymers such as butadiene, isoprene, and styrene, causing cracking, hardening and reduction in the life of tires, rubber insulation, and protective outdoor electrical coverings. Ozone inhibitors can be incorporated into elastomer production, resulting in considerable reduction in damage. Ozone also attacks the cellulose in textile materials as well as synthetic...
TABLE 1-7 Key Human Health Effects of Exposure to Nitrogen Dioxide (NO₂)

<table>
<thead>
<tr>
<th>NO₂ in ppm (Exposure Duration)</th>
<th>Observed Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2–0.5 (0.5–2.0 h)</td>
<td>Trend toward increased airway reactivity to challenges in asthmatics. No significant effects observed by same or other investigators at NO₂ levels up to 4 ppm. Small (2–6%) decreases in FEV₁ in FEV₁/FVC in adult and adolescent asthmatics, in response to NO₂ alone.</td>
</tr>
<tr>
<td>0.5 (1.5 h)</td>
<td>Small decreases (5–9%) in FEV₁ and FEV₁/FVC in COPD patients with mild exercise. No effects seen by other investigators for COPD patients at 0.5–2.0 ppm NO₂.</td>
</tr>
<tr>
<td>1.5–2.0 (1–5 h)</td>
<td>Increased airway reactivity to bronchoconstrictor in healthy adults. However, effects not detected by other investigators at 2–4 ppm.</td>
</tr>
<tr>
<td>2.0 (1–3 h)</td>
<td>Lung function changes (e.g., increased airflow resistance) in healthy subjects. Effects not found by others at 2–4 ppm.</td>
</tr>
</tbody>
</table>

Epidemiological Studies

- 0.05 ppm increase, where mean weekly concentrations in bedrooms in studies reporting levels were predominately between 0.005 and 0.006 ppm NO₂ in 1- and 2-week integrated average NO₂ concentration estimating an unspecified long-term average.

- 0.05 ppm increase in annual average of 2-week NO₂ levels, where mean weekly concentrations in bedrooms were predominately between 0.005 and 0.050 ppm NO₂.

- > 0.5 ppm (average exposure during workshift)
  - Mean exposure during hockey game to NO₂ levels of 1.5 ppm or higher.
  - 2% to 100 ppm (epidemic occupational exposure)
  - > 200 ppm (extreme epidemic exposure)

- FEV₁ – Forced expiratory volume in 1 s.
- FVC – Forced vital capacity
- COPD – Chronic obstructive pulmonary disease

TABLE 1-8 Effects Of Ozone And Photochemical Pollutants

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Exposure (h)</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>50</td>
<td>1 h</td>
</tr>
<tr>
<td>0.05</td>
<td>60</td>
<td>8 h</td>
</tr>
<tr>
<td>0.07</td>
<td>140</td>
<td>8 h</td>
</tr>
<tr>
<td>0.08</td>
<td>160</td>
<td>8 h</td>
</tr>
<tr>
<td>0.09</td>
<td>160</td>
<td>8 h</td>
</tr>
<tr>
<td>0.10</td>
<td>160</td>
<td>8 h</td>
</tr>
<tr>
<td>0.12</td>
<td>200</td>
<td>8 h</td>
</tr>
<tr>
<td>0.15</td>
<td>200</td>
<td>8 h</td>
</tr>
<tr>
<td>0.15</td>
<td>200</td>
<td>8 h</td>
</tr>
<tr>
<td>0.20</td>
<td>200</td>
<td>8 h</td>
</tr>
<tr>
<td>0.25</td>
<td>200</td>
<td>1–3 h</td>
</tr>
<tr>
<td>0.30</td>
<td>480</td>
<td>1–5 h</td>
</tr>
<tr>
<td>0.35</td>
<td>600</td>
<td>1–5 h</td>
</tr>
<tr>
<td>0.50</td>
<td>740</td>
<td>1–5 h</td>
</tr>
<tr>
<td>1.00</td>
<td>950</td>
<td>2 h</td>
</tr>
</tbody>
</table>

Concentration (ppm) | Exposure (h) | Effects |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>100</td>
<td>4 h</td>
</tr>
<tr>
<td>0.10</td>
<td>200</td>
<td>4 h</td>
</tr>
<tr>
<td>0.15</td>
<td>250</td>
<td>Maximum daily</td>
</tr>
<tr>
<td>0.20</td>
<td>350</td>
<td>1 h</td>
</tr>
</tbody>
</table>

FEV₁ – Forced expiratory volume

with ozone they irritate the nose and throat, cause chest constriction, and at high concentrations (3500 µg/m³) produce severe coughing and inability to concentrate. Table 1-11 presents a summary of the effects of ozone and photochemical oxidants [50].

Based on new findings reported in 1996, it was proposed that the National Ambient Air Quality Standard for ozone be changed from its present value of 0.12 ppm for 1 hour, to 0.08 ppm for 8 hours. The standard was promulgated in July 1997 based on findings that showed that there was decreased pulmonary function in children as measured by a decrement in the forced expiratory volume. These effects, as reported in the promulgated standard, are also summarized in Table 1-11.

Effects of ozone on vegetation were first noted in the late 1890s, when it attacks the male flower buds, and soon thereafter flowers and stamens also change. Conifer needle tips become brown and necrotic. Spinach, beans, tomatoes, and white.
Pines are especially sensitive [53]. A large number of pine trees in some of the western forests appear to be dying as the result of prolonged exposure to photochemical oxidants. The injury threshold for sensitive plants has been estimated at about 0.03 ppm (50 µg/m³) for 8-hr exposure. Damage to the plants cited above has been observed at concentrations of 0.1 ppm or less for time periods of 1 to 8 hr. A concentration of 0.06 ppm for 3 to 4 hr damages foliage. The retarding of citrus growth has also been attributed to ozone.

Peracetic acid nitrate (PAN) has also been found to affect vegetation. It attacks the spongy parenchyma cells surrounding the air spaces into which the stomata open. The principal visible effect is the silvering or bronzing of the lower leaf area. The threshold concentration for injury is estimated at 0.1 ppm for a 6-hr exposure, although petunias have been affected at 0.006 ppm for an 8-hr exposure. The youngest leaves in terms of maturity are most sensitive.

1-8-D Lead and Other Metals

Lead (Pb) is the only metal which is currently listed as a criteria pollutant. Lead is a gray-white metal with a low melting point that is soft, malleable, ductile, resistant to corrosion, and a relatively poor electrical conductor. For these reasons, lead was used as early as 2000 B.C. by the Phoenecians. It has been used in paints, piping, roofing, storage containers for corrosive materials, as a radiation shield, in lead-acid batteries, and as an organolead additive in gasoline to reduce knock and boost octane levels. Its primary use in this century has been as an additive to gasoline as tetraethyl lead (TEL) and tetramethyl lead (TML). As a result of its use for nearly 4000 years, trace concentrations of lead can be found worldwide in such remote locations as the Arctic and Antarctic (in the ice), in mountain ranges, in soil, and in water. Figure 1-10 illustrates the complexity of the various emission sources and pathways which have resulted in lead contamination from the environment to humans in the past [51]. Sources of lead resulting in concentrations in the air included industrial sources, auto emissions, crustal weathering of soils and deposition of lead-based paint into the soil followed by biological plant emissions (due to wind, construction, and other mechanical means of disturbing soils). While the use of lead as an additive has been banned in three of the five sources (paint pigments, auto gasoline, and solder), many existing painted surfaces and soldered pipes still contain lead and are potential sources of lead in the environment.

The document Air Quality Criteria for Lead (1986) [51] states that "it is clear from the wealth of available literature that there exists a continuum of biological effects associated with lead at a broad range of exposure." At low levels of exposure, biochemical changes begin to occur which affect enzyme activities involved in biosynthesis which has importance in the normal physiological functioning of the organs in the body. At higher levels, it begins to affect the nervous system and can disrupt reproductive functions and impair immunological functions. In cases of high exposure, disruptions of the nervous system and immunological functions can result in lead poisoning, permanent mental retardation, and even death. The severity of the effect has generally been related primarily to the concentration of lead in the blood stream. The national ambient air quality standard for lead is 1.5 µg/m³ (3-month average) and was established in 1978 based on conclusions that the maximum safe concentration in the bloodstream was 30 µg/dl of blood. Evidence obtained since that time suggests that effects may begin to occur at 10 to 15 µg/dl for prenatal exposure, resulting in reduced gestational length and possible other aspects of prenatal growth, as well as negative effects on postnatal neurobehavioral development [62]. Although the standard has not been modified to date, the emissions of lead into the environment in the U.S. have been drastically decreased since 1970 as a result of the ban on leaded gasoline, discussed in Section 1-10.

Although lead is the only metal that has been addressed under the criteria pollutants, it, along with a number of other metals, has been or are in the process of being addressed under Title III of the Clean Air Act Amendments of 1990 as Hazardous Air Pollutants. Compounds containing metals such as antimony, cadmium, chromium, manganese, and nickel, as well as other elements such as arsenic, cobalt, and selenium, are on a list of 180 toxic compounds for which maximum achievable control technologies are to be required.
1-9 Sources of Air Pollutants

Once selected substances have been carefully studied and determined to be air pollutants on the basis of the evidence available, it is of immediate interest to ascertain the major sources of these substances. The study conducted to determine the emissions of a particular pollutant is referred to as an emission inventory. The inventory may include only selected sources, all anthropogenic sources, or all sources, including natural sources, dependent on the specific objectives of the inventory. Preparation of an emission inventory, which is a key element in developing air quality management strategies, requires detailed knowledge of the emissions from the relevant sources. This is generally done through the use of emission factors. Emission factors are defined as the typical emissions (usually in mass/time or mass per unit of process input or output) that are emitted by a particular source type based on the specific pollutant, type of process, age, size, type of control technology in existence, and other pertinent factors affecting the emissions from the source. Historically, emission factors have been determined through evaluation of the various types of sources by numerous researchers. As a result of the critical need for emission factors as a fundamental building block in emission inventories, the U.S. EPA has compiled these factors into a single multiphase document *Compilation of Air Pollutant Emission Factors* (AP-42) that has been maintained on an ongoing basis since the early 1970s. (See the following section for more details.)

The nationwide emissions from the major sources of anthropogenic air pollution in the United States are presented in Table 1-9 for 1970, 1980, and 1991 [54]. From the table, we see that transportation sources (including the gasoline and diesel automobiles and aircraft emissions) are major sources of carbon monoxide and oxides of nitrogen due to incomplete combustion; electric utilities are the major sources of sulfur oxides through the combustion of fuels containing sulfur; and primary sources of electric utilities and transportation sources together comprise nearly 70 percent of the nitric oxide emissions (resulting from formation of NO, from nitrogen and oxygen at the high temperatures in the combustion chambers). Volatile organic compounds (VOCs) originate primarily from both transportation and industrial emissions such as dry cleaning, evaporation of industrial coatings, cleaning of manufactured parts, and evaporation of gasoline. Particulate matter is emitted by all of the major sources. In 1991, lead emissions were emitted primarily by industrial sources. The gradual conversion to the use of unleaded gasoline in the 1970s and 1980s and the ban in 1998 have reduced the emissions of lead from transportation sources by approximately 99 percent since 1970. These were primarily responsible for the overall 97 percent reduction in emissions of lead into the environment in the United States.

The importance of conducting emission inventories such as those reported in Table 1-9 is best illustrated by introducing the concept of a population growth curve as shown in Figure 1-11. The potential for pollution as measured by increases in "uncontrolled" emissions and subsequent increases in the ambient concentration of a pollutant tends to increase with time. This is due to factors such as (1) population growth, (2) technological changes which create new products, (3) social changes such as urbanization and spreading of urban areas into rural areas, and

---

**Table 1-9**

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Carbon Monoxide</th>
<th>Volatile Organic Compounds</th>
<th>Sulfur Dioxide</th>
<th>Nitrogen Oxides</th>
<th>Total Lead</th>
<th>Volatile Organic Compounds</th>
<th>Sulfur Dioxide</th>
<th>Nitrogen Oxides</th>
<th>Total Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970</td>
<td>724.4</td>
<td>274</td>
<td>2.5</td>
<td>3.7</td>
<td>10.4</td>
<td>29.3</td>
<td>6.6</td>
<td>10.5</td>
<td>2.1</td>
</tr>
<tr>
<td>1980</td>
<td>1,000</td>
<td>774</td>
<td>2.0</td>
<td>6.8</td>
<td>10.0</td>
<td>21.8</td>
<td>4.8</td>
<td>10.0</td>
<td>2.1</td>
</tr>
<tr>
<td>1991</td>
<td>1,000</td>
<td>774</td>
<td>2.0</td>
<td>6.8</td>
<td>10.0</td>
<td>21.8</td>
<td>4.8</td>
<td>10.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

---

and the passage of the Clean Air Act Amendments of 1970, emissions of $SO_x$, CO, NO$_x$, and VOCs were all increasing with time. Lead emissions were also increasing; although the data were not reported in the trend reports published by the U.S. EPA. Particulate emissions, in general, had already begun declining prior to 1970 due to state and local regulations that were initiated prior to 1970, particularly on large sources of particulate emissions such as coal-fired boilers. The most striking example of the effect of regulations is lead. The phasing out of leaded gasoline and emission standards required on industrial processes resulted in major reductions in the emission of lead into the environment in the period from 1970 to 1983. The emissions from sources of sulfur oxides, nitrogen oxides, carbon monoxide, and volatile organic compounds have all been reduced as a result of a number of regulations that will be discussed in Chapter 2. Clearly, substantial progress has been made in controlling the emissions of these pollutants since 1970.

There is a growing concern, however, that in the long term, some of the programs that have been made to date in reducing emissions may be eroded by increases in the number of sources and the greater energy demands projected for the future. This is of particular concern in areas that are experiencing rapid growth. Figure 1-12 shows the projection of emissions to the year 2015 for specific pollutants, based on U.S. EPA estimates [5]. Projections suggest that NO$_x$ and CO may reach minimum levels by the year 2000, followed by increases. To circumvent this potential increase in emissions, concepts such as placing "caps" on the total emissions of certain pollutants and/or reducing pollutant emission levels to a level that existed in a previous year, are now commonplace in terms of our regulatory vocabulary. These will be discussed in more detail in Chapter 5, in light of the acid rain provisions of the Clean Air Act Amendments passed in 1990.

Figure 1-13 illustrates the extent that the emission reductions shown in Figure 1-12 have had on ambient concentrations of the criteria pollutants. The data plotted in the figure are based on the results obtained from 40 to 149 monitoring sites located in the United States (1973–1984) and 205 to 748 sites (1985–1989). The data clearly show that the occurrence of high air pollutant concentrations has decreased during the last 20 years. It is important to realize, however, that the data represent the average value of the highest concentration observed at the sites (i.e., the highest value at each site is summed for all 748 sites and divided by 748). While the "average" maximum concentration is well below the standard for all six pollutants, there are still a significant number of areas in violation of air quality standards, referred to as nonattainment areas (as discussed earlier in Section 1–3). The projected increases in the emission of certain pollutants shown in Figure 1–12 are cause for additional concern that the trends of improved air quality shown in Figure 1–13 may not continue in all cases, based on the concepts that have been discussed. There is an ongoing need to evaluate and manage the quality of the air we breathe.

1-10 Global Issues Related to Air Pollution

Much of the discussion thus far in this text has centered around emissions of air pollution in the United States associated with localized air pollution problems and
Atmospheric Absorption

The earth's surface and the atmosphere above the earth's surface create a natural effect, referred to as the "greenhouse" effect. Without this effect, the earth would be quite different than we know it. If the earth had no atmosphere, its temperature would be much cooler than it is at the present time. The warmer temperatures that we experience on the earth's surface are due to the presence of greenhouse gases in our atmosphere. The radiation absorption bands for two such greenhouse gases, water vapor and carbon dioxide, are presented in Figure 1-14, in which the wavelength is given in micrometers. The wavelength range for ultraviolet light is less than 0.4 μm, the range for visible light is from 0.4 to 0.76 μm; and for infrared light the range is from 1 to 100 μm. During the normal diurnal cycle, solar radiation (primarily in the ultraviolet (UV), visible, and near infrared (IR) wavelengths between 0.2 and 4 μm) passes through the transparent atmosphere and is absorbed by the earth's surfaces. The heated surfaces of the earth, which are much cooler than the sun, lose the energy they absorb from the sun primarily by radiating in the longer wavelength infrared region (5 to 100 μm). While clouds, water vapor, carbon dioxide, and other greenhouse gases are relatively inefficient absorbers of the sun's radiation, they are more efficient at absorbing the longer wavelength radiation emitted from the earth's surface. When the atmosphere contains low concentrations of carbon dioxide and water vapor, the quantity of incoming solar energy is approximately equal to the outgoing terrestrial radiation and the equilibrium temperature of the earth's surface and lower atmosphere is thereby established.


their associated effects. As indicated earlier, however, air pollution and its transport are cause for concern on a global basis. In addition to a reduction in visibility caused by particles and gaseous pollutants, certain gaseous substances, because of their radiation absorption characteristics, have the potential for causing perturbations on a global basis. Some of these have already been classified as pollutants and others may come to be classified as pollutants in the future. The global concerns involve issues such as acid rain (discussed in Section 1-7-C), emission of gases which tend to cause global warming, and emission of compounds such as CFCs that can destroy the ozone layer in the stratosphere. The effects of these latter two issues are related to the absorption of radiation in the atmosphere.

FIGURE 1-14 Absorption bands of (a) carbon dioxide and (b) water vapor.
With an increase in the concentration of water vapor, carbon dioxide, or other greenhouse gases, the atmospheric absorption of the infrared is increased whereas the transmission of shortwave radiation is unchanged. The net result would be an increase in the average temperature of the earth's surface and lower atmosphere since the quantity of solar radiation during the day would be unchanged while the terrestrial radiation would be reduced. Water vapor is the most significant greenhouse gas and is responsible for the absorption of the outgoing IR radiation below 8 μm and above 20 μm as illustrated in Figure 1-14. Carbon dioxide is the second most significant greenhouse gas with primary absorption in the 12 to 18 μm IR region. Another category of greenhouse gases includes CFCs, which have absorption bands near 10 μm.

The World Meteorological Organization (WMO) has documented that concentrations of greenhouse gases such as CO₂, trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), methane (CH₄), and nitrogen oxide (N₂O) are increasing, as shown in Table 1-10 as reported by the National Research Council in Rethinking the Ozone Problem [66]. In some cases, such as with the CFCs and chlorinated gases, the compounds do not originate from the natural environment and are strictly anthropogenic emissions. In the 1980s, the increase in concentration of these compounds ranged from 0.6 percent/yr for CO₂ to 4 percent/yr for certain anthropogenic compounds. During the last 100 years, the global mean surface air temperatures have also risen by approximately 0.4 to 0.8°C as shown in Figure 1-15 [57]. Further speculation indicates that a continuation of global warming at these rates could eventually result in sufficient melting of ice in the polar regions to cause a substantial rise in the level of the oceans. On the basis of the preceding argument, it has been argued that CO₂ should be considered an air pollutant.

For the sake of argument, increased concentrations of CO₂ have been found to stimulate the growth of selected plants. Since plants absorb CO₂ from the atmosphere in their life cycle, the increased growth could cause a corresponding increase in CO₂ absorption, and a new static balance of the CO₂ content in the environment would be established. The massive destruction of rain forests around the world further decreases the potential to maintain the current CO₂ balance. The inadequacy of existing global transport models and uncertainties in the current understanding of the fate of greenhouse gases is a major cause for concern.

A major international Earth Summit was held in Rio de Janeiro in 1992. As a result, a number of countries signed the climate change treaty which called for voluntary reduction of CO₂ emissions by the year 2000 back to a level equivalent to 1990 emissions. The actual deadline for meeting these reductions was still being debated in the United Nations in 1996. Dates of 2002 and 2016 were being debated.

Ozone is another gas which absorbs the sun’s radiation. The presence of ozone in the lower stratosphere actually produces a very beneficial effect in that it absorbs a significant amount of the short wavelength ultraviolet radiation emitted by the sun. The ultraviolet energy is known to have been found to have a major potential for causing skin cancer and other detrimental effects on plants and animals in our earth's ecosystem. Ironically, tropospheric ozone formed as a result of photochemical reactions in the earth's surface boundary layer is a strong oxidizing agent and is damaging to both plants, animals, and materials and is therefore considered to be a pollutant. While greenhouse gases have been increasing in the atmosphere, the overall mass of ozone in the air surrounding the earth's surface has been decreasing for the last two decades. This is due primarily to the loss in stratospheric ozone due to the presence of anthropogenic gases such as chloro- and hydrochlorofluorocarbons (CFCs and HFCs). These gases, emitted at ground level have eventually dispersed into the atmosphere, causing ozone depletion. The observed depletion of ozone, or "ozone holes," has occurred in both the northern and southern hemispheres, although the greatest depletion has been in the stratosphere over Antarctica. CFCs and HCFCs are used extensively as coolants in heating, cooling, and refrigeration systems worldwide. Emissions to the environment occur accidentally due to leakage of coolant from the pressurized systems, or from intentional emission associated with the repair of the systems.

**TABLE 1-10 Changing Atmospheric Composition [56]**

<table>
<thead>
<tr>
<th>Species</th>
<th>Pre-industrial</th>
<th>Circa 1987</th>
<th>Annual rate of increase during the 1980s</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>~280 ppm</td>
<td>346 ppm</td>
<td>0.5%</td>
</tr>
<tr>
<td>CH₄</td>
<td>~660 ppb</td>
<td>1669 ppb</td>
<td>0.8%</td>
</tr>
<tr>
<td>N₂O</td>
<td>~265 ppb</td>
<td>307 ppb</td>
<td>0.2%</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>242 ppt</td>
<td>4%</td>
</tr>
<tr>
<td>CF₂Cl₂</td>
<td>0</td>
<td>415 ppt</td>
<td>4%</td>
</tr>
<tr>
<td>CF₄</td>
<td>0</td>
<td>147 ppt</td>
<td>1.5%</td>
</tr>
<tr>
<td>CCl₃</td>
<td>0</td>
<td>156 ppt</td>
<td>4%</td>
</tr>
<tr>
<td>CH₂CCl₂</td>
<td>0</td>
<td>600 ppt</td>
<td>0%</td>
</tr>
<tr>
<td>CH₄</td>
<td>0</td>
<td>90 ppb</td>
<td>1% (northern hemisphere)</td>
</tr>
<tr>
<td>CO</td>
<td>7</td>
<td>90 ppb</td>
<td>1% (northern hemisphere)</td>
</tr>
</tbody>
</table>

Source: WMO [1992].
The National Research Council's Committee on Tropospheric Ozone Formation and Measurement reported in 1991 [56] that the decrease in stratospheric ozone was "clearly one of the largest anthropogenic perturbations to our planet" that has occurred. The serious nature of the problem is exemplified by the policies practiced in the Australian school system in which school-age children are required to wear long-sleeve shirts, and long pants, and wide-brimmed hats when outside as a precaution against the threat of substantial increases in skin cancer and other related effects. Concerns over the depletion of ozone resulted in an international conference and cooperative agreements between countries to voluntarily reduce the use of chemicals found to deplete stratospheric ozone.

The Montreal Protocol, held in 1982, resulted in an international agreement among nations in which the use of CFCs was to be phased out by 1996 and HCFCs by the year 2028 in hopes of slowing and/or reversing the ozone depletion trend [58]. In that same year, the U.S. EPA banned the venting of CFCs during servicing of automotive air-conditioning systems and proposed a ban on venting of emissions during servicing of residential and commercial air-conditioning and refrigeration systems. In the period of 1987-1988 the rates of increase of CFCl3 (Freon-11) and CF2Cl2 (Freon-12) were 11 to 15 parts per billion (ppb), and 17 to 23 ppb per year, respectively, as reported by Khalil and Rasmussen [59] and as shown in Table 1-13. By 1990, ozone rates had slowed to approximately 3 to 6 ppb per year. Substantial reductions in the actual concentrations will occur in the future due to the phasing out of these compounds, although the lifetime of such compounds in the atmosphere is estimated to be 15 to 200 years.

Robinson and Robbins [60] and, more recently, Singh et. al [61] have pointed out that scavenging mechanisms exist in the natural environment for gaseous emissions such as CO, CO, NOx, sulfur compounds, and CFCs. These are summarized in Table 1-11. Based on these studies, an approximation was made for the residence time of the gases in the atmosphere. Although the scavenging mechanisms are important in controlling long-term accumulations of pollutants in the atmosphere, they do not operate fast enough to provide solutions for local urban air pollution situations. In fact, the existence of an air pollution condition is evidence that the available scavenging mechanism rates have been exceeded by the emission rate and/or formation of the pollutants due to secondary reactions in the atmosphere. The net rise in the global concentration of certain compounds, as shown in Table 1-15, indicates that the ability of scavenging mechanism may have already been exceeded for some compounds emitted into the atmosphere.

Table 1-11: Global Sources, Atmospheric Residence Times, Reactions and Sinks [59, 60]

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Anthropogenic Sources</th>
<th>Natural Sources</th>
<th>Atmospheric Residence Time</th>
<th>Removal Reactions and Sinks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2</td>
<td>Combustion of coal and oil</td>
<td>Volcanoes</td>
<td>4 days [59]</td>
<td>Oxidation to sulfate, after absorption by soils and liquid aerosols</td>
</tr>
<tr>
<td>NOx</td>
<td>Chemical processes, sewage treatment</td>
<td>Volcanoes, biological action in swamping areas</td>
<td>2 days [59]</td>
<td>Oxidation to SOx</td>
</tr>
<tr>
<td>CO</td>
<td>Combustion sources, incl. Auto exhaust, atm. oxidation of HCs and methane</td>
<td>Fossil fuels, methane and other HCs</td>
<td>0.2 years [59]</td>
<td>Oxidation to CO2</td>
</tr>
<tr>
<td>CH4</td>
<td>Landfills, rice, cattle, biogas burning</td>
<td>Wetlands, termites, geological emissions</td>
<td>9 years [59]</td>
<td>Oxidation to CO, CO2</td>
</tr>
<tr>
<td>CO2</td>
<td>Combustion, deforestation</td>
<td>Volcanoes, forests, biological decay, atm. oxid. of CO, CH4, NOx</td>
<td>150-200 years [59]</td>
<td>Absorption in oceans and biologically</td>
</tr>
<tr>
<td>NH3</td>
<td>Waste treatment</td>
<td>Biological decay</td>
<td>3-15 days [59]</td>
<td>Oxidation to nitrate and formation of ammonium sulfate</td>
</tr>
<tr>
<td>NO3/NO2</td>
<td>Combustion</td>
<td>Eutrophication in soil</td>
<td>5 days [60]</td>
<td>Oxidation to nitrate, photochemical reactions</td>
</tr>
<tr>
<td>CFCs</td>
<td>Refrigerants, foam manufact., propellants</td>
<td>none</td>
<td>50-150 years [59]</td>
<td>Photochemistry in atmosphere which release the chlorine fluoride</td>
</tr>
</tbody>
</table>

1-11 Air Pollution and Internet Resources

The computer technology revolution which has occurred during the last 25 years has led to the development of improved means of disseminating information on air pollution. Historically, federal documents related to air pollution were published by the U.S. Government Printing Office and made available to the general public through clearinghouses such as the National Technical Information Clearinghouse at the cost of reproduction. This included both printed publications as well as selected air quality models that could be ordered. With the almost exponential increase in information that has occurred since the first passage of the 1967 Clean Air Act, a number of computerized electronic means have been established to disseminate information. Electronic bulletin boards have been established to provide a wealth of information on environmental issues, regulations, and publications that are free (or provided at little cost) to those who have access through their company, or a personal computer with a modem, or—as is the case with students—through international linkages such as the Internet. This information
highway," as it has come to be known, provides immediate access to information that could otherwise have taken weeks or months to obtain, and then only at considerable expense.

One of the most comprehensive air pollution information systems is the U.S. EPA's Office of Air Quality Planning and Standards' Technology Transfer Network Bulletin Board System (TTNWeb). This network, although in its infancy, already contains 16 technical information bulletin boards, as shown in Table 1-12, that cover a wide range of air pollution information including guidance documents. air quality standards. air quality and emissions data. and a brief of air quality models that can be downloaded at little to no cost. The network also has a TTN user's manual that can be downloaded. Much of the information that can be viewed on the network can be downloaded in compressed or zipped files to a personal computer and decompressed to provide immediate access to the document in a word processor or spreadsheet. The data in Figures 1-11 and 1-12 were retrieved directly from the CAAA area of the OAQS' TTNWeb. as were many of the emission standards that will be discussed in future sections of this text. (See Reference 5.) For users who do not have access through university Internet connections. the OAQS' TTNWeb can be reached by modem 24 hours per day, 7 days a week (except Monday mornings) by calling 919-541-6742. Internet users can access the TTNWeb through the command http://www.epa.gov/tn. Users of this text may be particularly interested in the OAR Fac, SCRAM, and CHIEF bulletin boards, which contain the regulations. air quality models. and AF-42 (emission factors), respectively.

The above database and numerous other EPA data bases may also be reached through the World Wide Web (WWW): http://epa.gov/. Another reference document that can be accessed is Access EPA that helps users locate information available from EPA. Access EPA can be reached through telnet at epaoin.rnd.epa.gov followed by selection of Public Access Applications Menu, then EPA National Online Library System, then Access EPA.

**TABLE 1-12 TTNBBS Technical Information Areas**

<table>
<thead>
<tr>
<th>AAS</th>
<th>Acrometric Information Retrieval System Informaton</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMTTC</td>
<td>Ambient Monitoring Technology Information</td>
</tr>
<tr>
<td>APTI</td>
<td>Air Pollution Training Institute</td>
</tr>
<tr>
<td>OAQPS</td>
<td>Clean Air Act (Rules/Policy/Guidance)</td>
</tr>
<tr>
<td>CARF</td>
<td>Carrboro CASAR Dialogue</td>
</tr>
<tr>
<td>CHEIF</td>
<td>Emissions Inventories/Emission Factors Info.</td>
</tr>
<tr>
<td>COSPL</td>
<td>Compliance Information on Stationary Sources</td>
</tr>
<tr>
<td>CTC</td>
<td>General Technology Information</td>
</tr>
<tr>
<td>EMTC</td>
<td>Emission Measurement Technical Information</td>
</tr>
<tr>
<td>PAPA</td>
<td>On specifications, Federal and Region Emphasis Implementation</td>
</tr>
<tr>
<td>KCI</td>
<td>Industrial Combustion Control/Remediation</td>
</tr>
<tr>
<td>NELAC</td>
<td>National Environmental Accreditation Comm.</td>
</tr>
<tr>
<td>NSR</td>
<td>Non Source Review Information</td>
</tr>
<tr>
<td>DMS</td>
<td>Mobile Source Information</td>
</tr>
<tr>
<td>ORA</td>
<td>Radiation and Indoor Information</td>
</tr>
<tr>
<td>OTAG</td>
<td>Ozone Transport Assessment Group</td>
</tr>
<tr>
<td>RILC</td>
<td>RACT/BACT/LREER Clearinghouse</td>
</tr>
<tr>
<td>SCRAM</td>
<td>Regulatory Air Models/Information</td>
</tr>
<tr>
<td>SBAIP</td>
<td>Small Business Assistance Program Information</td>
</tr>
<tr>
<td>GIS</td>
<td>Geographic/Environmental Initiatives</td>
</tr>
</tbody>
</table>

**QUESTIONS**

1. Discuss the causes of air pollution.
2. What constitutes an air pollutant?
3. Why are water vapor and carbon dioxide not air pollutants in a conventional context?
4. List the pollutants for which air quality standards have been established.
5. What is the difference between TSP, PM10, and PM2.5?
6. Estimate the visual range in an atmosphere containing small particles having a concentration of 150 µg/m³.
7. Explain how the relation given by Equation (1-13) could be employed in the operation of a power plant to measure the smoke density of a Diesel engine.
8. What are the difficulties encountered in developing a meter to measure the particulate concentration in a flame based on light transmitted through the flame?
9. What are the effects of particulate matter on health? What particle size range is of major importance in impairing health?
10. What is the effect of CO on the human body?
11. Upon what basis was the air quality standard for the oxides of nitrogen set?
12. What was the major source of CO in the United States in the 1970s? Has this changed in the 1990s?
13. What was the source of lead (Pb) in the United States in 1970? How has this changed since 1970?
14. Describe why fossil fueled power plant plumes tend to have a reddish brown hue.
15. Review several recent issues of a "current issues" publication such as RNA's Environ Teleprint: Current Developments or Eloquent's "The Air Pollution Consultant" and write a brief 5 to 6 sentence summary of three different current air quality issues.
16. Connect by computer to the EPA OAQS' TTNWeb and review several of the current air quality issues that are being discussed. Write a 5- to 6-sentence summary of two different current issues.

**PROBLEMS**

1-1. The national ambient air quality standard for carbon monoxide (CO) is 9 ppm measured over a 1-hr averaging time. What is the equivalent concentration in milligrams per cubic meter at 25°C?

1-2. The primary air quality standard for sulfur dioxide (SO₂) as an annual average is 0.09 µg/m³. What is the equivalent concentration in parts per million at 25°C?

1-3. A vital statistics report shows that a daily summer day increased the particulate concentration in an urban area to a level of 150 µg/m³. Determine the equivalent concentration in grains per cubic foot, for conditions of 1 atm and 23°C.

1-4. The ozone (O₃) concentration sometimes reaches a value of 0.25 ppm over a 1-hr period in urban areas with photochemical smog problems. Determine by what percentage this
level exceeds the pre-1967 national ambient standard of 240 μg/m³ for the given time period, if the temperature is 20°C.

1.8. The concentration of carbon monoxide (CO) in cigarette smoke reaches levels of 400 ppm or higher. For this particular value, determine the percent by volume and the concentration in milligrams per cubic meter, at 25°C and 1 atm.

1.9. The primary air quality standard for NO₃ expressed as NO₂ as an annual average is 100 μg/m³. What is the equivalent concentration in parts per million at 25°C?

1.10. The particulate matter concentration in a large city is reported to be 160 μg/m³ on a particular day. (a) Correct this value, which is relatively high for an urban atmosphere, to grams per cubic foot. (b) In industrial situations where particles are being transported through ducts to collection equipment, the dust loading may be as high as 100 g/m³. In this situation, what is the equivalent concentration in micrometers per cubic meter?

1.11. The visibility of a light source is limited to 3.0 km. What percentage of light will pass through a length of 0.3 km if the limit of visibility is defined as (a) a 58 percent reduction and (b) a 50 percent reduction in the original light intensity?

1.12. If the limit of visibility is defined as the distance when f₅₀ reaches 0.60 in value, determine the percent extinction that occurs in the first (a) 10 percent, (b) 20 percent, and (c) 50 percent of the path length.

1.13. Air at 25°C and 1 atm has 78 percent by volume N₂, 21 percent by volume O₂, and 0.03 percent by volumeCH₄ (CH₂H₂OCH₂). The concentration of each component is in ppmv. (a) What is the concentration of each component in ppmv? (b) What is the concentration of each in micrometers/m³?

1.14. A stack gas analyzer is used to measure the concentration of nitrogen dioxide and nitrogen dioxide in the gas at a temperature of 300°F and a pressure of 30.29 in. Hg. The concentrations were reported as 450 and 20 ppm, respectively, at stack conditions. (a) What is the concentration of each in the stack gas at stack conditions in ppmv? Note that ppm stands for parts per million on a gas/volume basis. (b) What is the concentration of each in ppmv in the gas at stack conditions? (c) What is the concentration of the two gases in ppmv at standard conditions and under the assumption that the two gases mix according to their mole fractions? (d) What is the concentration of the two gases in micrometers/m³ at standard conditions and under the assumption that the two gases mix according to their mole fractions?

1.15. A uniform distribution of spheres with a diameter of 0.8 μm attenuates a light source by 85 percent at a test distance of 1000 m. The particle material density is 1.16 g/cm³ and the particle concentration in the air is 745 μg/m³. Determine (a) the scattering coefficient in m⁻¹ if absorption is neglected, (b) the value of the scattering ratio, Kₛ, for the substance, and (c) the limit of visibility in kilometers.

1.16. Consider droplets of 5 μm diameter with a refractive index of 1.5 suspended in air and exposed to daytime radiation. The density of the droplets is taken to be 1.1 g/cm³. The wavelength of visible light can be taken to be 0.5 μm. (a) What is the concentration of the droplets in micrometers per cubic meter for a visibility of 2 miles? (b) What is the concentration of droplets if the effective diameter is 1.0 μm and the visibility is 0.5 mi?

1.17. Particles have the following physical diameters and particle densities: (a) 5 μm with density of 2 g/cm³, (b) 6 μm with density of 2 g/cm³, (c) 10 μm with density of 4 g/cm³. Determine the effective aerodynamic diameter of each and state whether it would be collected in a PM₁₀ sampler.

1.18. Air has a concentration of 0.5 ppm of NO₂. The extinction coefficient is proportional to the concentration of NO₂ and the relationship between aₚ and the wavelength of light is shown in Figure 1-5. (a) Based on the relationship exhibited in Figure 1-5, determine the increase in the particle concentration of the light intensity that occurs in a distance of 3 km for wavelengths of 0.46, 0.55, and 0.65 μm. Explain why NO₂ gas appears brownish-yellow to brownish-red in the atmosphere.

1.19. Consider Equation (1-2) to be modified to the following form: \( I/I₀ = e^{-kC} \), where \( C \) is the concentration in parts per million, and \( k \) is a function of wavelength and has units of ppm⁻¹. (a) Based on a wavelength of 0.5 μm and Figure 1-5, determine the wavelength of the light that would be collected by a PM₁₀ sampler.

1.20. Dust with a density of 1.4 g/cm³, a scattering area ratio of 1.2, and an effective diameter of 1.4 μm has a concentration of 200 μg/m³ in the atmosphere. Estimate the limit of visibility in kilometers.

1.21. A PM₁₀ sampler was operated for a 24-hour period at a flowrate of 1.7 m³/min. At the end of the period, the filter had a weight gain of 0.55 grams after being desiccated. Determine the concentration of PM₁₀ in μg/m³.

1.22. Consider that cigarette smoke contains an average of 450 ppm carbon monoxide. If the average oxygen content in the air in the lungs is 19.6 percent, what percentage of the saturation level would the CO₂ concentration ultimately reach?

1.23. Assume that there are 450 ml of blood in the body and that blood normally contains 20 ml of CO per 100 ml of blood. A person under heavy exercise is breathing at a volume rate of 4.2 l/min, and the carbon dioxide concentration is 100 ppm carbon monoxide. Determine the time required, in minutes, for the blood to become 7 percent saturated with CO if the blood CO₂ level initially is (a) 0 percent and (b) 2 percent. Assume that all carbon monoxide is absorbed into the lungs and is absorbed.

1.24. Consider the situation where the gas in the lungs of a human contains 250 ppm carbon monoxide and the average oxygen content is 17.5 percent. If these concentrations were maintained, what percentage of the saturation level would the CO₂ concentration eventually reach?

1.25. Figure 1-8 shows a relationship between CO concentration, CO₂ in the blood stream, and exposure time. If a health-based standard is to be developed to keep the CO₂ below 1.5 percent, determine the approximate concentration of CO that should be the maximum allowable value for (a) a one-hour exposure and (b) an eight-hour exposure. Compare these to the air quality standard in Table 1-2 of the text.

REFERENCES


2 Federal Legislation and Regulatory Trends

2.1 Introduction

The existence of air pollution and the need for legislation to protect the health and welfare of the general populace are not modern phenomena. In thirteenth-century England, the burning of soft coal polluted the atmosphere in urban areas to such an extent that in 1273 England passed a law to reduce air pollution from this source. In the United States, it was not until the 1940s that efforts to control the degree of air pollution were initiated. Historically, the first measures against air pollution were taken by the state of California, in light of worsening conditions within the state, especially in the Los Angeles basin. It soon became apparent that other urban areas in the country were experiencing a decline in air quality, often for reasons different from those leading to the Los Angeles-type smog. As a result, federal intervention in the overall air pollution area was deemed necessary.

The major development of legislative and regulatory acts took place from 1955 to 1970. Without any precedents (except for some legislation in the water pollution area), legislators had to vary the approach of each succeeding act in order to overcome deficiencies in preceding acts. By the mid-1970s, the philosophical basis for national regulation of air pollution was well developed. The actual regulations are continually changing in the light of new technological and economic developments. Although regulatory changes in the 1980s were relatively few, the Clean Air Act Amendments of 1990 have resulted in significant regulatory changes, many of which will be phased in during 1990 to 2010.