

Air Quality

Fifth Edition



Thad Godish
Wayne T. Davis
Joshua S. Fu

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Under the Clean Air Act (CAA) Amendments of 1970, National Ambient Air Quality Standards (NAAQSs) were to be promulgated to protect public health and welfare. The former were to be primary standards, and the latter secondary. Public health protection has had the highest priority, whereas public welfare is less well defined. Welfare effects are air pollution effects not related to human health. Although it has always been clear what some welfare effects are (e.g., damage to crops, plants, and materials; malodors), others have evolved over time. In the latter case, these include visibility concerns, atmospheric deposition, possible ecosystem changes associated with stratospheric ozone (O_3) depletion, and global warming.

Welfare effects within the regulatory context are limited to pollutants for which air quality standards have been promulgated, the so-called criteria pollutants: carbon monoxide (CO), particulate matter (PM), sulfur dioxide (SO_2), nitrogen oxides (NO_x), O_3 , nonmethane hydrocarbons (NMHCs), and lead (Pb). The concept of welfare effects, as it is discussed in this chapter, is used more broadly. It includes non-health effects associated with other pollutants as well.

Most of the issues discussed in Chapter 4 (Atmospheric Effects) are welfare effects. Ecological changes and concerns associated with most of those issues, save visibility, are discussed in this chapter.

6.1 Effects on Agricultural Crops, Ornamental Plants, and Trees

Plants have long served as sentinels of the biological injury that air pollutants are capable of producing as a result of acute and chronic exposures. Phytotoxic responses to pollutants such as SO_2 , hydrogen chloride (HCl), and hydrogen fluoride (HF) have been reported in Europe since the middle of the nineteenth century. Particularly severe injury to, and destruction of, vegetation was associated with emissions of SO_2 and heavy metals from primary nonferrous metal smelters. In the United States, this included the Copper Hill Smelter in Ducktown, TN, a copper (Cu) smelter in Kellogg, ID, a zinc (Zn) smelter in eastern Pennsylvania, and other smaller smelters that have been long closed and would have been forgotten save for the despoiling of

the surrounding environment that persists although these men and their machines are long gone.

Smelter emissions have been a problem in Canada. In the 1920s, emissions from a smelter in Trail, British Columbia, were carried down the Columbia River Valley into the United States, causing significant damage to agricultural crops. This was one of the earliest recorded instances of a transboundary air pollution problem. The once-forested and subsequently devastated landscape downwind of the giant nickel (Ni) smelter near Sudbury, Ontario, is, to this day, a reminder of the significant effect that atmospheric pollutants can have on the environment. (On a historical note, emissions from the Sudbury smelter have been significantly reduced over the past two decades.)

Injury to agricultural plants and forests has been reported near uncontrolled nonferrous metal smelters in many parts of the world. Significant plant injury also occurs in developing countries around industrial sources, including coal-fired and oil-fired power plants, phosphate fertilizer mills, and glass plants.

Until the 1940s and 1950s, damage to agricultural crops, ornamental plants, and forests was, for the most part, a problem associated with point sources. As a result of intensive scientific investigation, the widespread injury to agricultural crops observed (as early as the mid-1940s) in the Los Angeles Basin was determined to be due to phytotoxic air pollutants such as O_3 and peroxyacetyl nitrate (PAN), produced in the atmosphere as a result of photochemical reactions. Plant biochemist Dr. Arie Hagen-Smit, often referred to as the father of air pollution, initiated studies to unravel the chemical complexities of smog formation.

Ozone injury on sensitive vegetation has since been observed throughout the United States and in many parts of the world. Ozone levels sufficient to cause injury on very sensitive vegetation are reported in most areas east of the Mississippi River. Because of its ubiquitous distribution and high phytotoxicity, O_3 is the most important phytotoxic air contaminant.

Control efforts and changes in operating practices have resulted in a significant reduction in the localized plant damage that had been associated with many point sources. Paradoxically, one of these changes, the use of tall stacks for more effective dilution of emissions from coal-fired power plants, has, as expected, resulted in decreased injury to vegetation in the vicinity of these sources, but inadvertently contributed to the problem of long-range transport and atmospheric deposition of strong acids and other pollutants.

Pollutants that have a history of causing significant plant injury under ambient exposure conditions include O_3 , SO_2 , PAN, fluoride (F), and ethylene (C_2H_4). Although it has been suspected of being a major plant-injuring pollution problem for some time, acidic deposition has only recently been determined to be, at least in part, causally related to plant injury under ambient conditions (e.g., the decline of red spruce in high-elevation forests).

Other pollutants are also known to cause injury to plants. They include nitrogen dioxide (NO_2), chlorine (Cl_2), hydrochloric acid (HCl), ammonia

(NH_3), and PM. They are classified as minor pollutants because their emissions from continuous point sources at levels sufficient to cause injury have, for the most part, been relatively limited. Plant injury associated with exposures to these pollutants is commonly associated with accidental releases in industrial operations or transportation. On the other hand, injury induced by particulate dusts is usually associated with continuous emissions from point sources.

6.1.1 Plant Injury

Injury to plants can be manifested as visible or subtle effects. The former are identifiable changes in leaf structure, which may include chlorophyll destruction (chlorosis), tissue death (necrosis), and pigment formation. Visible symptoms may result from acute or chronic exposures. Acute injury occurs from brief exposures (several hours) to elevated levels of a phytotoxic pollutant. Tissue necrosis is the dominant symptom pattern associated with acute exposures, with necrotic foliar patterns usually specific for a given pollutant.

Chronic injury results from intermittent or long-term exposures to relatively low pollutant concentrations, with chlorophyll destruction and chlorosis the major symptoms. Chlorosis, however, is a nonspecific symptom associated with a number of pollutants, natural senescence (aging), and injury caused by other factors such as nutritional deficiencies.

Some pollutants produce symptom patterns other than, or in addition to, the classic patterns of necrosis and chlorosis associated with acute and chronic injury. These are described as growth abnormalities. They may be subtle, such as growth reduction, or visible, such as accelerated senescence of flowers, bolting (breaking) of flower buds, abscission (breaking off) of plant parts, and a curvature of the leaf petiole called epinasty.

The severity of injury, that is, the amount of leaf surface affected, depends on pollutant concentration and duration of exposure. The greater the exposure, the more severe the injury. Entire leaves or, in extreme cases, the whole plant may be killed. The extent of injury also depends on the sensitivity of the species, variety, or strain to the pollutant. Considerable variability in the response of plants to different phytotoxic pollutants, as well as responses to a given pollutant, occurs. As a general rule, actively growing plants and the most actively growing tissue are most sensitive to pollutant exposures and are more likely to experience injury.

6.1.1.1 Sulfur Dioxide

Plants exposed to increased SO_2 levels develop characteristic acute symptoms within 48 h of exposure. Tissue in the internal center of leaves of broad-leaved species is killed, resulting in a pattern of ivory-to-white, red, or dead brown tissue between the veins. This interveinal necrosis extends outward from



FIGURE 6.1
Interveinal necrosis on pinto bean associated with exposure to SO_2 .

the veins to the leaf margin and is observable on both surfaces. In narrow-leaved species, for example, cereal grains, lilies, irises, and gladiolas, injury appears as irregular bifacial necrotic streaks between longer veins, and in some species, injury occurs at the tip of the leaf. Injury on coniferous plants is a reddish brown to brown tip necrosis with a banded appearance from repeated exposure. Chlorosis may occur on older needles under moderate exposures; such chlorotic needles are often prematurely shed. Interveinal necrosis on SO_2 -injured pinto bean leaves is illustrated in Figure 6.1.

6.1.1.2 Ozone

Unlike SO_2 , which initially injures tissues in the internal center of leaves, O_3 preferentially injures cells close to the upper surface (in broad-leaved species). The most common O_3 -induced symptom is "flecking," which is visible on the upper surface (Figure 6.2). These flecks are produced when groups of cells below the epidermis (surface cell layer) are injured or killed. They may be white, tan, or yellow in color. The upper surface may look chlorotic or



FIGURE 6.2
Ozone injury on tobacco.

"bronzed" if flecking is extensive. A variation of this symptom is stippling, wherein injured cells become unevenly pigmented, producing a red-purple to black-brown appearance (Figure 6.3). This injury is confined to interveinal areas. Injury in narrow-leaved species appears as small necrotic or chlorotic flecks between veins.

Ozone injury on coniferous species such as pine is common. It is the causal factor of emergence tipburn of eastern white pine, a disease observed on this species since the early twentieth century. The disease syndrome is characterized by the death of the tips of young elongating needles in spring and early summer. Killed needle tips become reddish brown. Ozone not only causes tip necrosis, but also other symptoms, ranging from chlorotic flecks to chlorotic mottling (small chlorotic patches). On O_3 -affected trees, older needles prematurely age, discolor, and are shed. Consequently, affected trees may possess only the current year's needles.

Ozone, along with SO_2 , seems to be responsible for the chlorotic dwarf disease of eastern white pine that has been observed in the northeastern United States for most of the twentieth century. In young, sensitive trees, current-year needles develop chlorotic flecks and mottling. Older needles become prematurely chlorotic and are shed before the new set of needles is fully developed. These trees are severely stunted and usually die before they reach 15 years of age.

In the San Bernardino Mountains of southern California, large numbers of ponderosa pines have been affected by what is called ozone needle mottle. The earliest symptoms are small chlorotic tissue patches that develop from the tip to the base in older needles. Death of the needle tip may also occur. As a consequence, O_3 -injured trees may possess only 1-year-old needles during the summer months rather than the 3-year to 5-year normal complement.



FIGURE 6.3
Ozone injury on grape.

swelling), and hyperplasia (excessive cell production) in the specific species exposed.

The most commonly reported symptom of acidic deposition injury on plants in laboratory studies is small necrotic lesions. These seem to be a result of the deposition of acidified water on the leaf surface and its subsequent evaporation. Repeated exposure to simulated acid rain events results in an increased number of lesions on affected leaves. Foliar injury has been observed at pH levels associated with recorded severe ambient deposition events. However, to this author's knowledge, there have been no confirmed reports of atmospheric deposition causing similar symptoms in plants under field conditions. Other effects not manifested as visible injury include reduced yield and leaching of metabolites and inorganic nutrients from plant surfaces. Leachates of such substances seem to be a common response to acid deposition. Leachates include amino acids, free sugars, organic acids, vitamins, a variety of essential mineral nutrients—nitrogen (N), calcium (Ca), phosphorus (P), magnesium (Mg)—alkaloids, growth regulators, and pectic substances.

A variety of potential effects of acidic deposition on forest element cycles and tree nutrition have been proposed. These include

1. Accelerated leaching of base cations from foliage and soils that may result in nutrient deficiency, root damage, and reduced drought tolerance
2. Increased mobilization of aluminum (Al) and other metals, also resulting in nutrient deficiency, root damage, and reduced drought tolerance
3. Inhibited microbiological processing of soil, possibly leading to reduced decomposition of organic matter, damage to mycorrhizae, nutrient deficiency, and altered pathogen–host relationships
4. Increased bioavailability of N, leading to accelerated organic matter decomposition and increased susceptibility to natural stresses such as freezing temperatures, drought, etc.

The importance of these mechanisms in altering tree and forest growth is not known.

6.1.1.7 Interaction Effects

Pollutants do not occur in the atmosphere singly. Therefore, it is possible, and even probable, that simultaneous, sequential, or intermittent exposures to several phytotoxic pollutants may result in plant injury. Available evidence indicates that simultaneous exposures to gaseous mixtures can produce synergistic, additive, or antagonistic effects. The type of interaction response is related to the plant species exposed, pollutant combinations and

concentrations, duration of exposure, and amount of injury caused by pollutants when exposed singly.

Plant exposures to mixtures of SO_2 + O_3 and SO_2 + NO_2 have reportedly decreased injury thresholds. Injury produced by exposure to gaseous mixtures may be more severe than the sum of the injury caused by exposure to individual pollutants (a synergistic response). Antagonistic responses are generally observed when injury caused by pollutants applied singly is severe; in these cases, the effect of mixtures is to reduce the severity of injury. Visible symptoms produced by gaseous mixtures are usually characteristic of a single pollutant.

6.1.2 Economic Losses

Numerous cases of significant pollutant-caused plant injury have been reported in the twentieth century. Excluding the photochemical oxidant problem in southern California and some areas of the northeast, most reports of air pollution-induced plant injury have been associated with point sources. With the exception of primary metal smelters, economic losses associated with point sources have often been insignificant. Many offending point sources in the United States have since been controlled. Nevertheless, because of photochemical oxidants such as O_3 and PAN, significant air pollution injury to vegetation is still widespread; associated economic losses, however, are often undetermined.

Scientists generally agree that O_3 causes 90% or more of the air pollution injury to crops in the United States. This recognition has led to the establishment of a National Crop Loss Assessment Network (NCLAN). From summaries of O_3 monitoring data; determination of the O_3 sensitivity of major crop plants such as corn, soy beans, wheat, cotton, grain, sorghum, and barley; and economic data, NCLAN-participating scientists have modeled the economic effect of O_3 on US agriculture. They have estimated that a 25% reduction in ambient tropospheric O_3 would result in a \$1.71 billion annual increase in agricultural production; a 40% reduction would result in a \$2.52 billion annual increase.

Quantification of economic loss is a difficult task. It requires surveys of suspected air pollution injury, confirmation of the causal factor, and estimation of the dollar costs. Loss estimates may be confounded by a number of factors. For example, the presence of visible injury on plants may not be translatable into economic loss. In many cases, plants with severe foliar injury may quickly recover, replacing injured leaves with younger healthy ones with no apparent lasting effects. In other instances, even a slight amount of injury can decrease the marketability of a crop. To deal with this reality, plant scientists use the concept of plant damage rather than plant injury when it relates to potential economic losses. It is implicit in the damage concept that economic losses have resulted. Plant injury does not have this connotation.

6.1.1.3 Peroxyacetyl Nitrate

Peroxyacetyl nitrate is the causal agent of what was described as smog injury on vegetable crops in the Los Angeles Basin from the 1940s to the early 1960s, where it was a major problem. Injury due to PAN has been observed around other western cities, but to a lesser degree; it has also been found in New Jersey and southeastern Canada.

PAN destroys tissue near the lower surface of leaves, resulting in what has been described as glazing on the underside of the leaf. A distinct pattern of banding is observed after repeated intermittent exposures. Injury is not commonly reported on narrow-leaved or coniferous species.

6.1.1.4 Fluorides

Fluoride injury may result from the uptake of gaseous hydrogen fluoride (HF) through leaves or from soluble particulate fluorides absorbed through leaves or roots. Whatever the route of exposure, fluorides are transported through veins to leaf margins and leaf tips, where they accumulate. Fluoride injury results from exposures to elevated tissue concentrations that occur as a result of the accumulation of F over a period of weeks to months. The severity of injury is directly related to the level of F accumulated in marginal leaf tip tissue.

In broad-leaved species, F injury appears as marginal (Figure 6.4) or tip necrosis. Necrotic tissue is often separated from healthy tissue by a narrow, sharply defined reddish band. It may have a characteristic wavy color pattern due to successive F-induced tissue death. Necrotic tissue may break away from uninjured tissue near the reddish band, giving the leaf a ragged appearance.

Fluoride injury on narrow-leaved species is characterized by tip necrosis that extends in irregular streaks down the leaf. Necrotic tissue may vary in color from ivory to various shades of brown. A band of dark brown tissue



FIGURE 6.4
Fluoride injury on Oregon grape.

sharply demarks injured from healthy tissues. Symptoms consist of chlorotic mottle at the margins and leaf tips. Small irregular chlorotic patches form between the veins and merge to form continuous bands as injury becomes extensive. Necrosis occurs when tissue injury is severe.

Tip necrosis is the characteristic symptom of F injury in conifers. Necrosis begins at the tip of current-year needles and progresses downward. The necrotic tip is usually reddish brown. This tip necrosis usually results in premature shedding of affected needles.

6.1.1.5 Ethylene

Plant injury caused by C_2H_4 was first reported when C_2H_4 was used in illuminating gas in greenhouses at the turn of the twentieth century. Because it is emitted in automobile exhaust, C_2H_4 is a ubiquitous pollutant in urban and suburban areas. Its concentrations in ambient air, although relatively low, may be sufficient to cause significant effects on plants.

Ethylene is a natural maturation hormone in plants, controlling the ripening and aging of fruits. The effects of ambient levels of C_2H_4 on plants growing in the urban environment are potentially great because C_2H_4 has significant biological activity at very low concentrations (e.g., ppbv).

One of the best-documented effects of C_2H_4 exposure is dry sepal of orchids, associated with use of C_2H_4 illuminating gas in greenhouses. Dry sepal has also been reported in urban areas, presumably from elevated levels of C_2H_4 associated with automobile emissions.

Other plants in the flowering stage may be sensitive to C_2H_4 exposures. Common C_2H_4 -induced responses include premature bud break, inhibition of flowering, and accelerated flower aging.

Because of its hormonal properties, C_2H_4 has the potential to cause widespread adverse effects on plants. However, field identification of injury resulting from such exposure may be nearly impossible because injury mimics natural senescence and changes induced by a variety of environmental factors. An interesting example of this problem is the widely observed premature pigmentation of tree and shrub leaves along many major highways.

6.1.1.6 Acidic Deposition

Acidic substances deposited on plants or the plant soil environment have the potential to cause direct injury or measurable changes in plant growth. Laboratory and greenhouse studies with simulated acidic rain events have shown that a wide variety of plants can be injured by exposure to acidic rainfall with a pH of approximately 3.0. Reported symptoms include (1) small (<1 mm) necrotic leaf lesions or marginal tip necrosis; (2) pitting, curling, wrinkling, shortening, and death of leaves; (3) premature abscission; (4) erosion of the waxy upper leaf surface; (5) chlorosis; (6) excessive adventitious (side) budding; (7) premature senescence; and (8) galls, hypertrophy (tissue

1986, symptoms of decline were seen in 14% of Swiss forests, 22% of Austrian forests, 22% of coniferous and 4% of deciduous trees in France, and 24% of forest areas in Holland.

Research studies indicate that air pollutants, through mechanisms that vary by site, are a significant causal factor in forest declines. A link to air pollution is suggested by the large number of species affected, rapid onset of symptoms, large geographical areas affected, and wide range of associated climates and soil conditions involved. The scientific consensus on these declines is that they are caused by a combination of direct foliar damage and nutrient imbalance, both due to pollutant exposures. Ozone, along with acid fogs, seems to be the principal cause of tree damage and decline of European forests.

6.2 Effects on Domesticated Animals

Retrospective studies of air pollution disasters, such as that which occurred in Donora, PA, in 1948, indicate that in addition to human deaths and illnesses, domesticated animals such as dogs and cats were affected. From epidemiological studies, it is evident that humans chronically exposed to high community air pollution levels have a higher incidence of respiratory disease. Although similar studies have not been done on domesticated animals, dogs and cats, which share the same basic environment as humans, are likely to be affected by such exposures.

6.2.1 Fluoride

Although it is no longer a problem in North America, F once caused more air pollution injury to domesticated animals than any other pollutant. Cases of F toxicity (fluorosis in cattle, sheep, horses, and pigs) resulted primarily from the ingestion of forage contaminated by gas, particulate, and soil sources. Fluorosis in livestock once was prevalent in Florida, Tennessee, Utah, Washington, and Oregon.

Fluorosis can be acute or chronic. Acute fluorosis is rare because livestock do not voluntarily consume heavily contaminated forage. Chronic fluorosis is still observed in livestock that ingest F-contaminated forage over time.

Because F interferes with normal Ca metabolism, chronic toxicity is characterized by dental and skeletal changes. There may be incomplete formation of enamel, dentine, or teeth themselves; teeth soften so that excessive dental wear occurs, interfering with proper mastication of food. These dental changes take place during tooth development and are not reversible.

microbial populations that may be occurring as a result of pollutant exposures on a regional level. This has been due, in part, to limited support for such studies and the inherent complexity of associating changes in species composition with exposure to atmospheric pollutants or other potential stress factors. For example, a progressive decline in flowering dogwood has been observed at Mammoth Cave National Park. It is not known whether such changes are natural or due to other factors such as phytotoxic air pollutants, acidic deposition, or a variety of other abiotic environmental stresses. A change is taking place, but the cause is unknown. Other unstudied changes in forest ecosystems are likely to be taking place as well.

6.3.2 Atmospheric Deposition

Atmospheric deposition poses significant ecological concerns. Major attention is given here to acidic deposition because of its well-recognized and documented environmental effects.

6.3.2.1 Acidic Deposition

Acidic deposition poses a threat to ecosystems that, because of local or regional geology (crystalline or metamorphic rock), have soils and surface waters that cannot adequately neutralize acidified rain, snow, and dry deposited materials. Such soils and waters contain little or no Ca or Mg carbonates and therefore have low acid-neutralizing capacity (ANC). Acid-sensitive ecosystems in North America are illustrated in Figure 4.8. These include mountainous regions of New York and New England; the Appalachian Mountain chain (including portions of Pennsylvania, West Virginia, Virginia, Kentucky, and Tennessee); upper Michigan, Wisconsin, and Minnesota; the Precambrian Shield of Canada, including Ontario, Quebec, and New Brunswick; and various mountainous regions of the North American west.

6.3.2.1.1 Aquatic Ecosystems

Chemical constituents that cause significant biological changes in aquatic ecosystems include H^+ , aluminum (Al^{3+}), and calcium (Ca^{2+}) ions. Increased H^+ (decreased pH) and Al^{3+} cause a variety of adverse biological effects that may be exacerbated by low Ca^{2+} concentrations. As pH decreases to less than 5.5, Al^{3+} concentrations increase to what are often toxic levels.

Changes in water chemistry associated with chronic or episodic acidification affect aquatic organisms at all ecological levels. Because of their large size and recreational importance, significant scientific attention has been given to the effects of acidification on fish populations. Declines in fish populations in acidic and low ANC lakes in the Adirondacks have been directly linked to atmospheric deposition-induced acidification. More than 200 lakes are now known to be fishless. Declines in fish populations in lakes and streams in New England and mid-Atlantic mountains have also

been reported. In Canada, thousands of lakes in Ontario, Quebec, and New Brunswick are fishless, apparently due to increased H^+ concentrations associated with acidic deposition.

Extinction of fish populations in freshwater lakes and decline of fish populations (and fish kills) in streams seem to be a result of episodic as well as chronic acidification. Sudden shifts in pH following spring snowmelt have reportedly caused fish kills. Long-term increases in H^+ and Al^{3+} concentrations result in recruitment failure; that is, few young fish reach maturity. Recruitment failure occurs because of the high mortality of eggs, larvae, and young fish that are particularly vulnerable to elevated H^+ and Al^{3+} concentrations. As a consequence, acidified waters show decreased population densities, with a shift of size and age toward larger, older fish. As acidification continues, a lake becomes fishless. Because acidification is a progressive phenomenon, the most sensitive fish species are affected first. Based on toxicity models developed from bioassay data, approximately 20% of lakes in the Adirondacks, 6% in New England, and 3% in the upper Midwest have H^+ , Al^{3+} , and Ca^{2+} index values unsuitable for the survival of sensitive fish species such as the common minnow and rainbow trout. Almost 10% of lakes in the Adirondacks have H^+ , Al^{3+} , and Ca^{2+} index values that make them unsuitable for the more acid-tolerant brook trout. In the mid-Atlantic coastal plain, an estimated 60% of upstream sites have H^+ and Al^{3+} levels during spring that would kill 50% of anadromous (ocean species that spawn in freshwater rivers and streams) fish species such as the larval stage of the blueback herring.

As with other stressed environments, species diversity reduction is one of the initial significant biological changes that occur in acidified waters. Although total biomass may initially remain unchanged, fewer species are present. Shifts in species composition occur at pH levels in the range of 6.0 to 6.5. Unicellular phytoplankton species decrease and certain filamentous species increase in abundance (and in severely acidified lakes, cover all surfaces with a thick mat). Acidification decreases the diversity and abundance of benthic (bottom-dwelling) invertebrates, which, because of their role as microdecomposers, are essential to nutrient cycling in aquatic systems. Reduced invertebrate populations result in fewer prey species for higher aquatic organisms.

Decreased decomposition by benthic organisms and bacteria results in the accumulation of organic debris, with less mineralization and release of organically bound nutrients. Strong acidity causes nutrient ions to bind to particles, decreasing their uptake by phytoplankton.

Acidification effects are profound, whether associated with acidic deposition or natural processes. As lakes become increasingly acidified, significant species changes and decreases in biomass production occur.

6.3.2.1.2 Terrestrial Ecosystems

Acidic deposition has the potential to directly and indirectly affect terrestrial plants and other organisms in natural ecosystems. Major scientific attention

Skeletal changes are usually manifested as diffuse thickening of long bones and calcification of ligaments, resulting in stiffness and lameness. Lame animals eat less because they have difficulty standing for any length of time. Affected animals become emaciated as a result of reduced food intake and difficult mastication. In dairy cattle this results in decreased milk production.

Although F poisoning is no longer a problem in North America and other developed countries, it may be occurring in developing countries where there is little or no environmental regulation.

6.2.2 Lead

Lead emissions from uncontrolled sources were a cause of livestock poisoning in North America in the recent past. Such Pb poisoning was also common in the early part of the twentieth century when lead arsenate insecticide was used as an orchard spray.

Air pollution-related poisoning of livestock in the United States was reported in the vicinity of primary and secondary Pb smelting operations up until the late 1960s. Poisoning was, for the most part, due to ingestion of Pb dust-contaminated forage. Lead poisoning may be acute or chronic depending on exposure level and duration. In cattle, early stages of acute Pb poisoning are characterized by excessive thirst, salivation, loss of appetite, constipation, delirium, and reduced milk production. Affected animals die when exposures are very high. Chronic poisoning results in a spectrum of symptoms, including diarrhea, colic, nervous disorders, swollen joints, lethargy, incoordination, bellowing stupor, rough coat, and emaciation, as well as a variety of metabolic changes similar to those observed in chronically exposed humans.

6.2.3 Other Toxic Exposures

In most cases when air pollution injury to livestock is confirmed, such injury has been associated with stationary sources processing minerals. These minerals contain biologically active elements that, when ingested in excessive amounts, produce toxic effects. Other elements in mineral dusts such as arsenic (As), selenium (Se), and molybdenum (Mb) have reportedly poisoned livestock and other animals.

6.3 Ecological Effects

Phytotoxic pollutants can cause injury to individual plants of a species, widespread injury to individual species (Ponderosa pine, red spruce, etc.), and, by

inference, whole ecosystems. In an ecosystem, the existence of all species is, to some extent, affected by the presence of all others. If a species such as Ponderosa pine is eliminated from forest stands in the San Bernardino Mountains, significant ecosystem changes will take place. Species that depend on Ponderosa pine for food and shelter must adapt to the new ecological order as Ponderosa pine is replaced by more O₃-tolerant species. Significant ecological changes would also occur as a result of other forest declines described previously.

When a population of a species is subject to an environmental stress, it responds in typical Darwinian fashion. The most sensitive, or least tolerant, individuals die and are eliminated. If the stress continues, the species survives, but individuals tolerant to the stress dominate the population. As such, the effect on ecosystems may be limited. Such responses can be expected for many species subject to low-level exposure to pollutants such as O₃, atmospheric deposition pollutants such as sulfuric and nitric acids (H₂SO₄ and HNO₃), increased exposure to ultraviolet (UV) light associated with stratospheric O₃ depletion, and climate changes associated with greenhouse gases.

Individual species, as well as ecosystems of which they are members, are relatively resistant to environmental stressors. If the stress is limited, they may genetically adapt without significant ecological changes. If the environmental stress is sufficient to eliminate one or more species or provide a competitive advantage to other species, significant ecological changes may take place. Major ecosystem changes are characteristic of aquatic systems undergoing significant acidification as a result of atmospheric deposition. They affect all levels of food chains, including plants and animals.

With the exception of acidic deposition, the effects of atmospheric pollutants on ecosystems have been little studied. The potential exists for subtle to major ecosystem changes as a result of

1. Direct exposures to phytotoxic pollutants such as O₃
2. Responses to components of atmospheric deposition (in addition to strong acids) such as nitrate N, elemental mercury (Hg), and methyl mercury (CH₃Hg); pesticides; endocrine disruptors such as polychlorinated biphenyls (PCBs) and dioxins; and other pollutants that accumulate in watersheds and estuaries
3. Increased UV radiation over portions of the southern and northern hemispheres
4. Global warming

6.3.1 Phytotoxic Pollutants

With the exception of major forest declines linked to O₃ exposures, few studies have been conducted to evaluate potential changes in plant, animal, and

has been given to evaluating potential causal connections between acidic deposition and "declines" of Norway spruce and beech in Germany and other countries of central Europe, high-elevation spruce and fir forests in the northern and southern Appalachian Mountains of the eastern United States, low-elevation spruce and fir forests in the northeastern United States, southern pines in the southeastern United States, and sugar maple in the northeastern United States and southeastern Canada.

As indicated in Section 6.1.3, acidic deposition has been implicated as a contributing factor to forest declines of high-altitude red spruce in the Appalachian Mountains and apparent widespread growth reductions in the southern Appalachian tree species. Acidic deposition has a significant potential to affect high-elevation eastern forest species because of acid cloud water (pH 2.8–3.8) exposures that occur upwards of 100 days/year. Such exposures result in alterations in plant nutrition, cold hardening of buds, and a variety of other physiological processes. Acidic deposition may cause reduced growth as a result of (1) foliar nutrient leaching; (2) reduced soil nutrient availability; (3) interference with normal root function associated with increased mobilization of Al^{3+} and inhibition of Ca^{2+} , magnesium (Mg^{2+}), and phosphorous (P^{2-}) uptake; (4) reduced carbon (C) levels due to reduced photosynthetic activity and increased respiratory C consumption; and (5) increased sensitivity to cold damage. Acidic deposition may also affect tree growth as a result of soil mobilization of Al^{3+} that causes direct toxic effects to roots. Acidification of forest soils results in interference with development of mycorrhizae, the symbiotic growth of roots and fungi essential for the normal growth of many forest species.

Direct effects of acidic deposition on forest species, as well as indirect effects resulting from changes in soil chemistry and microbiology, have the potential to cause significant changes in forest ecosystems. The magnitude of such effects over the long term (next half century) may be large.

6.3.2.2 Nitrogen

The atmosphere is a significant source of N input into terrestrial ecosystems, watersheds, and estuaries. Nitrogen is an important plant nutrient, as it is required for the synthesis of amino acids, proteins, nucleic acids, and chlorophyll. To a large extent, it governs the utilization of potassium (K), P^{2-} , and other nutrients.

6.3.2.2.1 Terrestrial Ecosystems

Until the industrial revolution, the availability of soil N was the limiting factor in the growth of trees and possibly other plants in forest ecosystems. Modern-day atmospheric inputs of N to forest environments is on the order of 5 to 20 times greater than that in the preindustrial era.

Nitrogen associated with atmospheric deposition serves as a plant nutrient in N-poor soils, particularly in forests. Such N inputs to forest ecosystems

may result in increased growth of some species and altered species composition and diversity because of changes in competitive relationships.

Soil N increases can change the vegetative structure of an ecosystem. When N becomes readily available in environments previously characterized by low N availability, plants adapted to such an environment will be replaced by those capable of using now-increased N levels. Such effects have been reported for heathlands in the Netherlands, where nitrophilous (nitrogen-loving) grass species have replaced slower-growing species. Herbaceous forest plant composition in the Netherlands has shifted in the past several decades to species commonly found on N-rich soils.

In other European countries, N deposition has altered the composition of nonwoody plants in mixed oak forests. Twenty of 30 species closely associated with high N deposition have increased in abundance.

Excessive N deposition may adversely affect the growth of forest trees. Decline of some tree species in German forests has been attributed to Mg^{2+} deficiencies caused by excessive N levels. Chronic N addition studies indicate that excessive N levels may result in decreased forest tree productivity and increased mortality. Studies in Vermont suggest that coniferous forest stands undergoing decline are being replaced by fast-growing deciduous forests that cycle N more rapidly. Plant succession and biodiversity are being significantly affected by chronic inputs of N into historically low-N-input environments.

A major evolving environmental concern is "N saturation" that results when atmospheric inputs to what are normally background soil N levels exceed the capacity of plants and soil microorganisms to utilize and retain it. Excess N "runs off," resulting in increased stream, river, and lake nitrate levels. Nitrogen saturation has been reported in spruce-fir ecosystems in the Appalachians, eastern hardwood watersheds in West Virginia, and mixed conifer and chaparral forests in the Los Angeles Basin.

A variety of ecosystem changes resulting from N saturation have been suggested. These include (1) permanent increase in foliage N and reduced P^{2-} and lignin in wood, (2) reduced productivity due to physiological disruptions, (3) decreased root growth, (4) increased nitrification and nitrate (NO_3^-) leaching, and (5) reduced soil fertility resulting from increased leaching.

Increased soil N can significantly alter nutrient cycling in terrestrial ecosystems. Processes affected include (1) plant nutrient uptake and allocation, (2) litter production, (3) release of N as NH_3 (ammonification) and conversion of NH_3 to NO_3^- (nitrification), and (4) leaching of NO_3^- and release of trace gases such as nitrous oxide (N_2O). In addition, under N saturation, soil microbial communities change from predominantly fungal (mycorrhizal) to those dominated by bacteria.

6.3.2.2.2 Aquatic Ecosystems

Nitrogen associated with atmospheric deposition changes the fertility, or nutrient condition, of lakes, rivers, streams, and estuaries (shallow water areas where rivers enter the sea). Increased plant nutrients in aquatic

Although organochlorine pesticides are, for the most part, no longer used in the United States, Canada, and Europe, they are still used in many parts of the world. Because of their persistence (half-life = ~12 to 15 years) and continued atmospheric transport, organochlorine pesticides are commonly measured in North American precipitation samples.

The environmental significance of this low-level contamination of the environment and movement through food chains is unknown. These substances have been reported to be endocrine disruptors in that they mimic estrogen, a female sex hormone. Major concerns have been expressed relative to their potential effect on male reproductive organs and processes, such as those observed in alligators associated with a spill of a large quantity of DDT.

The organochlorine pesticides, because of their persistence, mobility in the environment, and passage through food chains, have very likely contaminated every living thing on the planet and will likely continue to do so for some time.

6.3.2.4.2 Polychlorinated Biphenyls, Dioxins, and Furans

Although their use in the United States was discontinued in the 1970s, PCBs remain widespread contaminants of the Earth's environment. Like organochlorine pesticides, they are semivolatile and persistent. They are also biomagnified in food chains, with concentrations in aquatic organisms orders of magnitude greater than in the surrounding water. They affect the liver and nervous and reproductive systems and are animal carcinogens. The effects of PCBs on wildlife are largely unknown. Exposure through aquatic food chains is believed to be responsible for genetic or congenital abnormalities observed among fish-eating birds (particularly cormorants) in the Great Lakes Basin. Like other organochlorine compounds, PCBs seem to be endocrine disruptors.

Dioxins and furans are chlorinated organic compounds widely present in the environment at very low concentrations. They are characterized by their very high mammalian toxicity (LD_{50} [dose required to kill 50% of animals under test] = 2 ppb w/w), persistence, movement, and accumulation in food chains. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) has been shown to cause endocrine disruption, weaken immune systems, and cause adverse reproductive changes in wildlife species.

6.3.3 Stratospheric Ozone Depletion

The primary environmental concern associated with stratospheric O_3 depletion is increased UV-B radiation over Antarctica and potential increases over the northern hemisphere. UV light is a plant growth regulator; it controls cell elongation in terrestrial plants. As a consequence, plants tend to grow "shorter" in full sunlight. As a result of increases in UV-B exposure, plants may not grow as tall, and therefore, regions subject to increased UV-B levels

would not be as biologically productive. This could be a concern for annual crop plants and forest tree species.

Plants of species located at different latitudes are adapted to UV-B levels characteristic of their region. As such, it is likely that tolerant forms would, in a matter of a decade or so, begin to replace less tolerant forms in response to increased UV-B levels. Species would survive by adapting to the changed UV light conditions. Less tolerant or less genetically variable species may, however, be under severe environmental stress and be replaced by more tolerant species.

There is a significant potential for adverse biological changes in phytoplankton and other parts of the food chain in the upper zone of ocean water surrounding Antarctica. Exposures to UV-B can decrease photosynthesis and productivity in several marine species of algae and adversely affect various forms of larvae and other organisms. Algae or phytoplankton are the base of the Antarctic food chain that includes the very abundant krill (a small, shrimp-like animal) and higher-order species such as fish, birds, and sea mammals (e.g., seals and whales). As such, any major UV-B-related effects on phytoplankton could have major consequences for species in these food chains.

A worldwide decline in many amphibian species has been observed in the past several decades. The cause of this decline is not known. A few studies have shown that a number of amphibian species are very sensitive to near-surface UV-B levels. On this limited basis, a potential causal relationship between increased UV levels associated with stratospheric O_3 depletion and amphibian mortality has been proposed.

6.3.4 Global Warming

Atmospheric temperature is one of the most important environmental factors that affect the distribution of plant and animal communities around the planet. Temperature effects on individual plant or animal species and ecosystems are both direct and indirect (e.g., effects on water [H_2O] availability). Even slight changes in average atmospheric temperature can result in changes in the presence of a particular species in a given environment, its abundance, and its distribution. Limited evidence already exists that the near-surface planetary warming that has occurred in the past two decades has caused ecological changes. Projections of future global atmospheric warming, with associated effects in the polar regions (thinning of ice cover), coastal areas (sea level rises), and desert zones (increased desertification), as well as changes in precipitation patterns and migration of climatic zones, indicate that global warming will result in ecological changes, the likes of which the Earth has not experienced in thousands of years. These changes will affect, in varying degrees, most species that exist on our planet. The effects of global warming are expected to be particularly significant in polar regions and coastal areas.

ecosystems significantly increase the growth of algae and aquatic weeds. This increase in plant productivity results in increased biomass production at all levels of the food chain, including fish, and increases the turbidity of lakes and streams. Plant nutrients (e.g., NO_3^-), when present at elevated levels, may cause population explosions of algae called algal blooms. As these massive algal populations die, their decomposition results in episodic oxygen (O_2) depletion, with significant adverse ecological consequences. Plant nutrients contribute to the process of eutrophication, wherein freshwater lakes mature and fill in more rapidly as a result of increased biomass production and organic sediment deposition.

The atmosphere is but one source of plant nutrients that significantly affects the ecology of lakes, rivers, streams, and estuaries. Other sources such as agricultural runoff and wastewater treatment dominate the N budget of such systems. Nevertheless, in some stream, river, and lake waters, the atmosphere may be the source of 40% of nitrate N. Atmospheric deposition of NO_3^- to estuaries, such as those of the Chesapeake Bay, may be more significant in terms of ecological effects than in freshwater aquatic ecosystems. In the latter, the limiting factor for plant growth is P^{3-} , not N. This is not the case in estuaries.

6.3.2.3 Mercury and Other Trace Metals

Mercury deposition on land and water surfaces, and its accumulation in the muds of freshwater lakes, is an increasing environmental and public health concern. Although, in a relative sense, environmental Hg levels are low, their significance is greatly increased because Hg is biomagnified in food chains either as ionic Hg^{2+} or organic CH_3Hg . Methylmercury, produced by microorganisms as they transform Hg from its elemental form, tends to remain dissolved in water. As such, it moves upward through food chains and accumulates in fish tissues. This process is called biomagnification. It can result in CH_3Hg or Hg^{2+} levels in fish that are orders of magnitude higher than those found in water.

Because fish are at the top of most aquatic food chains, Hg levels in fish may be high. They are so high in some cases that the US government issues fish consumption advisories for many bodies of water, particularly in the Great Lakes Basin and Florida Everglades.

The primary environmental concern associated with Hg pollution has been the potential exposure of the fish-consuming public to unsafe Hg levels. Mercury is a very toxic substance in its elemental, ionic, and organic forms.

Emissions to the atmosphere from major Hg sources have been regulated under hazardous air pollutant standards since 1973, and significant limits have been placed on industrial water sources. Nevertheless, because of emissions from unregulated sources such as coal-fired power plants, Hg pollution of the environment is a major concern.

Although regulatory efforts have focused on public health, Hg poses an exposure/toxicity risk to a number of wildlife species that consume large quantities of fish. These include bald eagles, ospreys, loons, kingfishers, herons, and mink. It also poses a poisoning risk to sharks in near-shore waters. There is only limited evidence available on the chronic effects of Hg exposure on wildlife species. Significant neurological and reproductive system effects in populations of fish-eating birds and mammals may be occurring.

Atmospheric deposition contains a number of other trace metals that can accumulate in the environment. These include Zn, copper (Cu), Pb, Ni, tin (Sn), chromium (Cr), cadmium (Cd), silver (Ag), Mn, and vanadium (V). Heavy metals tend to accumulate in forest soil humus or soil layers immediately below where root activity occurs. As a consequence, they may be toxic to roots and soil microorganisms and interfere with nutrient cycles. Heavy metal deposition has affected the root growth of plants in heavily contaminated soils around smelters. The effects of low-level heavy metal contamination associated with atmospheric deposition have received only limited study. Some invertebrates (e.g., earthworms that consume leaf litter) are known to accumulate Cd, Pb, Zn, and Ni.

6.3.2.4 Organochlorine Compounds

6.3.2.4.1 Pesticides

The era of widespread use of persistent organochlorine pesticides in the United States began coming to a close with a 1972 ban on the use of DDT; cancellation of the registrations of other persistent pesticides or restrictions on their use followed in the next decade.

Because of their low volatilities ($\sim 10^{-4}$ mmHg), organochlorine pesticides have never been major atmospheric pollutants of concern. Nevertheless, as semivolatile and very persistent compounds, they have rather remarkable environmental mobility. For example, they have been found in fat tissue of Antarctic penguins 6,450 km (4,000 miles) from the nearest site of application.

Pesticides move through the atmosphere by a continual process of volatilization and deposition on particles and other surfaces. As such, they are commonly found in atmospheric deposition samples, albeit at very low levels.

Organochlorine pesticides, such as Hg, are bioaccumulated. Consequently, they are biomagnified in food chains, with the highest levels in fish and predator birds. The effects of pesticides on predator birds in the period 1950 to 1975 were dramatic, resulting in a precipitous decline in such species in North America. With the ban of DDT and other organochlorine pesticides, and restrictions in the use of other similar organochlorine compounds, pesticide levels in fish and birds began to decline, with the latter slowly recovering from its endangered species status (e.g., bald eagles, ospreys, peregrine falcons).



FIGURE 6.6
Erosion of carbonate column in Maltese square. (Courtesy of DHD Multimedia Gallery, <http://aj.hd.org>.)

A significant concern is the Acropolis, located downwind of Athens, Greece. Although chemical erosion of marble structures in the Acropolis has been occurring for more than 100 years, rapid population growth and use of high-S heating oils since World War II have greatly accelerated their destruction.

In addition to the Acropolis, the Colosseum in Rome and the Taj Mahal in India are in various stages of dissolution. In many European cities, marble statues have had to be moved indoors. Cities such as Venice have enacted legislation to preserve and restore hundreds of damaged piazzas, churches, and historical buildings. The grand cathedrals of Europe (e.g., Notre Dame, Chartres, and Cologne) are constantly undergoing restoration of acid-ravaged limestone statuary and other features on their external façades.

6.4.3 Paints

Paints consist of two functional components: vehicles and pigments. The vehicle consists of a binder and additives that hold the pigment to a substrate surface. The principal materials used as vehicles include hydrocarbon solvents, glycols, and resins, which may be natural, modified natural, or synthetic. Pigments, classified as white or colored, provide aesthetic appeal, hiding power, and durability. White Pb, titanium dioxide (TiO_2), and zinc oxide (ZnO) have been

widely used white pigments. Colored pigments are a variety of mineral, metal, and organic compounds. The function of paints is to provide an aesthetically appealing surface coating that protects underlying material from deterioration.

The appearance and durability of paints are affected by natural weathering processes. Paint weathering is accelerated by environmental factors such as moisture, temperature, sunlight (particularly UV light), and fungi. Paint appearance and durability may also be affected by air pollutants such as PM, H_2S , SO_2 , NH_3 , and O_3 .

Air pollutants affect the durability of painted surfaces by promoting chalking, discoloration, loss of gloss, erosion, blistering, and peeling. They may also decrease paint adhesion and strength and increase drying time. Sulfur dioxide can increase the drying time of some paints by reacting with drying oils and competing with auto-oxidative curing reactions responsible for cross-linking the binder. Erosion of oil-based house paint is reportedly enhanced by exposure to SO_2 and high relative humidity. Apparently, SO_2 reacts with extender pigments such as calcium carbonate (CaCO_3) and ZnO . Particles can also damage painted surfaces by serving as carriers for corrosive pollutants or by staining or pitting painted surfaces.

One of the more obvious effects of pollutants on paints is the dirty appearance that results from accumulation of aerosol particles. These may cause chemical deterioration of freshly applied paints that have not completely cured. Particles may also serve as wicks that allow chemically reactive substances to migrate into underlying surfaces, resulting in corrosion (if the underlying material is metallic) and subsequent paint peeling.

Exterior paints pigmented with white Pb may be discolored by reaction of Pb with low atmospheric levels of H_2S . Blackening of the paint surface by formation of lead sulfide (PbS) can occur at H_2S exposures as low as 0.05 ppmv for several hours. The intensity of discoloration is related not only to the concentration and duration of H_2S exposure, but also to Pb content of the paint and the presence of moisture.

There have been numerous reports over the last several decades of damage to automobile paints and coatings. Damage occurs on horizontal surfaces of freshly painted vehicles and appears as irregularly shaped and permanently etched areas. It is easily observed on dark-colored vehicles and appears after evaporation of moisture droplets. The consensus in the automobile industry is that this paint damage problem is due to environmental "fallout." The most likely cause is believed to be acid rain, as chemical analyses of exposed test panels have shown elevated levels of sulfate.

6.4.4 Textiles and Textile Dyes

Textiles consist of a basic fiber component and additives such as dyes, water repellents, and finishes. Each of these is subject to pollutant damage.

Exposures to atmospheric pollutants may result in significant deterioration and weakening of textile fibers. Fabrics such as cotton, hemp, linen, and

Air Quality and Emissions Assessment

The quality of air in our communities, countryside, and even remote locations changes from hour to hour, day to day, and over longer timescales. Concentrations of pollutants depend on the magnitude of emissions from individual sources, source emission density, topography, and state of the atmosphere.

Air quality can be defined qualitatively. It is poor when pollutants (1) cause a reduction in visibility, (2) soil building surfaces and damage materials, (3) damage crops and other plants, or (4) cause adverse health effects. It is deemed good when the sky appears clean and no adverse environmental effects are evident.

Qualitative assessments of air quality, although indicative of the nature of the atmosphere relative to pollution concerns, cannot be used to support regulatory programs designed to protect the environment. Air quality must therefore be characterized quantitatively. As such, it is defined in the context of concentrations of specific target pollutants and observed environmental and public health effects.

Protection of human health and the environment from adverse effects of pollutants is the primary goal of all air pollution control programs. Protection and enhancement of air quality require that good data on ambient concentrations of major pollutants and emissions from individual sources and groups of sources be available to regulatory authorities. Systematic efforts to monitor ambient pollutant concentrations both temporally and spatially, as well as to characterize and quantify emissions, are vital to the success of all air quality protection and pollution control programs. These efforts include ambient air quality monitoring, source emissions assessment, and modeling.

7.1 Air Quality Monitoring

Pollutant levels in North America are assessed using systematically conducted, long-term ambient air quality monitoring efforts. In the United States, monitoring provides data to

rayon are particularly sensitive to acid-forming gases and aerosols. Acids chemically break their cellulose chains, producing water-soluble products that have low tensile strength. Synthetic fibers such as nylon may also incur significant acid damage as well as undergo oxidation by NO_2 , which reduces the affinity of nylon fibers for certain dyes.

A number of pollutants can react with fabric dyes by oxidation or reduction reactions, causing them to fade. Fading of textile dyes associated with NO_2 exposure, particularly NO_2 , has had a long history. For example, NO_2 emissions from open electric-arc lamps and incandescent gas mantles caused fading of stored woolen goods in Germany prior to World War I. Nitrogen oxides emissions from gas heaters were also believed to be responsible for a serious fading problem on acetate rayon fabrics during the 1930s. During the 1950s, NO_2 emissions from home gas dryers caused fading of colored cotton fabrics. Nitrogen dioxide-induced fading has also been reported for fabrics exposed to urban environments.

Reports of NO_2 -induced fading of textile materials from ambient exposures were soon followed by observations that ambient O_3 levels were also a major fading cause. In the early 1960s, O_3 fading was reported for polyester-cotton permanent press slacks stored in warehouses or on retail shelves. Some manufacturers suffered significant economic losses. Fading of nylon carpets was a problem along the Gulf Coast from Florida to Texas. Blue dyes were particularly sensitive to a combination of ambient O_3 exposure and high humidity. This Gulf Coast fading was overcome by using O_3 -resistant dyes and modifying nylon fibers to decrease exposure to O_3 . Pollutant-induced fading of fabric dyes has posed significant challenges for textile manufacturers. Consequently, the industry had to develop resistant dyes and chemical inhibitors to mitigate such problems.

6.4.5 Paper and Leather

Papers that came into use after 1750 are very sensitive to SO_2 because of its conversion to H_2SO_4 by the metallic impurities in paper. Sulfuric acid causes paper to become brittle, decreasing its service life. This embrittlement is a major concern to libraries and museums in cities with elevated SO_2 concentrations, as it makes the preservation of historical books and documents more difficult.

Historical book preservation involves more than the paper component. Air pollution damage to leather-bound books is also a major concern. Damage to leather is initially seen as cracking. Cracking results in increased leather exposure, thus accelerating deterioration. Leather eventually loses its resiliency and turns to a reddish brown dust.

6.4.6 Rubber

Ozone can induce cracking in rubber and plastic compounds, most notably those under stress. The depth and nature of cracking depends on O_3

concentration, rubber or plastic formulation, and degree of stress. Unsaturated natural and synthetic rubbers, for example, butadiene-styrene and butadiene-acrylonitrile, are especially vulnerable to O_3 cracking. Ozone reacts with the double bonds in such products. Saturated compounds such as thiokol, butyl, and silicon polymers are relatively resistant to O_3 cracking. Rubber compounds are often formulated by the addition of antioxidants to reduce cracking. This is particularly important in rubber tires.

Rubber cracking was one of the first effects of smog observed in the Los Angeles area. During the 1950s, it was used to monitor O_3 concentrations. Under standardized conditions, O_3 concentrations could be directly related to the depth of O_3 -induced cracks.

6.4.7 Glass

With the exception of F, glass is resistant to most air pollutants. Fluoride reacts with silicon (Si) compounds to produce a familiar etched appearance. Etching of glass has been observed in the vicinity of major F sources such as phosphate fertilizer mills, Al smelters, enamel frit plants, and even steel mills. Continuous exposure to F may render glass opaque.

6.4.8 Economic Losses

Economic losses due to air pollution-induced damage to materials are difficult to assess; it is very difficult to distinguish between natural deterioration and that caused or accelerated by air pollutants. Only limited efforts have been made to quantify the costs associated with air pollution damage to materials. It is probable, however, that such costs are in the tens of billions of dollars.

6.5 Odor Pollution

The welfare effects described in this chapter generally do not affect people directly. Odor, on the other hand, does. Although exposure to malodorous substances may cause symptoms in some individuals, the problem of odor, or odor air pollution, is usually viewed as being one of annoyance.

The term *odor*, as used in everyday speech, commonly carries with it an unpleasant connotation. The term defined by scientists is neutral; it connotes only that some volatile or semivolatile substance is sensed by the human olfactory system.

The ability to smell chemical substances is common among members of the animal kingdom. In many species, the olfactory sense plays an important role in locating food, attracting individuals of the opposite sex for breeding,

1. Determine compliance with National Ambient Air Quality Standards (NAAQSs) for seven pollutant categories (criteria pollutants) in air quality control regions (AQCRs) or portions thereof
2. Determine long-term trends
3. Determine human exposures
4. Support the Air Quality Index (AQI) program
5. Support emissions reduction programs
6. Determine effectiveness of emission control programs
7. Support environmental assessments such as visibility impairment and degradation of watersheds
8. Support research efforts designed to determine potential associations between pollutant levels and adverse health and environmental effects

Air quality monitoring efforts are important in identifying new pollutant-related environmental problems (e.g., mercury [Hg] deposition) and tracking changes in tropospheric and stratospheric concentrations of ozone (O_3), destroying chemicals (as well as O_3 itself) and atmospheric concentrations of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs).

7.1.1 Monitoring Considerations

Air quality monitoring involves numerous measurements of individual pollutants over time at a number of locations in organized, systematic programs. Concentration measurements are made from samples of small volumes of ambient air.

7.1.1.1 Sampling

Because of the vastness and dynamic nature of the atmosphere, it is not possible to determine the infinite number of concentration values typical of individual pollutants. As in other instances where a population of values is potentially large, pollutant concentrations must be inferred from a relatively limited number of samples. Consequently, they must be determined from fixed-site monitors whose locations reflect the objectives of air quality monitoring programs.

Concentrations are determined by collecting pollutants in or on a sampling medium or in automated continuous systems, where they are drawn through a sensing device. In manual methods, sampling and analysis are discrete events, with sample analysis occurring days to weeks after collection. In automated systems, sampling and analysis are simultaneous or near-simultaneous events and concentrations are measured in real time.

In manual methods, a sufficient amount of pollutant must be collected to meet the lower limit of detection (LOD) requirements of the analytical procedure used. This quantity will depend on the atmospheric concentration and sample size (the volume of air that passes through or comes in contact with the sampling medium). Sample size is a direct function of sampling rate and duration; samples are collected intermittently.

Sampling rates for individual pollutants using manual methods reflect collection efficiencies and instrument limitations. Collection efficiency is the ratio of pollutant collected to the actual quantity present in the air volume sampled. It depends on the sampling technique employed and on the chemical and physical properties of individual pollutants. For gases, collection efficiency decreases as flow rate increases above the optimum value. Optimum collection efficiencies are often achieved at relatively low sampling rates for gas-phase contaminants (<1 L/min). Because of low flow rates or low collected pollutant mass, sampling duration may be extended to collect a sufficient quantity of pollutant for analysis. For some gas-phase substances, refrigeration or use of preservatives is necessary to minimize pollutant loss before samples are analyzed.

In continuous real-time sampling, the analytical technique is usually sensitive enough that the sample size or volume needed to accurately detect and quantify specific pollutants is relatively small (typically milliliters). As a consequence, flow rates used in such instruments are also relatively low (milliliters per minute), and optimal rates of flow are used to achieve the sensitivity and accuracy for which the instruments are designed.

7.1.1.2 Averaging Times

Collection and analytical limitations associated with manual, intermittent methodologies often require extended sampling durations; thus, concentration values are integrated or averaged over the sampling period. Sampling durations required to collect samples, and intended use of the data, determine the averaging time. For example, 24-h averages are appropriate for long-term trends.

The real-time air quality monitoring instruments used for more than four decades provide a continuous record of fluctuating concentrations. Although such data are deemed more useful than integrated data obtained from intermittent samples, real-time data are so voluminous that they are, for the most part, uninterpretable. As a consequence, data from real-time monitoring instruments are integrated to provide hourly average concentrations or concentrations reflective of the needs of NAAQSs. For pollutants such as O_3 , in which peak levels occur for a limited period, 8-h averaging times are used. Differences in average concentrations associated with real-time data are illustrated in Figure 7.1.

Averaging times are specified for regulated air pollutants. For example, the averaging times for particulate matter with aerodynamic diameters of

The precision of a sampling/analytical technique is determined from calculations of the mean of repeated measurements and its standard deviation. In a normally distributed population, approximately 67% of sample values are within approximately 1 standard deviation (σ) of the mean; 95% are within 2σ values.

Standard deviation can be calculated from the following equation:

$$\sigma = \left[\sum_{i=1}^n (X_i - \bar{X})^2 / N \right]^{0.5} \quad (7.8)$$

where $\bar{X}$ is the mean, X_i is the individual measured value, and N is the total number of measurements.

By using a programmable calculator or spreadsheet software, 1σ is determined to be 0.048. Therefore, the precision of our sampling results is more or less 0.048 ppmv. Precision, however, is usually reported as a percentage by calculating the coefficient of variation (CV), where $\bar{X}$ is the sample mean.

$$\begin{aligned} CV &= (\sigma/\bar{X})(100) \\ &= 5.2\% \end{aligned} \quad (7.9)$$

Using approximately 1σ as a reference, the precision of our measurements was more or less 5.2%.

In this case, our sampling/analytical technique had high relative accuracy (92.5%) and good precision (low variability). Sample precision values within more or less 10% of the measured value are considered to be good.

Differences in the concepts of accuracy and precision can be seen in Figure 7.5. In the first target (a), values are scattered and do not come close to the target's center. In the second (b), all values are close to the middle of the

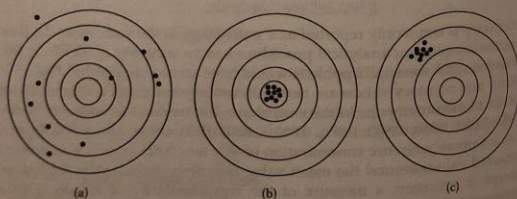


FIGURE 7.5
Graphical illustration of accuracy, precision, and bias.

target. In the former, accuracy is relatively low, with poor precision. In the latter, results are both accurate and precise.

The third target (c) illustrates the concept of bias. Results show good to excellent precision but deviate from the true value in a systematic way. Bias occurs as a result of calibration errors (the instrument may be out of calibration), but may also be due to hardware problems associated with instrument electronics or systematic software problems.

Accuracy in the context of air quality monitoring activities includes a combination of random (precision) and systematic (bias) errors. The term accuracy is used when these two types of error cannot be separated. As a consequence, accuracy values are stated in the same format as precision. Reported accuracy values include precision determinations. For most ambient air quality monitoring activities, accuracies (which take precision into account) within more or less 10% of the true value are considered acceptable. For passive sampling techniques, accuracy values within approximately 25% are considered acceptable.

7.1.2.2 Calibration

All sampling and monitoring instruments must be periodically calibrated to reduce bias-associated errors and assure data reliability. Calibration is a process in which measured values are compared with standard reference values (in the case of pollutant concentrations) or volume airflows are measured using standard airflow measuring techniques and devices. When bias-type errors are identified, instrument adjustments are made to reduce observed errors, that is, bring the instrument back into calibration.

In some manual sampling methods, instrument calibration is limited to measuring airflow rates. Such calibration may be conducted using flow-measuring instruments based on primary or secondary standards. A primary standard is one that is directly traceable to the National Institute of Standards and Technology (NIST). A primary standard would be, e.g., a bubble meter (gas burette and soap solution used for low flows) or volumetric flask. In the latter case, the volumetric flask may be used to calibrate wet or dry test meters that may be used to calibrate rotometers. Wet and dry test meters and rotometers are secondary standards. Because of their portability and ease of use, field instruments are commonly calibrated with secondary standard devices (such as rotometers). Based on U.S. Environmental Protection Agency (U.S. EPA) regulations, airflow rate measurements must be made using instruments traceable to an authoritative volume (e.g., NIST).

Monitoring instruments for gas-phase pollutants such as O_3 , NO_2 , CO , and SO_2 must be periodically calibrated to determine whether measured values are consistent with reference values. Concentration calibrations are made using gas standards traceable to a NIST reference material or a NIST-certified gas manufacturer's internal standard.

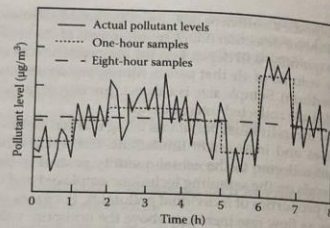


FIGURE 7.1

Pollutant concentrations associated with different averaging times applied to real-time data.

less than or equal to $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) are 24 h and 1 year, but for those with diameters of less than or equal to $10 \mu\text{m}$ (PM_{10}), it is 24 h; for carbon monoxide (CO) it is 1 and 8 h; for ozone (O_3), 8 h; for sulfur dioxide (SO_2), 1 h and 3 h; for nitrogen dioxide (NO_2), 1 h and 1 year; and for lead (Pb), 3 months. Concentrations averaged over the entire year may be based on a continuous record of measurements or, in the case of PM_{10} and Pb, a more limited number of samples.

7.1.1.3 Sampling Techniques

The principal objective of sampling is to collect a pollutant or pollutants for subsequent analysis or provide a sensing environment for real-time measurements. Both require a system whereby gases or particles are drawn to the surface of a collecting medium or into a sensing environment. These functions are accomplished by sampling trains that include a vacuum pump, flow regulator, and collecting device or sensing unit. Sampling trains for gases may also utilize filters to prevent particles from entering the collection unit, scrubbers for interfering gases, and the like.

Based on the type of information desired, as well as the collection and analytical limitations, sampling may be conducted by passive, intermittent, or continuous procedures. Such procedures provide air quality data representing a range of averaging times, from the instantaneous values of continuous systems to the 7-day average employed for some passive samplers.

Because of low cost and ease of use, passive sampling techniques were widely used in the early years of pollution control. These early techniques included the capture of particles on sticky paper, collection of settleable particles in dustfall jars or buckets, and measurement of sulfation rates on lead dioxide-impregnated gauze-covered cylinders (Pb candles). These

techniques were relatively crude and abandoned with the advent of dynamic sampling methods.

New developments in passive sampling technology in the past three decades have made passive sampling a widely accepted and used methodology for personal exposure monitoring in occupational environments, measurement of indoor air contaminants such as formaldehyde (HCHO) and radon (Rn), and air quality and health research studies. Such sampling devices include small badge-type devices, tubes, canisters, and the like (Figure 7.2). Because of its low cost, passive sampling techniques would be appropriate for use in ambient monitoring activities of developing nations.

In grab sampling, air samples are collected in a relatively short time (seconds or minutes) using a variety of devices. Grab sampling is typically used in problem environments (e.g., chemical spills) as a means of identifying pollutants and their concentrations present at the time samples were collected. Grab sampling using evacuated canisters for collection and identification of volatile organic compounds (VOCs) is an integral part of Photochemical Assessment Monitoring Stations (PAMS) network activities.

Intermittent sampling using dynamic sampling methods (i.e., manual methods) came into widespread use in air quality monitoring networks in the United States in the 1950s through the early 1970s, both for PM and gases such as SO_2 and nitrogen oxides (NO_x). Intermittent sampling has the advantage of relatively low cost and provides reasonably useable data. It has the disadvantage of relatively long averaging times (typically 24 h), historically viewed by regulators as undesirable for gas-phase pollutants. Intermittent sampling continues to be the sampling method of choice for PM_{10} , $\text{PM}_{2.5}$, Pb, and atmospheric deposition networks. Because of its relatively low cost, intermittent sampling is often used to supplement continuous monitoring systems. Intermittent sample collections at multiple locations may provide more useful data than a continuous record at a few locations. It is particularly useful where resources for pollutant monitoring are limited.



FIGURE 7.2

Passive ozone sampler. (Courtesy of Ogawa & Company, USA Inc.)

Nominal regulatory efforts to control air pollution in the United States began in the late nineteenth and early twentieth centuries when several large cities approved ordinances to control "smoke" produced by a variety of industrial activities. Although largely ineffectual because they lacked enforcement authority, these smoke ordinances nevertheless served as forerunners of present-day regulatory programs.

In response to the increasingly worsening smog problem in its southern coastal area, California began serious efforts to control air pollution in the 1950s. As scientists unraveled the chemistry of smog, regulatory efforts changed from controlling emissions from stationary sources to those from automobiles. As a consequence, by the late 1960s, both California and the federal government began to earnest their significant and continuing regulatory efforts to reduce emissions from motor vehicles.

By the 1960s, there was increasing recognition at all governmental levels that air pollution was a serious environmental problem. Many state and local governments began to form agencies and develop regulatory frameworks to control air pollution. These efforts (in retrospect) were relatively timid and, for the most part, not very effective.

As the modern environmental movement evolved, the premise that polluted cities and countryside were a price of progress was no longer accepted. A major change occurred in American attitudes. The economic well-being that provided Americans the so-called good life was seen to diminish the quality of the environment in which fruits of economic prosperity were to be enjoyed. The desire of Americans to prevent further deterioration and improve environmental quality gave rise to the significant regulatory efforts to control air pollution and other environmental problems that have taken place since 1970.

8.1 Nonregulatory Legal Remedies

Before modern regulatory air pollution control programs, individuals or groups of citizens were limited in what they could do to abate the pollution adversely affecting them. They could ask corporate officers and others responsible for managing sources to be better neighbors and appeal to their

8.3.1 1955 Clean Air Legislation

Legislation enacted in 1955 authorized the Public Health Service, of the Department of Health, Education, and Welfare (DHEW), to conduct air pollution research and training programs and provide technical assistance to state and local governments. It affirmed that state and local governments had the fundamental responsibility for air pollution control. Amendments to this law in 1960 and 1962 called for special studies relating to health effects associated with motor vehicle-related pollutants.

8.3.2 1963 Clean Air Act

In response to the deteriorating quality of air in postwar United States, Congress passed the CAA of 1963. The CAA broadened the federal role in abating air pollution. Specifically, it provided for (1) grants for program development and improvement of state and local air pollution control efforts; (2) accelerated research, training, and technical assistance; (3) federal enforcement authority to abate interstate air pollution problems; and (4) federal research responsibility for automobile and sulfur oxides (SO_x) pollution. Although the federal role was considerably expanded, state and local governments were primarily responsible for air pollution control.

8.3.3 Motor Vehicle Air Pollution Control Act

In 1965, Congress amended the 1963 CAA. These amendments were described as the Motor Vehicle Air Pollution Control Act. It authorized the secretary of the DHEW to promulgate emission standards for motor vehicles. As a consequence, federal emission standards were established for all 1968 model light-duty motor vehicles. The 1965 amendments also established the National Air Pollution Control Administration (NAPCA) within the DHEW to provide regulatory leadership in the nation's efforts to control air pollution.

8.3.4 Air Quality Act of 1967

Although some progress was made under the CAA of 1963, control programs at all governmental levels remained relatively weak and air pollution problems continued, for the most part, unabated. In 1967, Congress attempted to strengthen this country's air pollution control efforts by enacting the Air Quality Act. Many of the regulatory concepts developed in the 1967 legislation continue to provide the framework for current control efforts. Of special significance were the institution of a regional approach to air pollution control and the development and implementation of air quality standards.

The Air Quality Act of 1967 required NAPCA to designate AQCRs and develop and issue air quality criteria and control technique information. After the federal agency completed these mandated requirements, individual

states were to develop state air quality standards and plan for their implementation on a fixed time schedule. Air quality criteria documents were to serve as the scientific basis for development of air quality standards.

The Air Quality Act also provided for the continuation of the federal role in air pollution research and development, training programs, and grants-in-aid to state and local air pollution control programs. Although federal authorities were given significant new powers to initiate lawsuits whenever interstate violations occurred, states maintained primary responsibility for enforcement.

Progress under the Air Quality Act was slow and limited. States could not promulgate air quality standards until the NAPCA designated AQCRs and issued air quality criteria and control technique documents for specific pollutants. These tasks took considerable time; for example, air quality criteria documents for SO_x and PM were not issued until 1969; for HCs, carbon monoxide (CO), and oxidants, 1970; and for nitrogen oxides (NO_x), 1971. The process of designating AQCRs was also very slow. Publication of control technique documents was carried out more expeditiously.

8.3.5 1970 Clean Air Act Amendments

In 1970, public concern for environmental quality had reached its zenith. In response to limited progress under the Air Quality Act of 1967 and public support for strong legislation, Congress enacted tough new CAA Amendments. The NAPCA was eliminated and its air pollution control functions were transferred to the U.S. EPA, an independent federal agency created by executive order of the president.

The CAA Amendments of 1970 sought to remedy deficiencies of earlier legislation. Most importantly, they completed federalization of air pollution control efforts, provided significant federal enforcement authority, and placed air pollution control on a rigorous timetable.

Specific provisions of the 1970 CAA Amendments included (1) setting uniform national ambient air quality standards (NAAQSs), (2) immediately designating AQCRs, (3) requiring state implementation plans (SIPs) to achieve NAAQSs, (4) setting stringent new automobile exhaust emission standards and standards for fuel additives, (5) setting emission standards for new or significantly modified sources and HAPs, (6) allowing the right of citizen suits, and (7) providing for federal enforcement authority in air pollution emergencies and interstate and intrastate air pollution violations.

8.3.6 1977 Clean Air Act Amendments

The goal of the 1970 CAA Amendments was to achieve clean air for all regions of the country by July 1, 1975. Although significant progress for some pollutants was made, many AQCRs did not achieve one or more NAAQSs by the congressionally mandated deadline.

be the most sensitive, that is, asthmatics, children, the aged or infirm, those with existing cardiovascular disease, and the like. As a consequence, ambient air quality standards are much more stringent than occupational standards designed to protect nominally healthy working adults.

Because air quality management strategies are based on the premise that a safe level of exposure (a threshold) exists, they are generally not applied to contaminants not known to have threshold values. It has been widely accepted in both the scientific and regulatory communities that there is no generally safe level of exposure to carcinogens.

Once an air quality standard for a pollutant or pollutant category has been promulgated, regulatory authorities at federal, state or provincial, and local levels are responsible for developing and implementing control and management practices (tactics) that will ensure that air quality standards are not exceeded.

Air quality management, although generally assumed to be a cost-effective approach to achieving air quality goals, is a relatively complicated undertaking. Its complexity involves both technical and political dimensions. Regulatory authorities must select and implement tactics that, in their best judgment, will achieve each air quality standard. In the case of ozone (O_3), control efforts have been confounded because of uncertainties associated with the contributions of anthropogenic and biogenic sources of hydrocarbons (HCs) to tropospheric O_3 chemistry, as well as other factors. In efforts to achieve particulate matter (PM) standards, regulatory authorities attempted to employ a control tactic that made both technical and economic sense but was not politically popular. Such was the case with prohibitive bans on leaf burning in autumn. Although relatively cost-effective, it has been politically unacceptable to some communities. On paper, air quality management is a highly practical and cost-effective control strategy. However, as is the case with many things in life, "the devil is in the details."

8.2.1.2 Emission Standards

In an emissions standards strategy, limits are placed on the maximum quantity (typically mass per unit time or thermal input) of a pollutant or pollutants that can be emitted from specific sources. The same emission standard is applied equally to all sources in a source category; that is, all members of a category must comply with the emission limit without regard to existing air quality. The same emission limits apply to sources in "clean" or "dirty" air regions.

With the exception of hazardous or toxic pollutants in the United States, emission standards, when used as a strategy, are governed by practicability; that is, emission standards reflect the highest degree of pollution reduction achievable taking cost of control into consideration.

The "best practicable means" or "good practice" approach is widely used for the development of emissions standards in the United States and other

developed countries. The term *practicable* indicates economic, technical, and political practicality. The "best practicable means" in practice may be the degree of emission reduction achieved by the best industrial plants in a source category, or technology that can be reasonably applied by borrowing from other industries. Implicit in this approach is that emissions standards may become more stringent (at least for new sources) as control technology improves and becomes more affordable. "Best practicable means," the traditional approach to air pollution control in Europe, would be equivalent to what is described in the United States as "reasonably available control technology" (RACT). Such requirements are generally applied to new or significantly modified existing sources under new source performance standards (NSPSs), to be discussed later in this chapter, and to achieve air quality standards in some air quality control regions (AQCRs).

An emission standards strategy may also require very stringent emission limits. For pollutants that pose unique health hazards, for example, mercury (Hg), beryllium (Be), benzene, radioactive isotopes, and asbestos, emission reduction requirements reflect "best-available control technology" (BACT). The objective of BACT standards is to achieve the highest degree of emission reduction that technology is capable of, with a more limited consideration of capital and operating costs. New coal-fired utilities in Class I prevention of significant deterioration (PSD) regions (see Section 8.4.6) are required to use BACT.

The 1990 Clean Air Act (CAA) Amendments require setting maximum achievable control technology (MACT) standards for toxic or hazardous air pollutants (HAPs). This concept, in theory, suggests a higher degree of emission control than BACT. This is because emissions reductions can be achieved by a variety of control practices other than treating just waste gas streams.

Emissions standards are usually specified in some numerical form. In the case of coal-fired power plants licensed under the 1972 NSPS for sulfur dioxide (SO_2), the emission limit is 1.2 lb of SO_2 /MBtu (million British thermal unit). Numerical standards can be based on heat input (lb/MBtu), unit of time (lb/h), weight per unit air volume (grains/standard cubic foot), or weight of process material (lb/ton). They may also be prescribed in metric units; in some cases, mixed units (US and metric) are used (e.g., g/mi).

Emission standards have the advantage of simplicity. There is no need for extensive and expensive air quality monitoring networks, modeling to determine compliance, and complex technical and public policy decisions. All sources in the source category must meet the same requirements regardless of existing air quality. It is a highly attractive control strategy from an administrative standpoint. As used in the United States, it has the advantage of being applied to special pollution concerns such as new sources and pollutants believed to pose uniquely hazardous or toxic exposure problems.

Use of emission standards as a control strategy also has limitations or problems. Although costs are taken into consideration in setting emission limits,

sense of civic responsibility. Such appeals (if many of them were indeed made) would, for the most part, have gone unheeded. Pollution abatement requires the allocation of what many economists and corporate financial officers describe as unproductive resources, that is, money that does not add to product value.

In the absence of strong governmental regulatory programs, a citizen or group of citizens has a right to file suit against a source employing common-law legal principles. Although significant air pollution control regulations have been in place for more than four decades, we continue to have this right.

Individuals claiming injury from emissions produced by a source can file a civil suit against the source in an effort to recover damages and abate the problem. Such suits are called torts. Tort law involves a system of legal principles and remedies that attempts to address harm to individuals or their property. Historically, both nuisance and trespass principles of tort law have been used to address claims of harm associated with air pollution.

8.1.1 Nuisance

A nuisance is an intentional or negligent act that results in an unreasonable interference with the use and enjoyment of one's property. It may be private (affecting some individuals and not others) or public (affecting everyone equally). Under the private nuisance concept, the plaintiff, or injured party, must convince a judge or jury that the action is unreasonable. If the suit is successful, he or she is entitled to recover damages. To abate the problem, however, the plaintiff must seek an injunction against the source.

In deciding whether to grant such an injunction, the court must balance the equities; that is, it must take into account the following: (1) extent of damage, (2) cost of pollution abatement, (3) whether the pollution source was on the scene first, and (4) the economic position of the polluting source in the community. If the dispute is between a corporation with a large local work force and a single party, or even a group of landowners, courts invariably balance the equity in favor of the polluting source and refuse to grant an injunction. In such cases, courts reason that injunctive relief, if granted, will result in great economic harm to the local community. Although damages are awarded to the affected party or parties, injunctive relief is only rarely provided.

If all members of a community are equally affected, then no individual citizen can sue. In such cases, a public authority, such as a local prosecutor, would have to file a public nuisance suit against the pollution source that is causing "an unreasonable interference with a right common to the general public." As in private suits, courts must assess the seriousness of alleged harm relative to the social utility of the source's conduct. Public authorities have historically been reluctant to file such actions.

8.1.2 Trespass

The trespass concept applies to cases in which there is a physical violation of a landowner's right to exclusive possession of his or her property. Particulate-laden smoke could be considered to violate trespass provisions of common law. Historically, in determining liability, courts have not required that the invasion be proven unreasonable or that damages be proven.

8.2 Regulatory Strategies and Tactics

Successful abatement of air pollution and protection of public health and welfare requires the selection of appropriate regulatory strategies and tactics to implement them. A variety of air quality regulatory strategies may be employed. These include air quality management (air quality standards), emission standards, and economics-based approaches. Air quality management and emission standard strategies are the mainstay of pollution control efforts in the United States and other developed countries. Several economics-based pollution control approaches have been proposed and adopted. Some have been incorporated into air pollution control laws and regulatory practice.

8.2.1 Strategies

8.2.1.1 Air Quality Management

Air quality management strategies are based on the widely accepted toxicological principle that pollutant exposures below threshold (lowest dose at which toxic effects are observed) values are relatively safe, and therefore some level of atmospheric pollution is acceptable and thus legally permissible. Pollutants identified as posing potentially significant public health risks and welfare concerns may be regulated by the promulgation of ambient air quality standards.

Air quality standards are legal limits on atmospheric concentrations of regulated pollutants. Promulgation of an air quality standard for an ambient air pollutant is typically characterized by intensive review of scientific studies, recommendations on acceptable levels, and ultimate decision making by a regulatory authority.

Setting ambient air quality standards is a difficult and arduous process. In many cases, the relationship between pollutant levels, adverse health effects, and the level of protection necessary is subject to some degree of uncertainty. In the United States, the Environmental Protection Agency (U.S. EPA) is required to promulgate air quality standards that provide an "adequate margin of safety," with special consideration for those individuals who may

their deliberations was an ambient air pollution control strategy based on setting NAAQSs, with the proviso that states develop implementation plans to achieve them. Additionally, national emission standards would be established for major new sources and for existing and new sources of HAPs. As a consequence, the nation's ambient air pollution control program has been based primarily on strategies employing both air quality management and emission standards concepts.

8.4.1 Air Quality Standards

Under the 1967 Air Quality Act, states were required to set air quality standards for AQCRs within their jurisdiction. These standards were to be consistent with air quality criteria developed and issued by the NAPCA. Development of state air quality standards under the 1967 legislation was slow, due in part to the slowness of the NAPCA to publish air quality criteria and designate AQCRs. In addition, states were concerned that the adoption of stringent standards would result in their industries relocating to states with weaker standards. This concern created a great deal of uncertainty, confusion, and ultimately inaction.

Under the CAA Amendments of 1970, the federal government was charged with the responsibility of developing uniform NAAQSs. These were to include primary standards designed to protect health and secondary standards to protect public welfare. Primary standards were to be achieved by July 1, 1975, and secondary standards "at a reasonable time thereafter." Implicit in this dual-standard requirement was the premise that pollutant levels protective of public welfare were to be more stringent than those for public health and that achievement of primary health-based standards had immediate priority. In 1971, the U.S. EPA promulgated NAAQSs for six air pollutants. In 1978, an air quality standard was also promulgated for lead (Pb). Also in 1978, the 1971 photochemical oxidant standard was revised to an O_3 standard, with an increase in permissible levels. In 1987, the suspended PM standard was revised and designated a PM_{10} (PM with an aerodynamic diameter of $\leq 10 \mu m$) standard. This revision reflected the need for a particle size-based PM standard that better reflected respiratory health risks. In 1997, the U.S. EPA promulgated a new 8-h standard for O_3 and a $PM_{2.5}$ standard (in addition to the existing PM_{10}). The latest NAAQSs (including the most recent additions of the SO_2 and NO_2 1-h standards in 2010 and the change in the $PM_{2.5}$ annual standard), and the averaging times and forms of the standards are summarized in Table 8.1. The table and detailed summaries of the changes in the standards since their establishment as criteria pollutants can be found on the U.S. EPA website at <http://www.epa.gov/air/criteria.html>. The ozone standard is anticipated to be reduced further in 2014 to less than 80 ppb.

wind speeds. This is ironic in the sense that urban areas, because of their relatively high pollutant emissions, are in greater, not lesser, need of being ventilated by the wind.

Winds have directional aspects. These include the prevailing northeasterly flows in the subtropics, southwesterly flows in the middle latitudes, and easterly flows at high latitudes in the northern hemisphere. They also include the cyclonic (clockwise) and anticyclonic flows associated with migrating low-pressure and high-pressure systems. Because flows are somewhat circular, wind direction will depend on one's position in the circulating pressure cell. It also depends on local topography. At night in river valleys, airflows are downslope and downriver; they are upslope during daylight hours. Along sea and lake coasts, winds during clear weather flow inland during the day and waterward at night.

Wind direction is quite variable, with large changes often occurring over relatively short periods of time. A change in wind direction of 30° or more in 1 h is not uncommon. Over a period of 24 h, it may shift by 180° . Seasonal factors may cause wind direction variations of 360° .

Wind direction and variability can have significant effects on air quality. Areas downwind of point sources where winds are relatively persistent may experience relatively high ground-level concentrations compared with other areas at similar distances. If the wind is more variable, pollutants will be dispersed in a larger volume of air and be more equally distributed around the source; ground level concentrations are therefore likely to be lower.

Wind direction is particularly important in the transport and dispersion of pollutants over large geographical areas. It is the southwesterly airflows that carry acid precursors from the US Midwest to the northeastern states and southeastern Canada. Similar flows have transported pollutants from countries in southeastern Asia to the West Coast of the United States.

3.1.2 Turbulence

Airflows within the PBL are influenced by prevailing high-altitude air motion, frictional drag of the Earth's surface, and vertical airflows. Turbulence is characterized by circular eddies that may be vertical, horizontal, or various other orientations. These eddies represent air movements over shorter timescales than those that determine mean wind speeds. Turbulent eddies are produced by both mechanical and thermal forces.

Mechanical turbulence is induced by wind moving over and around structures and vegetation. It increases with wind speed and surface roughness. It is also produced by the shearing effect of fast-moving air aloft as it flows over air slowed by friction.

Thermal turbulence results from the heating or cooling of air near the Earth's surface. On clear days, solar heating of ground surfaces transfers heat to the air above it. Convection cells of rising warm air and descending cooler air develop. Under intensive surface heating, convective eddies are

generated that extend vertically on the order of 1,000 to 1,500 m ($\sim 3,600$ to 5,000 ft).

For the most part, mechanical and thermal turbulence are daytime phenomena. Both are dampened by nighttime radiative cooling of the ground and the air adjacent to it.

The effect of both mechanical and thermal turbulence is to enhance atmospheric mixing and pollutant dispersion. As a consequence, pollutant concentrations are significantly decreased. An exception is the downwash phenomena that causes plumes to be brought to the ground near smokestacks (by mechanical turbulence). In most cases, turbulence has a positive effect on air quality.

Downwash results in high pollutant concentrations in the turbulent wake downwind of a source. Downwash can also occur as a consequence of the shearing effect of high-velocity winds (>70 km/h, ~ 40 mi/h).

3.1.3 Atmospheric Stability

The atmosphere, particularly in the PBL, is characterized by highly variable horizontal and vertical air movements. In turbulent flows (described previously), the atmosphere is unstable and pollutants are rapidly dispersed. Turbulent flows associated with heating of the Earth's surface are dampened on cloudy days. Under such conditions, the atmosphere is more stable and pollutants are less rapidly dispersed.

When an entity is undergoing rapid change or has the immediate potential to do so, it is said to be unstable. When it is undergoing little or no change, and is even resistant to change, it is said to be stable. Stability and instability represent opposite ends in a continuum of possibilities. This continuum is implicit in the phrase *atmospheric stability*.

Vertical air motion is significantly affected by temperature gradients. The rate of temperature change with height is described as the lapse rate. Tropospheric temperatures, on average, decrease with height (Figure 1.7). This decrease, or normal lapse rate, is $-6.5^\circ\text{C}/\text{km}$ (18.9°F) or $-0.65^\circ\text{C}/100$ m.

The normal lapse rate differs from what would be expected if a parcel of warm, dry air were released into a dry atmosphere. In this theoretical case, the buoyant parcel would rise and expand adiabatically (i.e., no energy is transferred to surrounding air). As it rises, its temperature decreases at a constant rate. This theoretical change of temperature with height is called the adiabatic lapse rate. It has values of $-10^\circ\text{C}/\text{km}$ (-29°F) or $-1^\circ\text{C}/100$ m.

Because parcels of air released into the lower atmosphere contain H_2O vapor, the adiabatic lapse rate is used to describe how air cools when it rises in a dry atmosphere. Under real-world conditions, air contains a significant amount of H_2O vapor that cools as the air parcel rises. When air reaches its saturation vapor pressure, heat is released as H_2O vapor condenses (heat of vaporization is released). Air is warmed, resulting in a somewhat smaller decrease of temperature with height than that predicted for adiabatic conditions.

species from one region of the atmosphere to another. Transport enhances dispersion and provides an opportunity for pollutants from different sources to interact.

Pollutant transport and dispersion are affected by atmospheric dynamics, fluid physical phenomena that occur in the atmosphere, and the physical laws that govern them. These may facilitate or constrain transport and dispersal.

Pollutants are initially released into the planetary boundary layer (PBL), that portion of the atmosphere most directly affected by the Earth's surface. The PBL is subject to fluxes of heat and water (H_2O) vapor from the surface, and other physical forces. Its depth, on average, ranges from a few hundred meters to 1 to 2 km. Above the PBL is a relatively stable layer of air that separates it from the free troposphere above.

Pollutant transport and dispersion are affected by different scales of motion. These are the microscale, mesoscale, synoptic scale, and macroscale or planetary scale (Table 3.1). Microscale refers to air motion in the near vicinity of a source and includes phenomena that affect plume behavior; mesoscale refers to atmospheric motions on the order of tens to hundreds of kilometers and such phenomena as fronts, airflows in river valleys, and coastal airflows; synoptic scale refers to systems on the order of 10^6 km² or more such as high-pressure and low-pressure systems responsible for day-to-day weather variations; and planetary scale refers to atmospheric motions on the order of continents or larger. These scales of air motion are useful in describing atmospheric phenomena. It is important to note that the atmosphere is one continuous flowing fluid and all motions are a part of this larger flow.

In the context of a few months, the PBL is relatively well mixed. However, on shorter timescales and near the Earth's surface (where pollutants are emitted), transport and dispersion are often limited by atmospheric conditions.

TABLE 3.1
Meteorological Scales of Air Motion

Scale	Geographical Area (km ²)	Period	Phenomena
Microscale	2-15	Minutes	Plume behavior Downwash
Mesoscale	15-160+	Hour to days	Sea, lake, and land breezes Mountain valley winds
Synoptic scale	>10 ⁶	Days	Migratory high-pressure and low-pressure systems Cold and warm fronts Semipermanent high-pressure systems
Planetary scale		Weeks to months	Hadley cell flows Tropical storms Jet stream meanders

Some atmospheric conditions result in increased ground-level pollutant concentrations that may potentially harm humans and our environment. Consequently, they are discussed in detail below. Particular attention is given to horizontal wind (speed and direction), turbulence, topography, atmospheric stability, and inversions.

3.1.1 Wind

Horizontal winds are characterized by both velocity (wind speed) and direction. As seen in Chapter 1, wind speed is affected by horizontal pressure and temperature gradients (the higher the pressure gradient, the higher the wind speed) and friction, which is proportional to the roughness of the Earth's surfaces (surface roughness). Relationships between surface roughness and wind speed for urban, suburban, and rural areas can be seen in Figure 3.1. The maximum height of each wind profile indicates where surface effects end and the gradient wind (wind affected by pressure differentials and the Coriolis effect) begins. For the urban area depicted, this occurs at approximately 500 m (1650 ft); for the suburban area, at approximately 300 m (990 ft); and for the rural area, at approximately 250 m (825 ft).

For continuously emitting stack sources, dilution begins at the point of release. This plume dilution is inversely proportional to wind speed, that is, by doubling wind speed, pollutant concentration is decreased by 50% of its initial value. The effect of wind speed is to increase the volume of air available for pollutant dispersal. As seen in Figure 3.1, urban areas are characterized by relatively high surface roughness and, as a consequence, diminished

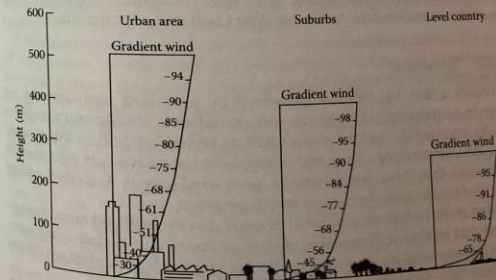


FIGURE 3.1
Effect of surface roughness on wind speed as a function of height over urban, suburban, and rural areas. (Adapted from *Atmospheric Dispersion Emissions*, EPA Publication 600/4-90-010a)

Atmospheric Dispersion, Transport, and Deposition

The atmosphere has served as a sink for emissions of volcanoes and a variety of geological processes, forest and grassland fires, and decomposition and other biological processes for hundreds of millions (if not billions) of years. It has also served as a sink for pollutants generated by human activities, proceeding from man's first use of fire to the smelting of metal ores and use of fossil fuels such as coal, oil, and natural gas to motor vehicle and other emissions from our very industrialized and technologically advanced modern times.

Despite its vastness, the atmosphere (at least in the short term) is not a perfect sink. Its ability to carry away (transport), dilute (disperse), and ultimately remove (deposition) waste products released to it is limited by various atmospheric motion phenomena. Pollutant concentrations may reach unacceptable levels as a result of local or regional overloading of the near-surface atmosphere, topographical barriers, and mesoscale, mesoscale, and macroscale air motion phenomena.

The atmosphere serves as a medium for atmospheric chemical reactions that ultimately serve to remove contaminants. These reactions may produce pollutants that may themselves pose significant environmental concerns. Levels of long-lived pollutants such as methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2) may increase, causing global warming and, in the case of halogenated hydrocarbons, stratospheric ozone (O_3) depletion.

Because of technological and economic limitations, we have little choice but to use the atmosphere for the disposal of airborne wastes. Like other natural resources, our use of the atmosphere has to be a wise one, recognizing its limitations and using it in a sustainable way.

3.1 Dispersion and Transport

Pollutants released from ground level and elevated sources (smokestacks) are immediately subject to atmospheric processes, with dispersion in ever-increasing volumes of air by both vertical and horizontal transport. Transport is the process by which air motions carry gas-phase and particulate-phase

MHs are affected by semipermanent marine high-pressure systems (note Los Angeles in Figure 3.6) and migrating high-pressure systems. Subsidence of air and formation of inversions cause MHs to decrease. MHs are an important variable used in air quality modeling (see Chapter 7).

3.1.6 Topography

Both microscale and mesoscale air motions are affected by nearby topographical features. Topography can have significant effects on both air movement and pollutant levels. These include differential vertical airflows associated with forests, plowed agricultural fields, parking lots, and the like. Such flows affect the behavior of smokestack plumes.

In river valleys, downslope airflows at night intensify (deepen) surface-based inversions, and valley winds during the day help move pollutants upslope and out of the valley. Mountains also serve as barriers to air movement. In the Los Angeles basin, the San Bernardino Mountains retard airflow in northerly and easterly directions, further intensifying smog and haze conditions. Mountains also increase surface roughness, thereby decreasing wind speeds.

The smog problem over the Los Angeles basin is also affected by the adjacent cool waters of the Pacific. When sea breezes bring cool air in from the ocean, warmer air is pushed aloft, further intensifying the elevated inversion.

Mesoscale airflow patterns occur on relatively calm days in coastal areas as a result of differential heating and cooling of land and water surfaces. During summer, when skies are clear and prevailing winds are light, land surfaces warm more rapidly than sea and lake water. The subsequently warmed air flows up and waterward. As a consequence of temperature and pressure differences, air flows landward at the surface from the water, forming a sea or lake breeze. Air moving from the land cools and descends to form a weak circulation cell. At night, rapid radiational cooling of the land results in surface airflows toward water, forming a land breeze. These land breezes are generally lighter than lake and sea breezes.

Land, sea, and lake breezes, and the circulation patterns that form with them, occur only when prevailing winds are light. They are overridden when winds are strong. In the case of the south coast of California, sea breezes intensify subsidence inversions. They may also cause advective inversions, which commonly occur in late spring when large bodies of water are still cold relative to adjacent land areas. As water-cooled air moves inland, it warms; the inversion is broken up and replaced by superadiabatic lapse rate conditions. The weak circulation cells associated with land, lake, and sea breezes may allow pollutants to be recirculated to some degree and carried over from one day to the next.

3.1.7 Pollutant Dispersion from Point Sources

Point sources may occur at ground level, or as is often the case, pollutants are emitted from smokestacks that vary in height. The subsequent history of

plumes formed depends on (1) the physical and chemical nature of pollutants, (2) meteorological factors such as wind speed and atmospheric stability, (3) location of the source relative to physical obstructions, and (4) topographical factors that affect air movement. As these affect plume rise, its spread horizontally and vertically, and its transport, they also affect maximum ground-level concentrations (MGLCs) and the distance of MGLCs from the source.

3.1.7.1 Pollutants and Diffusion

In many cases, point source plumes are a mixture of gas-phase and particulate-phase substances. Particles with aerodynamic diameters of greater than or equal to $20\ \mu\text{m}$ have appreciable settling velocities, and as a consequence, deposition occurs relatively close to their sources. Smaller particles, particularly those with aerodynamic diameters of less than or equal to $1\ \mu\text{m}$, have very low settling velocities and dispersion behavior similar to that of gases and vapors. The gaseous nature of plumes, given sufficient time, may allow for dispersion by simple diffusion, whereby the random motion of molecules results in pollutants migrating from areas of high concentration (the center of the plume) to areas of low concentration (the plume's periphery). Diffusion causes plumes to spread both horizontally and vertically. As a consequence, the effect of diffusion can be seen to increase with downwind distance.

3.1.7.2 Plume Rise and Transport

Dispersion from a smokestack source is significantly affected by its physical height as well as plume rise. In Figure 3.7, the plume is seen to rise to a maximum height and then level off. The distance from the top of the stack to the center of the plume is described as plume rise. The distance from the ground to the center of the plume (including the stack) is the effective stack height.

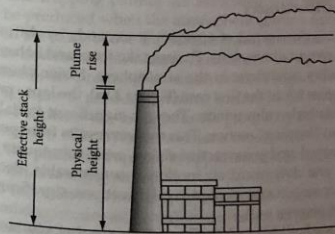


FIGURE 3.7
Plume rise and effective stack height.

Dispersion is enhanced with increasing stack height and plume rise. Ground-level concentrations will be lower, and at constant wind speed, the distance at which MGLCs occur will be increased as effective stack height increases.

The height of the plume at the point it levels off depends on the exit temperature of stack gases, cross-sectional diameter of the stack, emission velocity, horizontal wind speed, and atmospheric stability (as indicated by the vertical temperature gradient).

The effective stack height for a source can be increased by building taller stacks. Tall-stack technology has been used since the 1960s by electrical utilities operating large coal-fired power plants. Such stacks are commonly 250 to 300 m (850–1,000 ft) high, with some stacks approximately 400 m (1,300 ft). They were designed and operated on the principle that pollutants could be dispersed from such facilities without causing unacceptable downwind ground-level concentrations.

Wind speed in the horizontal dimension significantly affects both plume rise and ground-level concentrations. Higher wind speeds decrease effective stack height. However, due to the increased volume of air associated with increasing wind speeds, ground-level concentrations are usually reduced. Higher wind speeds decrease the distance at which MGLCs occur. At very high speeds (~80 km/h, 50 mi/h), plume rise may be negligible; the plume may be brought to the ground immediately downwind of the source.

Tall stacks are designed to take advantage of the higher wind speeds that occur aloft as the frictional drag of the Earth's surface is diminished. Pollutant dispersion is enhanced as a result of these higher wind speeds.

Plume rise, as indicated, is subject to atmospheric stability. Under unstable conditions, significant plume rise occurs; under stable conditions, plume rise is markedly reduced. In the latter case, dispersion is decreased and higher ground-level concentrations can be expected.

3.1.7.3 Plume Characteristics

As a plume moves downwind of a source, it expands by diffusion in both horizontal and vertical dimensions. Plumes take form and behavior patterns that reflect stability conditions in the atmosphere. Major plume types are illustrated in Figure 3.8. In the first case (Figure 3.8a), the lapse rate is superadiabatic with relatively calm winds. There is significant initial plume rise and a subsequent "looping" motion. This motion results from portions of the plume being buoyed up by convective rising, with subsequent descending of air. Upward and downward air motion is considerable. Because eddies that produce this motion are oriented in all directions, significant horizontal dispersion takes place as well.

A coning plume is illustrated in Figure 3.8b. Coning plumes form when lapse rates are neutral to isothermal. As such, the atmosphere is slightly unstable to slightly stable. Such lapse rates occur on cloudy or windy days or

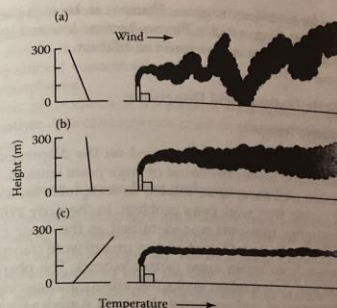


FIGURE 3.8

Plume form and behavior associated with different atmospheric stability conditions. (a) Looping, (b) coning, and (c) fanning.

at night. Atmospheric turbulence is primarily mechanical; turbulent eddies may have different orientations that result in dispersion in a relatively symmetrical pattern.

A fanning plume is illustrated in Figure 3.8c. It is produced under stable conditions in which the top of a ground-based inversion is well above the stack. The plume rises slightly, there being little vertical air movement and dispersion. Horizontal motions, however, are not inhibited. As a consequence, the plume may be characterized by varying degrees of horizontal spreading.

Other plume forms and behaviors (not illustrated here) occur. Lofting, fumigating, and trapping plumes are associated with inversions. A lofting plume may be produced when the atmosphere above a surface inversion is unstable, with the stack above the surface-based inversion. The plume rises upward as its downward movement is restricted by the inversion beneath it. Lofting plumes are produced at sunset on clear nights, over open terrain. A fumigating plume is produced when a surface-based inversion breaks up after sunrise. Pollutants are brought to the ground by the downward movement of convective cells. When inversions occur both above and below a smokestack, the plume is trapped; in appearance, it is somewhat similar to, but deeper than, a fanning plume.

As plumes move downwind, they generally mix with air that is less polluted. Such mixing occurs as a result of diffusion, advection, displacement, convection, and mechanical turbulence. Consequently, concentrations decrease with downwind distance. Depending on their height and atmospheric stability, plumes may reach the ground within a few kilometers of a source or may

fog droplets; and (3) collision of rain droplets and particles both within and below clouds. In the last case, collisions with, and subsequent incorporation of, gas-phase substances can also occur. This process is called washout. The removal of particles in the rain-making process is called rainout.

3.3 Meteorological Applications: Air Pollution Control

As seen in previous discussions in this chapter, a variety of meteorological factors affect the dispersion of pollutants from individual sources as well as urban areas. Thus, meteorology has significant applications in air pollution control programs. These include episode prediction, planning, and community responses. These also include the determination of whether, under worst-case atmospheric conditions, proposed sources will be in compliance with air quality standards and visibility protection requirements for the prevention of significant deterioration provisions of clean air legislation. Compliance is determined from air quality modeling.

3.3.1 Episode Planning

In the late 1950s and early 1960s, the U.S. Weather Service (now the National Weather Service) observed that increased pollutant levels in urban areas were associated with slow-moving migratory high-pressure systems. As a consequence, it began a program of issuing air pollution potential forecasts when such systems covered an area of at least 90,000 km² (~35,000 mi²) and were expected to persist for at least 36 h.

Despite the fact that regulatory efforts to control air pollution have significantly reduced health threats associated with ambient air pollution, such stagnant high-pressure systems occur periodically, as do the semipermanent high-pressure systems over southern California. As such, they can cause significant increases in ground-level concentrations that may adversely affect the health of individuals at special risk (e.g., asthmatics, those ill with respiratory or cardiovascular disease, and the elderly). Therefore, there is a continuing need to forecast air pollution episodes. When the National Weather Service forecasts a developing episode, regulatory authorities at the local, state, and national levels begin to implement episode control plans, which may include requiring phased reductions in emissions of one or more primary pollutants and issuing community health warnings (see Chapter 8).

3.3.2 Air Quality Modeling

New and existing stationary sources regulated under New Source Performance Standards, and National Emission Standards for Hazardous Air