14

Effects on the Atmosphere, Soil, and Water Bodies

I. THE PHYSICS OF VISIBILITY

Impairment of visibility involves degradation of the ability to perceive the environment. Several factors are involved in determining visibility in the atmosphere (Fig. 14.1): the optical characteristics of the illumination source; the viewed targets; the intervening atmosphere; and the characteristics of the observer's eyesight [1].

To see an object, an observer must be able to detect the contrast between the object and its surroundings. If this contrast decreases, it is more difficult to observe the object. In the atmosphere, visibility can decrease for a number of reasons. For example, we may be farther away from the object (e.g. an airplane can move away from us); the sun's angle may change with the time of day; and if air pollution increases, the contrast may decrease, reducing our ability to see the object.

Objects close to us are easily perceived, but this diminishes as a function of distance. The lowest limit of contrast for human observers is called the *threshold contrast* and is important because this value influences the maximum distance at which we can see various objects. Thus, it is closely related

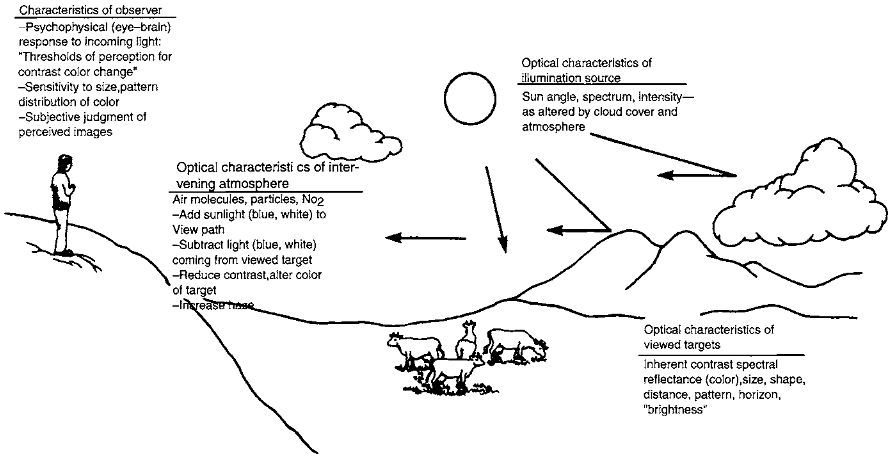

Fig. 14.1. Factors determining visibility in the atmosphere. *Source*: US Environmental Protection Agency, *Protecting Visibility*, EPA-450/5-79-008. Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1979.

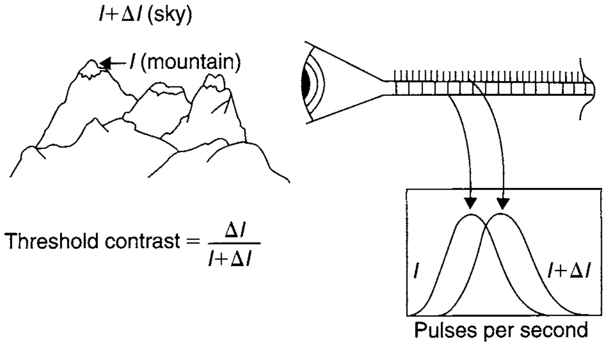

Fig. 14.2. Threshold contrast in distinguishing an object from its surroundings. The eye responds to an increment in light intensity by increasing the number of signals (pulses) sent to the brain. The detection of threshold contrast involves the ability to discriminate between the target (I) and the brighter background ($I + \Delta I$). *Source*: Gregory, R. L., *Eye and Brain: The Psychology of Seeing*. Weidenfeld and Nicolson, London, 1977.

to our understanding of good versus bad visibility for a particular set of environmental conditions.

Threshold contrast is illustrated in Fig. 14.2. I is the intensity of light received by the eye from the object, and $I + \Delta I$ represents the intensity coming from the surroundings. The threshold contrast can be as low as 0.018–0.03 and the object can still be perceptible. Other factors, such as the physical size of the visual image on the retina of the eye and the brain's response to the color of the object, influence the perception of contrast.

Let us consider the influence of gases and particles on the optical properties of the atmosphere. Reduction in visibility is caused by the following interactions in the atmosphere: light scattering by gaseous molecules and particles, and light absorption by gases and particles [2].

Light-scattering processes involve the interaction of light with gases or particles in such a manner that the direction or frequency of the light is altered. Absorption processes occur when the electromagnetic radiation interacts with gases or particles and is transferred internally to the gas or particle.

Light scattering by gaseous molecules is wavelength dependent and is the reason why the sky is blue. This process is dominant in atmospheres that are relatively free of aerosols or light-absorbing gases. Light scattering by particles is the most important cause of visibility reduction. This phenomenon is dependent on the size of the particles suspended in the atmosphere.

Light absorption by gases in the lower troposphere is limited to the absorption characteristics of nitrogen dioxide. This compound absorbs the shorter, or blue, wavelengths of visible light, causing us to observe the red wavelengths. We therefore perceive a yellow to reddish-brown tint in atmospheres containing quantities of NO_2. Light absorption by particles is related principally to carbonaceous or black soot in the atmosphere. Other types of fine particles such as sulfates, although not good light absorbers, are very efficient at scattering light.

A. Light Extinction in the Atmosphere

The interaction of light in the atmosphere is described mathematically in Eq. (14.1):

$$-\mathrm{d}I = b_{\mathrm{ext}} I \,\mathrm{d}x \tag{14.1}$$

where $-dI$ is the decrease in intensity, b_{ext} is the extinction coefficient, I is the original intensity of the beam of light, and $\mathrm{d}x$ is the length of the path traveled by the beam of light.

Figure 14.3(a) shows a beam of light transmitted through the atmosphere. The intensity of the beam $I(x)$ decreases with the distance from the illumination source as the light is absorbed or scattered out of the beam. For a short period, this decrease is proportional to the intensity of the beam and the length of the interval at that point. Here b_{ext} is the extinction or attenuation coefficient and is a function of the degree of scattering and absorption of the particles and gases which are present in the beam path.

Figure 14.3(b) illustrates a slightly more complicated case, but one more applicable to atmospheric visibility. In this example, the observer still depends on the ability to perceive light rays emanating from the target object and on the scattering and absorption of those rays out of the beam. In addition, however, the observer must contend with additional light scattered into the line of sight from other angles. This extraneous light is sometimes called

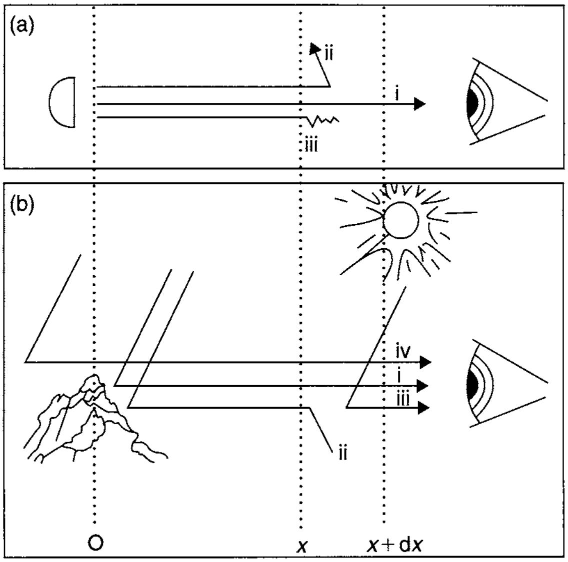

Fig. 14.3. (a) A diagram of extinction of light from a source such as an electric light in a reflector, illustrating (i) transmitted, (ii) scattered, and (iii) absorbed light. (b) A diagram of daylight visibility, illustrating (i) residual light from a target reaching an observer, (ii) light from a target scattered out of an observer's line of sight, (iii) air light from the intervening atmosphere, and (iv) air light constituting horizon sky. *Source*: US Environmental Protection Agency, *Protecting Visibility*, EPA-450/5-79-008. Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1979.

air light. Equation (14.1) is modified to account for this phenomenon by adding a term to represent this background intensity.

$$-\mathrm{d}I = -\mathrm{d}I(\text{extinction}) + \mathrm{d}I(\text{air light}) \tag{14.2}$$

This air light term contributes to the reduced visibility we call *atmospheric haze*.

A simplified relationship developed by Koschmieder which relates the visual range and the extinction coefficient is given by

$$L_\mathrm{v} = 3.92/b_\mathrm{ext} \tag{14.3}$$

where L_v is the distance at which a black object is just barely visible [3]. Equation (14.3) is based on the following assumptions:

1. The background behind the target is uniform.
2. The object is black.
3. An observer can detect a contrast of 0.02.
4. The ratio of air light to extinction is constant over the path of sight.

While the Koschmieder relationship is useful as a first approximation for determining visual range, many situations exist in which the results are only qualitative.

The extinction coefficient b_{ext} is dependent on the presence of gases and molecules that scatter and absorb light in the atmosphere. The extinction coefficient may be considered as the sum of the air and pollutant scattering and absorption interactions, as shown in the following equation:

$$b_{\text{ext}} = b_{\text{rg}} + b_{\text{ag}} + b_{\text{scat}} + b_{\text{ap}} \tag{14.4}$$

where b_{rg} is scattering by gaseous molecules (Rayleigh scattering), b_{ag} is absorption by NO_2 gas, b_{scat} is scattering by particles, and b_{ap} is absorption by particles. These various extinction components are a function of wavelength. As extinction increases, visibility decreases.

The Rayleigh scattering extinction coefficient for particle-free air is $0.012\,\text{km}^{-1}$ for "green" light ($\gamma = 0.05\,\mu\text{m}$) at sea level [4]. This permits a visual range of ~320 km. The particle-free, or Rayleigh scattering, case represents the best visibility possible with the current atmosphere on earth.

The absorption spectrum of NO_2 shows significant absorption in the visible region (see Fig. 14.4) [5]. As a strong absorber in the blue region, NO_2 can color plumes red, brown, or yellow. Figure 14.5 shows a comparison of extinction coefficients of 0.1 ppm NO_2 and Rayleigh scattering by air [6]. In urban areas, some discoloration can be due to area-wide NO_2 pollution. In rural areas, the biggest problem with NO_2 is that in coherent plumes from power plants, it contributes to the discoloration of the plume.

Suspended particles are the most important factor in visibility reduction. In most instances, the visual quality of air is controlled by particle scattering and is characterized by the extinction coefficient b_{scat}. The size of particles plays a crucial role in their interaction with light. Other factors are the refractive index and shape of the particles, although their effect is harder to measure and is less well understood. If we could establish these properties, we could calculate the amount of light scattering and absorption. Alternatively, the extinction coefficient associated with an aerosol can be measured directly.

Light and suspended particles interact in the four basic ways shown in Fig. 14.6: refraction, diffraction, phase shift, and absorption. For particles with a diameter of 0.1–1.0 μm, scattering and absorption can be calculated by using the Mie equations [7]. Figure 14.7 shows the relative scattering and absorption efficiency per unit volume of particle for a typical aerosol containing some light-absorbing soot [8]. This clearly shows the importance of atmospheric particles in the diameter range 0.1–1.0 μm as efficient light-scattering centers. With

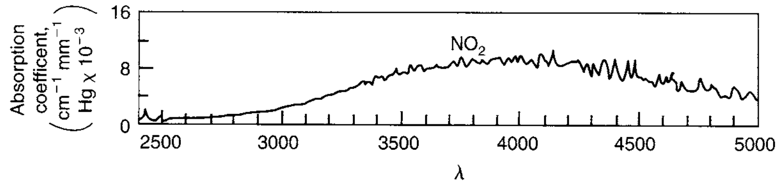

Fig. 14.4. Absorption spectrum of NO_2. *Source*: Hall Jr., T. C., and Blacet, F. E., *J. Chem. Phys.* **20**, 1745 (1952).

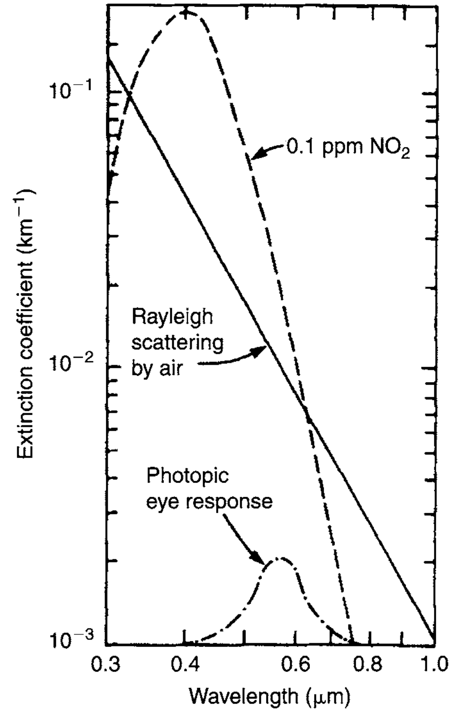

Fig. 14.5. Comparison of b_{ext} for 0.1 ppm NO_2 and Rayleigh scattering by air. The photopic eye response represents the range of wavelengths over which the eye detects light. *Source*: Husar, R., White, W. H., Paterson, D. E., and Trijonis, J., *Visibility Impairment in the Atmosphere.* Draft report prepared for the US Environmental Protection Agency under Contract No. 68022515, Task Order No. 28.

particles of larger and smaller diameters, scattering decreases. Absorption generally contributes less to the extinction coefficient than does the scattering processes. Atmospheric particles of different chemical composition have different refractive indices, resulting in different scattering efficiencies. Figure 14.8 shows the scattering-to-mass ratio for four different materials [9]. Clearly, carbon or soot aerosols, and aerosols of the same diameter with water content, scatter with different efficiencies at the same diameter.

Visibility is also affected by alteration of particle size due to hydroscopic particle growth, which is a function of relative humidity. In Los Angeles, California, the air, principally of marine origin, has numerous sea salt particles. Visibility is noticeably reduced when humidity exceeds about 67%. In a study of visibility related to both relative humidity and origin of air (maritime or continental), Buma [10] found that at a set relative humidity, continental air reduced visibility below 7 km more often than did air of maritime origin. This effect is presumably due to numerous hygroscopic aerosols from air pollution sources. Some materials, such as sulfuric acid mist, exhibit hygroscopic growth at humidity as low as 30%.

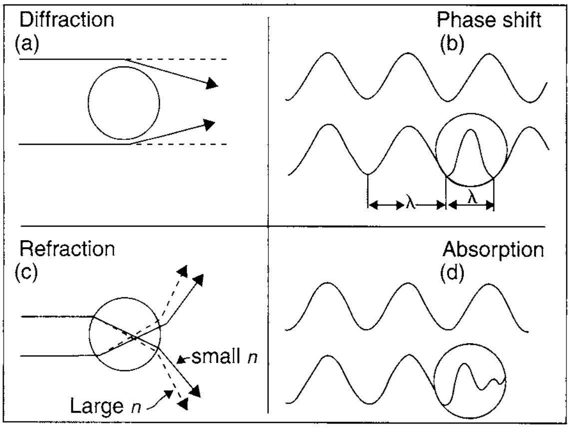

Fig. 14.6. Four forms of particle light interaction. Light scattering by coarse particles (>2 μm) is the combined effect of diffraction and refraction. (a) Diffraction is an edge effect whereby the light is bent to fill in the shadow behind the particle. (b) The speed of a wavefront entering a particle with refractive index $n > 1$ (for water, $n = 1.33$) is reduced. (c) Refraction produces a lens effect. The angular dispersion resulting from bending incoming rays increases with n. (d) For absorbing media, the refracted wave intensity decays within the particle. When the particle size is comparable to the wavelength of light (0.1–1.0 μm), these interactions (a)–(d) are complex and enhanced. *Source*: US Environmental Protection Agency, *Protecting Visibility*, EPA-450/5-79-008. Office of Air Quality Planning Standards, Research Triangle Park, NC, 1979.

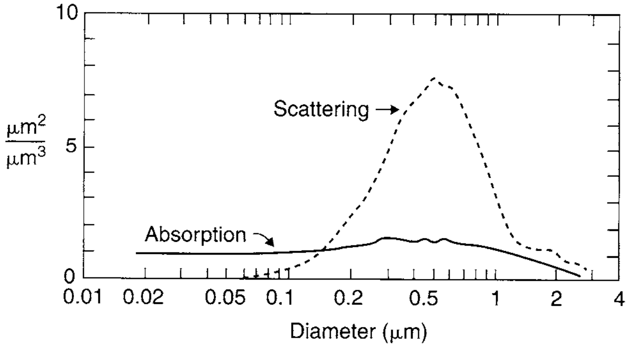

Fig. 14.7. Scattering and absorption cross section per unit volume as a function of particle diameter. *Source*: Charlson, R. J., Waggoner, A. P., and Thielke, H. F., *Visibility Protection for Class I Areas. The Technical Basis*. Report to the Council on Environmental Quality, Washington, DC, 1978.

B. Turbidity

The attenuation of solar radiation has been studied by McCormick and his associates [11, 12] using the Voltz sun photometer, which makes measurements at a wavelength of 0.5 μm. The ratio of the incident solar transmissivity to the extraterrestrial solar intensity can be as high as 0.5 in clean atmospheres but can drop to 0.2–0.3 in polluted areas, indicating a decrease

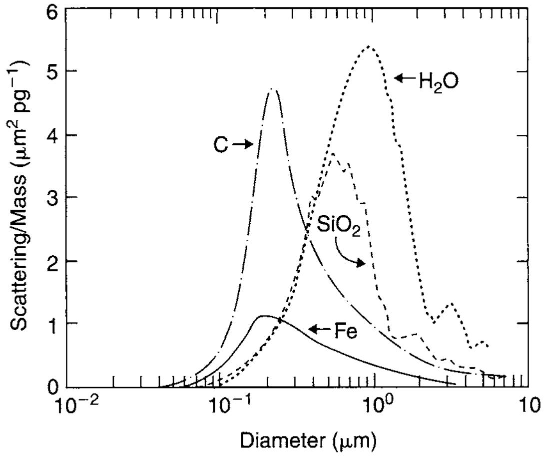

Fig. 14.8. Single particle scattering to mass ratio for particles of four different compositions. Carbon particles are also very efficient absorbers of light. *Source*: US Environmental Protection Agency, *Protecting Visibility*, EPA-450/5-79-008. Office of Air Quality Planning Standards, Research Triangle Park, NC, 1979.

of 50% in ground-level solar intensity. The turbidity coefficient can also be derived from these measurements and used to approximate the aerosol loading of the atmosphere. By assuming a particle size distribution in the size range 0.1–10.0 μm and a particle density, the total number of particles can be estimated. The mass loading per cubic meter can also be approximated. Because of the reasonable cost and simplicity of the sun photometer, it is useful for making comparative measurements around the world.

C. Precipitation

Pollution can cause opposite effects in relation to precipitation. Addition of a few particles that act as ice nuclei can cause ice particles to grow at the expense of supercooled water droplets, producing particles large enough to fall as precipitation. An example of this is commercial cloud seeding with silver iodide particles released from aircraft to induce rain. If too many particles are added, none of them grow sufficiently to cause precipitation. Therefore, the effects of pollution on precipitation are complex.

II. FORMATION OF ATMOSPHERIC HAZE

Atmospheric haze is the condition of reduced visibility caused by the presence of fine particles or NO_2 in the atmosphere. The particles must be 0.1–1.0 μm in diameter, the size range in which light scattering occurs. The source of these particles may be natural or anthropogenic.

Atmospheric haze has been observed in both the western and eastern portions of the United States. Typical visual ranges in the East are <15 miles and in the Southwest >50 miles. The desire to protect visual air quality in the United States is focused on the national parks in the West. The ability to see vistas over 50–100 km in these locations makes them particularly vulnerable to atmospheric haze. This phenomenon is generally associated with diffuse or widespread atmospheric degradation as opposed to individual plumes.

The major component of atmospheric haze is sulfate particulate matter (particularly ammonium sulfate), along with varying amounts of nitrate particulate matter, which in some areas can equal the sulfate. Other components include graphitic material, fine fly ash, and organic aerosols.

The sources of particulate matter in the atmosphere can be primary, directly injected into the atmosphere, or secondary, formed in the atmosphere by gas-to-particle conversion processes [13]. The primary sources of fine particles are combustion processes, e.g., power plants and diesel engines. Power plants with advanced control technology still emit substantial numbers and masses of fine particles with diameters $<1.0\,\mu m$. The composition of these particles includes soot or carbonaceous material, trace metals, V_2O_5, and sulfates. In addition, large quantities of NO_2 and SO_2 are released to the atmosphere.

A. Particle Formation in the Atmosphere

The secondary source of fine particles in the atmosphere is gas-to-particle conversion processes, considered to be the more important source of particles contributing to atmospheric haze. In gas-to-particle conversion, gaseous molecules become transformed to liquid or solid particles. This phase transformation can occur by three processes: absorption, nucleation, and condensation. *Absorption* is the process by which a gas goes into solution in a liquid phase. Absorption of a specific gas is dependent on the solubility of the gas in a particular liquid, e.g., SO_2 in liquid H_2O droplets. *Nucleation* and *condensation* are terms associated with aerosol dynamics.

Nucleation is the growth of clusters of molecules that become a thermodynamically stable nucleus. This process is dependent on the vapor pressure of the condensable species. The molecular clusters undergo growth when the saturation ratio, S, is greater than 1, where *saturation ratio* is defined as the actual pressure of the gas divided by its equilibrium vapor pressure. $S > 1$ is referred to as a *supersaturated condition* [14].

The size at which a cluster may be thermodynamically stable is influenced by the Kelvin effect. The equilibrium vapor pressure of a component increases as the droplet size decreases. Vapor pressure is determined by the energy necessary to separate a single molecule from the surrounding molecules in the liquid. As the curvature of the droplet's surface increases, fewer neighboring molecules will be able to bind a particular molecule to the liquid phase, thus increasing the probability of a molecule escaping the liquid's surface. Thus, smaller droplets will have a higher equilibrium vapor pressure. This would affect the minimum size necessary for a thermodynamically stable cluster, suggesting that components with lower equilibrium saturation vapor pressures will form stable clusters at smaller diameters.

Condensation is the result of collisions between a gaseous molecule and an existing aerosol droplet when supersaturation exists. Condensation occurs at much lower values of supersaturation than nucleation. Thus, when particles already exist in sufficient quantities, condensation will be the dominant process occurring to relieve the supersaturated condition of the vapor-phase material.

A simple model for the formation and growth of an aerosol at ambient conditions involves the formation of a gas product by the appropriate chemical oxidation reactions in the gas phase. This product must have a sufficiently low vapor pressure for the gas-phase concentration of the oxidized product to exceed its saturation vapor pressure. When this condition occurs, nucleation and condensation may proceed, relieving supersaturation. These processes result in the transfer of mass to the condensed phase. Aerosol growth in size occurs while condensation is proceeding.

Coagulation, i.e., the process by which discrete particles come into contact with each other in the air and remain joined together by surface forces, represents another way in which aerosol diameter will increase. However, it does not alter the mass of material in the coagulated particle.

The clearest example of this working model of homogeneous gas-to-particle conversion is sulfuric acid aerosol formation. Sulfuric acid (H_2SO_4) has an extremely low saturation vapor pressure. Oxidation of relatively small amounts of sulfur dioxide (SO_2) can result in a gas-phase concentration of H_2SO_4 that exceeds its equilibrium vapor pressure in the ambient atmosphere, with the subsequent formation of sulfuric acid aerosol. In contrast, nitric acid (HNO_3) has a much higher saturation vapor pressure. Therefore, the gas-phase concentration of HNO_3 is not high enough to permit nucleation of nitric acid aerosol in typical atmospheric systems.

Atmospheric haze can occur over regions of several thousand square kilometers, caused by the oxidation of widespread SO_2 and NO_2 to sulfate and nitrate in relatively slow-moving air masses. In the eastern United States, large air masses associated with slow-moving or stagnating anticyclones have become sufficiently contaminated to be called *hazy blobs*. These blobs have been tracked by satellites as they develop and move across the country [15].

The evolution of regional hazy air masses has been documented in several case studies. The development of one such system is shown in Fig. 14.9. During a 10-day period in the summer of 1975, a large region of the eastern United States had decreased visibility associated with the presence of fine particles in the atmosphere. The phenomenon occurred in association with a slow-moving high-pressure system. Because it seldom rains during the passage of these systems, the fine particles may have stayed airborne for a longer period of time than usual.

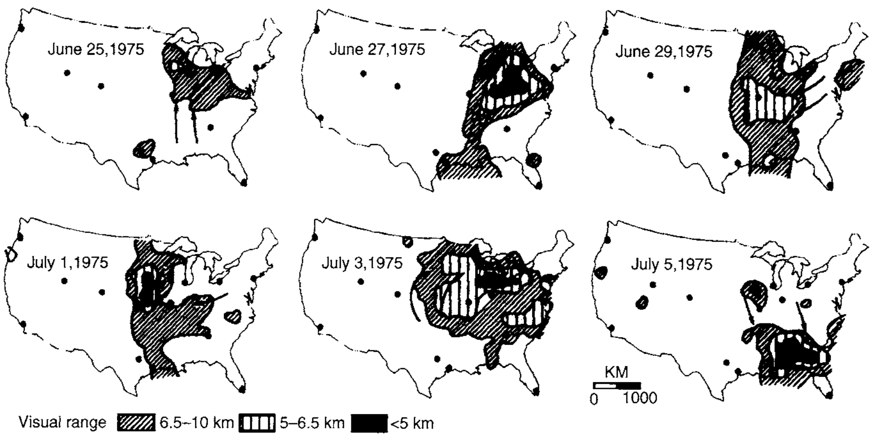

Fig. 14.9. The evolution and transport of a large hazy air mass. Contour maps of noon visibility for June 25–July 5, 1975. *Source*: Lyons, W. A., and Husar, R. B., *Mon. Weather Rev.* **104**, 1623–1626 (1976).

III. EFFECTS OF ATMOSPHERIC HAZE

The United States Clean Air Act of 1977 set as a national goal the prevention of any future degradation and the reduction of any existing impairment of visibility in mandatory class I federal areas caused by anthropogenic air pollution. The Clean Air Act Amendments of 1990 reinforce the support of these goals (see Chapter 24 for a discussion of federal classes of areas). These areas include most of the major national parks, such as the Grand Canyon, Yosemite, and Zion Park. This portion of the Clean Air Act addresses the problem of visibility degradation by atmospheric haze of anthropogenic origin. This legislation recognizes atmospheric haze as a cause of degradation in visual air quality.

All nations contain areas of exceptional scenic beauty. The value of these areas is largely determined by society. Many nations, determined to protect these areas, have established parks or preserves where only limited development can occur, in many instances limited to facilities such as food and lodging for visitors to the area.

The Grand Canyon National Park in the southwestern United States is a prime example of an area of natural beauty. This park is ~250 km long, varying in width up to ~45 km. The actual canyon is ~10 km at its widest point, with the Colorado River running in the bottom of the canyon, 1600 m below the edge of the outer rim. Visitors go to parks for many reasons, such as hiking, camping, wildlife, and the enjoyment of solitude, but the overwhelming majority visit the Grand Canyon to enjoy the magnificent views from its rim. These views have detail in the foreground (0–5 km), with colored layers of rock strata on canyon walls perhaps 5–25 km distant and in the far background (25–50 km) additional geologic features which contribute to the viewers' appreciation of the scene. To enjoy these views, one must have good visibility over the entire path length from the details in the foreground to the objects in the distant background.

A survey by national park personnel indicates that large areas of the United States are subject to varying degrees of visibility degradation [1]. The middle portion of the eastern half of the country and the Florida Gulf Coast are subject to widespread hazy air masses associated with stagnation conditions. Large portions of the western half of the country are subject to atmospheric haze problems associated with power plants, urban plumes, and agricultural activities.

Average airport visibilities over the eastern half of the United States have been determined over a period of approximately 25 years (1948–1974) [6]. Although seasonal variations occur, the long-term trend has been decreased visual air quality over the time period.

IV. VISIBILITY

Holzworth and Maga [16] developed a technique for examining the trend in visibility and analyzed data for several California airports. Bakersfield's visibility deteriorated over the period 1948–1957 and Sacramento's visibility decreased over the period 1935–1958. Los Angeles had decreasing visibility from 1932 to 1947, with little change over the period 1948–1959.

Holzworth [17] reported on the frequency of visibility of less than 7 miles for 28 cities. Two periods of records were compared for each city. There were increases in low visibility in only 26% of the comparisons from the early period (around 1930–1940) to a later period (around the mid-1950s).

Miller *et al.* [18], using analyses for Akron, Ohio; Lexington, Kentucky; and Memphis, Tennessee, concluded that "summer daytime visibilities were significantly lower during the period 1966–1969 than visibilities for the preceding 4-year period."

Faulkenberry and Craig [19], in examining the trends at three Oregon cities, utilized a modification of the Holzworth–Maga technique by which a single statistic can be calculated for each year, indicating the probability of observing better visibility at Salem, Oregon, with no trends at Portland and Eugene, Oregon over the period 1950–1971.

Arizona has traditionally been a large copper-producing state. SO_x emissions from copper smelters near Phoenix and Tucson are shown in Fig. 14.10 [1]. Phoenix is located 100 km from the nearest smelter, and Tucson is 60 km from the nearest smelter. The improvement in visibility in the 1967–1968 period was due to a decrease in SO_x emissions when there was a 9-month shutdown caused by a strike. Improvement in visibility in the mid-1970 was the result of better control technology and process changes.

Zannetti *et al.* [20] did an analysis of visual range in the eastern United States again showing the importance of humidity but also showing the importance of air mass type, which is usually related to its direction of origin.

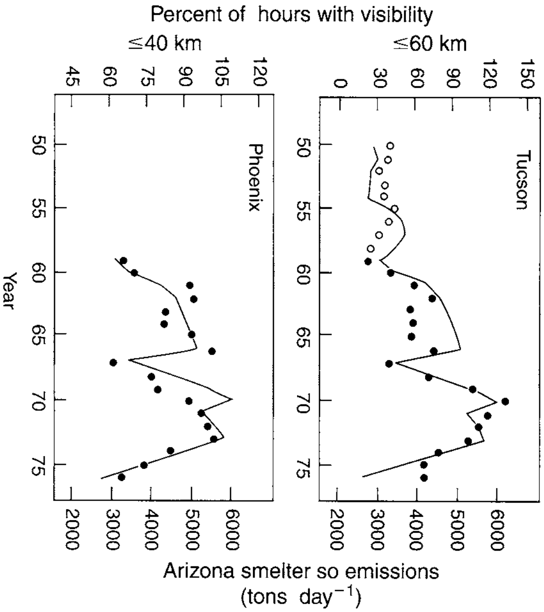

Fig. 14.10. Historic trends in hours of reduced visibility at Phoenix and Tucson, Arizona, compared to trends in SO_x emissions from Arizona smelters. The solid lines (———) represent yearly SO_x emissions. The dots (...) represent yearly percentages of hours of reduced visibility. Note the open dots used to represent different locations in Tucson before 1958. *Source*: US Environmental Protection Agency, *Protecting Visibility*, EPA-450/5-79-008. Office of Air Quality Planning Standards, Research Triangle Park, NC, 1979.

Mathai [21] summarized the specialty conference on atmospheric visibility. With the exception of water content of particles and the measurement of organic species, analytical laboratory techniques are readily available for particle analysis. Regulatory approaches to mitigate existing visibility impairment and to prevent further impairment are being formulated. A significant problem for regulation is the lack of proven techniques to quantify the contributions due to various sources.

V. ACIDIC DEPOSITION

Over the past 25 years, evidence has been accumulated on changes in aquatic life and soil pH in Scandinavia, Canada, and the northeastern United States. Many believe that these changes are caused by acidic deposition traceable to pollutant acid precursors that result from the burning of fossil fuels. Acid rain is only one component of *acidic deposition*, a more appropriate description of this phenomenon. Acidic deposition is the combined total of wet and dry deposition, with wet acidic deposition being commonly referred to as acid rain.

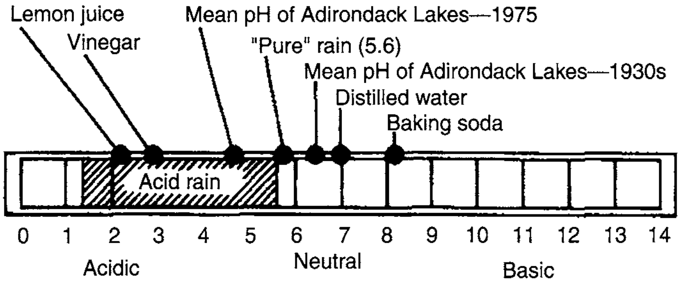

Fig. 14.11. The pH scale is a measure of hydrogen ion concentration. The pH of common substances is shown with various values along the scale. The Adirondack Lakes are located in the state of New York and are considered to be receptors of acidic deposition. *Source*: US Environmental Protection Agency, *Acid Rain—Research Summary*, EPA-600/8-79-028. Cincinnati, OH, 1979.

Acidity is defined in terms of the pH scale, where pH is the negative logarithm of the hydrogen ion $[H^+]$ concentration:

$$pH = -\log[H^+] \tag{14.5}$$

In the simplest case, CO_2 dissolves in raindrops, forming carbonic acid. At a temperature of 20°C, the raindrops have a pH of 5.6, the value often labeled as that of clean or natural rainwater. It represents the baseline for comparing the pH of rainwater which may be altered by SO_2 or NO_x oxidation products. Figure 14.11 illustrates the pH scale with the pH of common items and the pH range observed in rainwater. The pH of rainwater can vary from 5.6 due to the presence of H_2SO_4 and HNO_3 dissolved or formed in the droplets. These strong acids dissociate and release hydrogen ions, resulting in more acidic droplets. Basic compounds can also influence the pH. Calcium (Ca^{2+}), magnesium (Mg^{2+}), and ammonium (NH_4^+) ions help to neutralize the rain droplet and shift the overall H^+ toward the basic end of the scale. The overall pH of any given droplet is a combination of the effects of carbonic acid, sulfuric and nitric acids, and any neutralizers such as ammonia.

The principal elements of acidic deposition are shown in Fig. 14.12. Dry deposition occurs when it is not raining. Gaseous SO_2, NO_2, and HNO_3 and acid aerosols are deposited when they come into contact with and stick to the surfaces of water bodies, vegetation, soil, and other materials. If the surfaces are moist or liquid, the gases can go directly into solution; the acids formed are identical to those that fall in the form of acid rain. SO_2 and NO_2 can undergo oxidation, forming acids in the liquid surfaces if oxidizers are present. During cloud formation, when rain droplets are created, fine particles or acid droplets can act as seed nuclei for water to condense. This is one process by which sulfuric acid is incorporated in the droplets. While the droplets are in the cloud, additional gaseous SO_2 and NO_2 impinge on them and are absorbed. These absorbed gases can be oxidized by dissolved H_2O_2 or other oxidizers, lowering the pH of the raindrop. As the raindrop falls

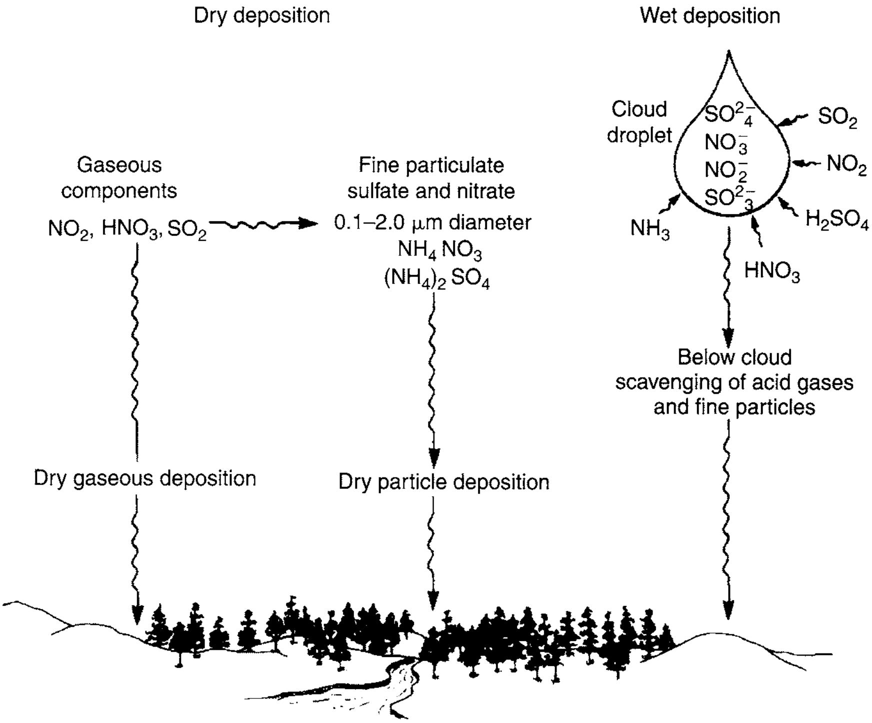

Fig. 14.12. Atmospheric processes involved in acidic deposition. The two principal deposition pathways are dry deposition (nonrain events) and wet deposition (rain events).

beneath the cloud, additional acidic gases and aerosol particles may be incorporated in it, also affecting its pH.

The United States has established a National Atmospheric Deposition Program (NADP), and Canada has established the CANSAP program, which consists of sampling networks and organizational and support structures to obtain quantitative information on the spatial and temporal distribution patterns of acid deposition [22, 23]. The lowest rainwater pH isopleths are associated with the regions of highest SO_2 emissions. Although there is considerable controversy over the quality and strength of the link between SO_2 and NO_x emissions from stationary sources and subsequent acid deposition hundreds of kilometers downwind, the National Research Council has concluded that a 50% reduction in the emissions of sulfur and nitrogen gases will produce about a 50% reduction in the acids deposited on the land and water downwind of the emission source. They also state that current meteorological models of atmospheric transport cannot identify specific sources with acid deposition at a particular downwind location [24].

A field study, the Eulerian Model Evaluation Field Study (EMEFS) [25], has been used to evaluate two models: the acidic deposition and oxidant model (ADOM) [26] and the regional acid deposition model (RADM) [27].

For both models the calculated values, such as air concentrations, are volume averages over grid cells which are 127 km on a side for the ADOM and 80 km for the RADM. These are compared with point measurements at a possible 97 locations. The ADOM tended to overestimate ground-level SO_2 and underestimate ground-level sulfate. Two factors not included in the model that may contribute to these results are consideration of conversion during surface fog and conversion in nonprecipitating clouds. The RADM also overestimated SO_2 and underestimated aerosol sulfate.

In the eastern United States, acid rain consists of ~65% sulfuric acid, ~30% nitric acid, and ~5% other acids. In the West, windblown alkaline dusts buffer the acidity in rains occurring over many rural areas, whereas in urban areas 80% of the acidity is due to nitric acid [28]. Average pH in rainfall over the eastern United States for the period April 1979–March 1980 was less than 5.0, with some areas less than 4.2 [29]. The lowest annual pH recorded was 3.78 at De Bilt, The Netherlands, in 1967, and the lowest in an individual rainfall was 2.4 at Pitlochry, Scotland, on April 10, 1974 [30].

One of the major effects of acidic deposition is felt by aquatic ecosystems in mountainous terrain, where considerable precipitation occurs due to orographic lifting. The maximum effect is felt where there is little buffering of the acid by soil or rock structures and where steep lakeshore slopes allow little time for precipitation to remain on the ground surface before entering the lake. Maximum fish kills occur in the early spring due to the "acid shock" of the first meltwater, which releases the pollution accumulated in the winter snowpack. This first melt may be 5–10 times more acidic than rainfall.

Although the same measurement techniques for rainfall acidity have not been used over a long period of time and sampling has been carried out at relatively few locations, the trend between 1955–1956 and 1975–1976 was for the area with a pH of less than 4.6 to expand greatly over the eastern United States. The largest increases occurred over the southeastern United States, where industrialization grew rapidly during the period. The last several decades have also seen an increased area of lower pH over northern Europe.

VI. EFFECTS OF ACIDIC DEPOSITION

Land, vegetation, and bodies of water are the surfaces on which acidic deposition accumulates. Bodies of freshwater represent the smallest proportion of the earth's surface area available for acidic deposition. Yet, the best-known effect is acidification of freshwater aquatic systems.

Consider a lake with a small watershed in a forest ecosystem. The forest and vegetation can be considered as an acid concentrator. SO_2, NO_2, and acid aerosol are deposited on vegetation surfaces during dry periods and rainfalls; they are washed to the soil floor by low-pH rainwater. Much of the acidity is neutralized by dissolving and mobilizing minerals in the soil. Aluminum, calcium, magnesium, sodium, and potassium are leached from the soil into surface waters. The ability of soils to tolerate acidic deposition is very dependent on the alkalinity of the soil. The soil structure in the northeastern United States and eastern Canada is quite varied, but much of the area is covered with thin soils with a relatively limited neutralizing capacity. In watersheds with this type of soil, lakes and streams are susceptible to low pH and elevated levels of aluminum. This combination has been found to be very toxic to some species of fish. When the pH drops to ~5, many species of fish are no longer to reproduce and survive. In Sweden, thousands of lakes are no longer able to support fish. In the United States the number of polluted lakes is much smaller, but many more may be pushed into that condition by continued acidic deposition. In Canada, damage to aquatic systems and forest ecosystems is a matter of considerable concern.

Aquatic systems in areas of large snowfall accumulation are subjected to a pH surge during the spring thaw. Acidic deposition is immobilized in the snowpack, and when warm springtime temperatures cause melting, the melted snow flows into streams and lakes, potentially overloading the buffering capacity of the aquatic system.

A second area of concern is reduced tree growth in forests, discussed in Chapter 13. As acidic deposition moves through forest soil, the leaching process removes nutrients. If the soil base is thin or contains barely adequate amounts of nutrients to support a particular mix of species, the continued loss of a portion of the soil minerals may cause a reduction in future tree growth rates or a change in the types of trees able to survive in a given location.

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SUGGESTED READING

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QUESTIONS

1. Define threshold contrast.
2. List the four components which contribute to the extinction coefficient b_{ext}. Describe the circumstances in which each component would dominate extinction.
3. Derive the Koschmieder relationship from Eq. (14.1).
4. Compare visibility measurements at a nearby airport with those of particle-free clean air.
5. Explain why stringent emission standards for particulate matter based on mass/heat input will do little to improve visual air quality.
6. Explain the differences in visual air quality between the western and eastern portions of the United States.
7. Compare the wavelengths of visible light with the range of particle diameters which most efficiently scatter light.
8. Describe the impact of future visibility degradation on your area (e.g. on specific areas of scenic attraction).
9. In the 1980s and 1990s, where were the greatest increases in rainfall acidity in the United States? What is the suspected reason?