External Review Draft No. 1
April 1980

Draft
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Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume III
Welfare Effects

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Preface to Volume III

A concern for human welfare implies a concern for the biological and physical realms of man's environment. This volume assesses the effects of sulfur oxides and particulate matter on human welfare by examining four specific topics: effects on vegetation and ecosystems (Chapter 7), acidic precipitation (Chapter 8), visibility and climate (Chapter 9), and materials (Chapter 10).

Sulfur oxides and particulate matter induce a variety of specific symptoms in vegetation. These effects range from visible injury to latent declines in yield or, conversely, beneficial effects under certain conditions. Several variables influence these outcomes, including pollutant concentration, mode of exposure, ambient conditions, and various characteristics of the vegetation itself. In addition, the specific form of particulate matter is, of course, an important variable.

As the level of SO_2 increases, plants develop more predictable and visible symptoms of injury. In research tests, important agricultural crops such as alfalfa, timothy, range grasses, soybean, barley, wheat, cabbage, lettuce, spinach, tobacco, cucumber, eggplant, pea, and kidney bean suffered necrotic leaf injury or reduced yield.

Acidic precipitation is relevant to an evaluation of the impact of sulfur oxides on human welfare. The pH of precipitation in various regions appears to have declined (become more acidic) in recent history. An increase in the acidity of rain and snow has serious implications for terrestrial and aquatic ecosystems. Thus, in this volume, the effects of acidic precipitation on aquatic organisms and terrestrial vegetation and soils are considered in some detail. In addition, the causes and characteristics of acidic precipitation are examined.

The precipitation (wet deposition) of acidic oxides of sulfur and nitrogen is only one aspect of atmospheric deposition. Dry deposition also distributes similar chemical substances in gases, aerosols, and particulate matter. Thus, the biological effects of acidic precipitation or dry deposition are chemically indistinguishable. But geographically, acidic precipitation has been associated with regions in which man-made emissions of sulfur and nitrogen oxides are highest. The combustion of fossil fuels, certain industrial processes (such as smelting of ore), auto exhausts, and nitrogen fertilizers used in agricultural and forest lands are primary man-made sources of acidic precipitation pollution.

The reduction (or extinction) of fish populations in hundreds of Minnesota, New York State, and Canadian lakes is believed to be associated with aquatic acid stress. Similar reports concern lakes and streams in other U.S. and Canadian regions.

One of the most conspicuous effects of air pollution, especially particulate matter, is the degradation of man's view of his environment. Atmospheric particles scatter and absorb light, creating haze which reduces the clarity and range of vision and which distorts aesthetic features of the landscape. In addition, atmospheric particles can potentially affect meteorological conditions, including precipitation quantity and quality, cloudiness, and solar radiation.

Sulfates primarily exist in the atmosphere as fine particles. Being hygroscopic (able to absorb moisture from the air), their effect on visibility varies with degrees of humidity. This complicates predicting the effect of sulfates on visibility reduction. Increasing emissions of sulfur oxides have, however, been linked with similar increases in haziness.

Do increased concentrations of airborne particulate warm or cool the earth? There is little agreement on an answer to that question. However, in urban areas, inadvertent changes in cloudiness have been well established. Haze is also strongly suspected (though it is not yet proved) to affect agricultural productivity by causing solar radiation decreases.

Finally, this volume examines the tangible effects of sulfur oxides and particulate matter on man's artifacts. The corrosion and the soiling of materials are damaging processes that can have significant economic implications. For example, corrosion of specific metal coatings, such as zinc (as in galvanized metal), is accelerated by sulfur dioxide (SO_2) and acid sulfates. Experiments indicate that one part SO_2 will react with iron and form about 40 parts of rust.

Sulfur oxides and particulate matter also deteriorate and soil buildings and painted surfaces. Deterioration of limestone and marble is evident, but the economic loss, especially to works of art, is difficult to assess.

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7. EFFECTS ON VEGETATION

7.1 GENERAL INTRODUCTION AND APPROACH

This chapter reviews pertinent and useful literature on the effects of particulate matter and sulfur oxides on all forms of plant life. Information of only historical interest has been kept to a minimum and emphasis has been given to more recent studies that have employed modern technologies and statistical procedures. Information on each pollutant is presented separately since few interactive effects have been demonstrated Interactions that have been reported are covered in the appropriate chapter section.

7.1.1 Origin and Distribution of Particles

Particles are defined as solid particles or liquid droplets ranging in diameter from 0.00 to 500 μm (134). The size limits are arbitrary but are meant to indicate that particles can be as small as a cluster of several molecules or as large as a visible dust unit. Particles constitute a significant fraction of the atmospheric air pollutants. This chapter discusses all types of particles other than acidic rain and biological particles (fungal spores, bacteria, viruses, etc.).

Particles have been classified as fine (<2 μm in diameter) and coarse (>2 μm in diameter) (470). Very fine particles exhibit Brownian motion, follow fluid streamlines, and can coagulate and condense. Larger particles are strongly influenced by gravity and seldom coalesce or condense (134). The chemical behavior of particles may be determined by the composition of the particles themselves and by the gases adsorbed on their surfaces.

Particles are generally categorized as primary and secondary. Primary particles are usually 2 to 20 μm in size and are injected directly into the atmosphere by chemical or physical processes. Secondary particles are produced by chemical reactions in the atmosphere. They are smaller than primary particles and can be classified as sulfates, nitrates, or hydrocarbons.

There is increasing evidence that particles and gases that produce particles when injected into the atmosphere in one location can be deposited several hundred miles away from this source. According to Whitby (470), "It is now well established that a significant fraction of sulfur, emitted into the atmosphere either as a primary aerosol or as a product of gas to particle phase conversion, ends up in the atmosphere as stable sub-micron aerosol." At present, the heaviest concentrations of particles seem to be located along the coastline and in the heavily industrialized Mid-Central States.

7.1.2 Phytotoxic Forms of Particles

The effects of air pollutants on vegetation can be considered in terms of source, transport, deposition, and plant uptake. Except where the residence time of the pollutant in the air is very short, chemical transformation of the pollutant may be involved. There are exceptions, in which effects may occur without significant uptake, as is the case with certain types of water-insoluble particles.

Particles may affect vegetation directly or indirectly through changes in soil chemistry and physics, or both.

The surfaces of vegetation provide a major collection surface for the transfer of particles to the biosphere (401). The capacity of plants to act as a sink for air contaminants has been reviewed by several investigators (31, 68, 181, 403).

Toxic effects result when the rates of exposure or deposition and accumulation exceed the rates of detoxification through metabolism. Phytotoxic forms of both inorganic and organic chemical species occur as particles. Among the constituents of inorganic particulates, the following elements are considered to be phytotoxic: Al, As, B, Cd, Cu, Pb, Mg, Mn, Hg, K, Na, Zn, and F. In addition, acid ($H_2SO_4.HNO_3$) and saline (NaCl) aerosols are phytotoxic. Organic particles such as herbicides are phytotoxic to target, as well as to nontarget, organisms when air drift occurs (370).

7.1.3 Origins and Distribution of Sulfur

Sulfur in the atmosphere has been found in as many as 23 different chemical forms (70). Of all sulfur compounds directly emitted into the atmosphere through man's activities, sulfur dioxide is emitted in the largest quantity (325).

Hydrogen sulfide is believed to be emitted into the atmosphere in large but uncertain quantities, mainly from natural sources such as swamps and estuaries. Most of it is rapidly oxidized to SO_2 and sulfuric acid (64). Charlson et al. (70) proposed a flow diagram for the cycling of sulfur compounds through the atmosphere (Figure 7-1). The likelihood of simultaneous coexistence of several sulfur-containing species (possibly in different oxidation states) in single or separate atmospheric particles may further confuse evaluation of cause and effect relationships in plant response.

7.1.4 Phytotoxic Forms of Sulfur

In laboratory and field tests, the following sulfur compounds have been shown to be phytotoxic at appropriate doses: sulfur dioxide, hydrogen sulfide, and sulfuric acid as mist, submicron aerosol, or in aqueous solution. At other concentrations, over time, these sulfur compounds have demonstrated stimulatory or beneficial effects.

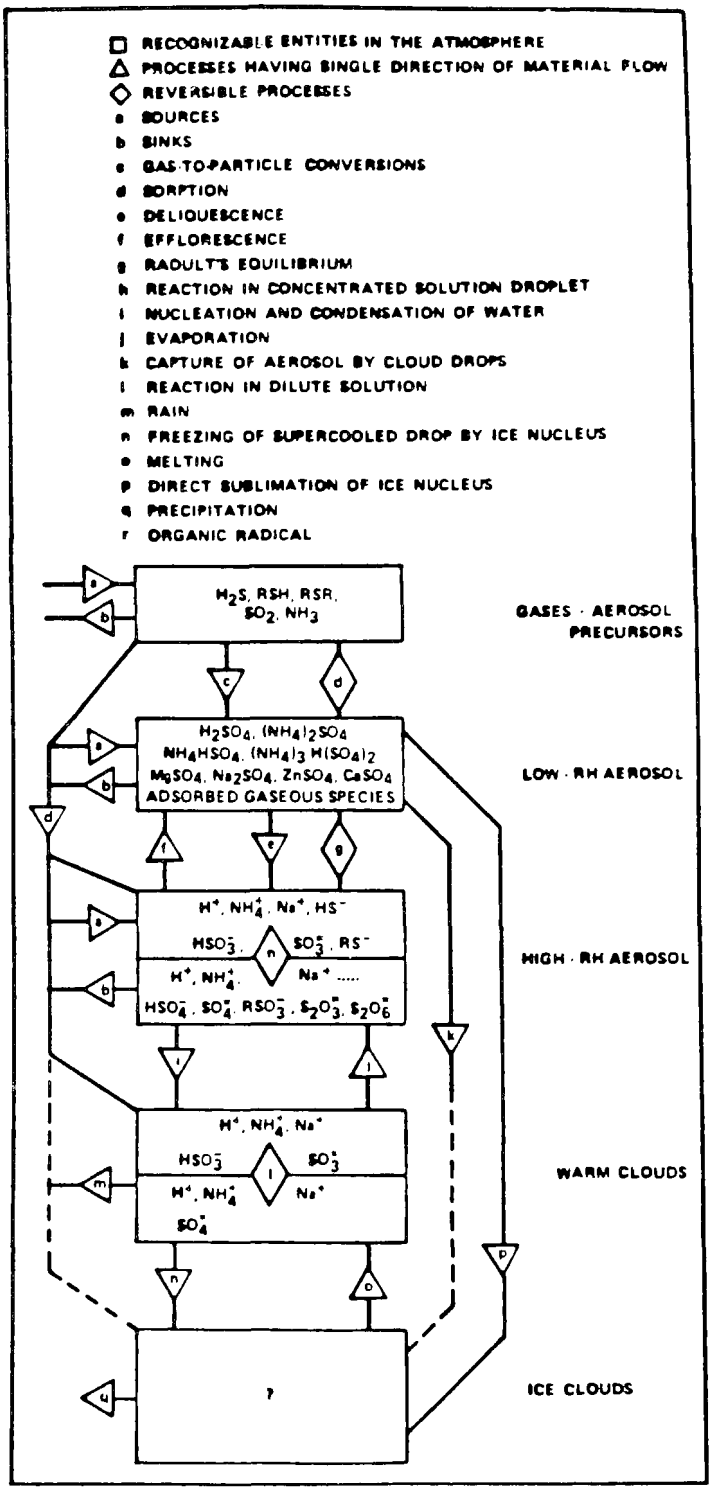

Figure 7-1. Flow diagram shows the tropospheric sulfur cycle.

Source: Charlson et al. (1978).

The phytotoxic effects of SO_2 have been studied since 1871 (410). In recent years, some effort has been directed towards the understanding of the direct effects of other sulfur compounds such as hydrogen sulfide, carbonyl sulfide, sulfates or sulfuric acid aerosols, and sulfuric acid in aqueous media (447).

7.1.5 Relationships Between Particles and Sulfur

No comprehensive summary of the chemical composition and size distribution of sulfur-containing primary particles is available. Several reports have emphasized the interrelationships of sulfur compounds and particles.

Studies on the chemical composition of fly ash as a function of particle size show that toxic elements such as lead, cadmium, manganese, and arsenic increase markedly in concentration with decreasing particle size (108, 259). Dzubay and Stevens (123) found that in urban aerosols, 75 percent of the sulfur along with zinc, bromine, selenium, and lead occurred in fine particles. Sulfur dioxide in a point-source plume is considered to be converted to particulate sulfur at the rate of 0.5 to 4 percent per hour (199).

It is believed that solid phases containing sulfur are numerous. Particulate matter such as ferric oxide, manganese oxide, and carbon can capture SO_2 by physical absorption, as well as by catalyzed oxidation (79, 215, 398). The principal sulfur compounds include $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4HSO_4, $CaSO_4$, $MgSO_4$, and Na_2SO_4, sulfates of transition metals, and organic sulfur compounds (refer to Atmospheric Environment, vol. 12, 1978). Dry and wet removal of sulfur from the atmosphere is considered to be important relative to ground-level effects. Because the chemical composition of particles and their effects on vegetation are very varied (263), published literature on the interactive effects of particles and other air pollutants is scarce (235, 236, 474).

7.2 SYMPTOMATOLOGY OF SO_2-INDUCED PLANT INJURY

7.2.1 Introduction

Exposure to SO_2 may cause visible injury to a plant. Below the threshold for visible damage, SO_2 causes physiological injury that is not visible but is nonetheless real. Such injury has been called "latent," "hidden," "invisible," "physiological" and "subtle"; the term "latent" is used here. For example, exposure to SO_2 concentrations that cause no visible effects may depress growth and reduce the yield of the usable part of the plant.

In evaluating the impact of a pollutant on vegetation, latent injury may be more important than visible injury (24, 222, 237, 353).

When preclinical visible injury is manifested as yellowing of tissues, pigmentation, or visible stunting of growth, then chronic injury has occurred. If plant death does occur under such exposure conditions, other mitigating factors may also be involved, i.e., abiotic or biotic disease inducing agents or insect attack.

However, once a sufficient dose of pollutant has occurred to induce necrosis of individual cells, tissues, organs, or entire plants then acute injury has occurred and irreversible effects may be observed. Plant death may result from continual exposure to high pollutant doses.

Latent injury involves effects on the normal physiological activity of the plant without manifestation of visible symptoms. Chronic injury is detectable visually but does not involve necrosis and acute injury entails death of tissues. Depending upon the plant species, exact conditions of the seasonal stage of crop growth, pollutant dose and environmental conditions, many forms of injury may take place and their relative impact may vary. Symptoms of acute and chronic injury may occur on a given plant simultaneously.

The distinction between latent and acute or chronic injury may not always be clear. Dead cells (acute injury) have been found in SO_2-exposed soybean leaves in the absence of visible (unaided eye)

foliar injury (207). Under the definitions set forth herein, such injury could still be classified as acute since it is visible and need not be compared with an unexposed plant to be detected.

Three terms have frequently been used to describe the effects of air pollutants on vegetation: injury, damage, and impact. These are herein defined for purposes of this chapter as follows:

Injury - one or more physiological effects as manifested by one of the symptoms discussed above or direct yield losses in specific vegetation species. No economic value incurred or no economic value loss estimates made and available.

Damage - injury (as defined above) that results in measurable economic losses to specific crops, i.e., yield reduction in soybeans; radial increment decreases in forest trees, and visible injury to orchids and ornamental quality from an esthetic sense of value.

Impact - the total influence (detrimental or beneficial) of air pollutants on all aspects of vegetation as used for food, fiber, and esthetic considerations. Impact on a forest may include ecosystem shifts, watershed effects, and recreational value due to reductions in visibility; impact in crop situations may include indirect losses such as shifts in planted species, farm machinery purchase as part of new crop production, or land-use values as reduced or increased by pollutant loading in the area.

Many reviews of SO_2 effects on vegetation have been prepared (58, 97, 159, 202, 272, 318, 325, 434, 442, 447, 452). Additional reports of SO_2 effects on plants for use in diagnostic situations have also been prepared (103, 104, 248, 396, 444).

7.2.2 Cellular and Biochemical Changes

There is evidence that the anions formed from SO_2 affect the membranes of chloroplasts and other organelles (154). Fisher et al. (136) found that in leaves of Vicia faba exposed to SO_2, granulation of the stroma and swelling of the fret membranes of the chloroplasts were the first observable changes at the ultrastructural level. Wellburn et al. (464), using Vicia faba, also observed a swelling of the fret membranes and granal compartments of the chloroplasts. This swelling was more extensive for higher concentrations and for longer durations. It was followed by the swelling of the chloroplast and degradation of the chloroplast envelope. In the final stages of response, the density of the cell contents increased, with an aggregation of cellular material, although the granal membranes persisted for a long period of time.

Sulfur dioxide has been shown to increase or decrease stomatal resistance and thus affect the photosynthetic performance (164). When it enters the leaf, SO_2 is readily dissolved in the water surrounding the mesophyll cells and is then converted into bisulfite, sulfite, and sulfate. Silvius et al. (395) exposed isolated spinach chloroplasts to 0.5 mM concentrations of either SO_2, sodium bisulfite, sodium sulfite, or sodium sulfate, and measured oxygen evolution as an indicator of photosynthesis. Photosynthesis was inhibited most by sulfite, bisulfite, and SO_2, and least by SO_4. No inhibition of photosynthesis was observed when the chloroplasts were exposed to hydrochloric acid at comparable mM concentrations. Silvius et al. (395) also observed that all of the compounds they tested inhibited ATP formation.

More recently, Legge et al. (260) showed a direct but reversible decrease in ATP levels in lodgepole x jack pine with exposures to ambient SO_2 below 0.20 ppm for 15 min. These same levels of SO_2, however, did not produce measurable changes in the photosynthetic rates in this study.

Horsman and Wellburn (190) prepared the most complete listing of reported metabolic or enzymatic effects of SO_2 on plants or plant tissues. In only one of ten studies was an increase in photosynthesis ($^{14}CO_2$ fixation) in response to the exposure to SO_2 or its derivatives reported; in five of seven studies listed however, ATP concentrations dropped after exposure to SO_2. Ziegler (495) showed an inhibition of the enzyme ribulose-1,5,-diphosphate carboxylase in isolated spinach chloroplasts, and Horsman and Wellburn (189) found a slight reduction in the activity of the same enzyme in pea seedlings at a concentration of 0.20 ppm SO_2. Since ribulose-1,5-diphosphate carboxylase fixes CO_2 in the pentose pathway, any reduction in its activity would be reflected in reduced photosynthetic rates.

Recent studies have shown a variety of SO_2-induced biochemical effects: enzyme inhibition (343, 344, 495); interference with respiration (162); energy transduction (18, 395); lipid biosynthesis (286); alterations in amino acid content and quality (151); increase in phenolic compounds and soluble sugars (157); altered mineral nutrients status (261); and chlorophyll loss (260, 366). Pahlich (345) has rationalized some of this diverse list of effects in terms of sulfite and sulfate accumulation by the exposed plant tissue. However, it is not clear what these biochemical responses mean in terms of visible injury or growth and productivity effects.

Vogl et al. (455) have attempted to integrate the biochemical response and the type and magnitude of the resultant plant effect (Table 7-1). Development of models is necessary to relate changes in physiology (biochemical responses) of specific plant species to altered growth and productivity of that species relative to chronic, long-term exposures to fluctuating SO_2 concentrations. Thus frequent simultaneous measurements of the pollutant concentration and a number of physiological parameters are required to interpret plant response to the stress (226).

7.2.3 Growth and Yield Effects Without Expression of Visible Symptoms

Invisible injury was originally associated with (1) reduced photosynthesis, (2) early senescence, (3) an overall unthrifty appearance without actual lesions on the leaves, (4) reduced growth and yield, and (5) increased susceptibility to disease (411). Respiration of spruce was inhibited but there was not visible injury to the leaves (411). A later review defined invisible injury as interference with growth, photosynthesis, respiration, reproduction, enzyme function, or demonstrable increase in susceptibility to disease without lesions or discoloration of leaves, stems, or roots of the plant (419).

New techniques and instrumentation have aided the demonstration of physiological effects without visible symptoms for many crops. Ryegrass (S23) exposed to ambient air in a greenhouse weighed between 16 and 57 percent less than plants grown in similar air that had been passed through a water scrubber to remove SO_2. However, lack of continuous SO_2 concentrations (0.067 ppm SO_2) for a 26-week exposure period reduced the growth of (S23) ryegrass and led to a 52 percent reduction in dry-weight production over control-treated plants which received an average of 0.005 ppm SO_2 for the same period. The plants exposed to SO_2 were slightly chlorotic, but it is doubtful whether the symptom could have been detected in the absence of control plants.

TABLE 7-1. RELATIONSHIPS BETWEEN CERTAIN BIOCHEMICAL EFFECTS AND PLANT INJURY

Degree of Injury	Description of injury					
			Injury to:		Ability to recover in:	
	Visible symptoms	Symptoms of biochemical injury in leaf cells	Assimilation organs	Whole plant	Assimilation organs	Whole plant
A	None	Stress on buffer systems	None	None		
B	Not detectable	Photosynthesis adversely affected, diminished assimilation rate	Temporary reduction of gaseous exchange	Not detectable	Very quick, completely	
C	Loss of assimilation capacity through: (1) premature death of assimilation organs (leaves, needles) (2) diminished growth of new tissues (shorter needles, etc.)	Diminished activity of enzymes Effect on chlorophyll	Prolonged impedance of gaseous exchange	Reduced growth (deficiency conditions)	Slowly, completely	Slowly, completely for perennials
D	Necrosis of the assimilating and active plant tissues	Death of cells through protein and enzyme degradation	Irreversible injury: necrosis of some assimilatory organs or parts thereof	Loss of assimilation capability	Quickly, not completely; sometimes, not at all for isolated tissues	Slowly, completely for perrennials
E	Destruction of all important assimilatory plant tissues	Death of organs	Irreversible injury to all assimilation organs	Destruction of assimilation capability	Not any more	Sometimes (for isolated tissues)

source: Vogel et al., 1965 (455).

Detached leaves of pea (Pisum sativum) were exposed to 0.05, 0.10, and 0.25 ppm SO_2 and resulting changes in photosynthetic rates were measured (10, 25, and 50 percent, respectively) (62). The SO_2 at first stimulated and later inhibited photosynthesis but there was no visible injury to the leaves. Pea plants were continuously exposed to 0.1, 0.15, and 0.25 ppm SO_2 for 18 days (204). Accumulation of inorganic sulfur, a reduced buffer capacity of the cells, and a stimulation of glutamate dehydrogenase activity were reported. There was a decrease in fresh and dry weight of plants exposed to the lower concentrations, and visible signs of injury on older leaves. The same effects were noted at 0.25 ppm SO_2 but were accompanied by considerable necrosis.

Soybeans (cultivar wells) in field plots exposed to fluctuating concentrations of SO_2 for 4 to 4.5 hr daily for 24 and 18 days in 1977 and 1978, respectively, gave reduced yields but showed no visible injury to the leaves (311, 407). Mild symptoms were noted only on the plants exposed to high SO_2 concentrations, but reduced yields were recorded for all of the fumigated plots. Yield reductions resulted mainly from decreases in seed size, numbers of filled seeds per pod, and number of pods per plant. In 1977, photosynthesis was reduced by as much as 63 percent at the highest concentrations, and a short-lived stimulation of photosynthesis was noted occasionally at the lowest levels of SO_2 (311).

Photosynthesis in barley and oat plant canopies was reduced in response to a 2-hr exposure to 0.20 ppm SO_2, but no leaf damage was observed (30). The yield of durum wheat and barley exposed to SO_2 concentrations of 0.03, 0.05, 0.10, and 0.15 ppm SO_2 for 3 consecutive days per week for 12 weeks

of the 1977 growing season was reduced by as much as up to 44 percent in the 0.10- and 0.15-ppm treatment (473). The yield of spring wheat was unaffected by similar treatments. Shorter exposures of 3 hr per week to 1.20 ppm SO_2 had no effect on yield.

Leaf injury and radial growth were evaluated on Douglas fir (Pseudotsugae menziesii) and yellow pine (Pinus ponderosa) growing in nursery plots exposed to sulfur dioxide (SO_2) in controlled fumigations (221). Slightly injured yellow pine (0.10 percent foliar symptoms) exhibited no significant deviations in growth while slightly injured Douglas fir (0.10 percent foliar symptoms) showed a definite growth retardation when compared with control plants. The growth retardations were evident for 3 years after SO_2 exposure, followed by substantial recovery.

Piskornik (354) exposed six tree species (Quercus robur, Aesculus hippocastanum, Acer pseudoplatanus, Fraximus excelsior, Betula verrucosa, and Acer platanoides) to 0.10, 0.40, and 1.30 ppm SO_2 for 24 hr. Exposure to 0.10 ppm SO_2 resulted in a significant reduction in photosynthesis only in the oak (Quercus robur), with no visible symptoms. At 0.40 ppm, all species had reduced photosynthesis (36, 60, 86, 16, 24, and 26 percent, respectively), and a few symptoms appeared on planetree maple (Acer pseudoplatanus), some on oak, and some on horsechestnut (Aesculus hippocastanum). A decrease in the rate of photosynthesis (measured by carbon dioxide assimilation) occurred even in leaves that did not exhibit any visible injury, and premature aging of some leaves and decreased water content of tissues was also noted.

Spruce may respond to low SO_2 concentrations by metabolic changes and increased susceptibility to other pests and parasites without visible symptoms (296); losses in growth under such conditions have been reported to amount to 10 percent. Significant reductions in the growth of trees in Austrian forests occurred in response to a variety of pollutants at relatively low

concentrations (117). Radial increment studies revealed growth reductions in many trees, some of which exhibited no typical macroscopic visible symptoms.

Growth in a mixed white pine stand and a yellow poplar (Liriodendron tulipifera) stand near a source of SO_2 and nitrogen oxides was examined using a simple linear regression analysis to evaluate the relationship between annual radial increment (1936-71) and annual industrial production level (amount of coal burned) (412). A significant inverse relationship between growth and air pollution was demonstrated in both white pine and yellow poplar. Experiments were extended to three stands of loblolly pine, using multiple linear regression analysis, annual radial increment growth being the dependent variable and annual industrial production level (SO_2 and NO_x pollution), total annual rainfall, annual seasonal rainfall, and age as independent variables to evaluate pollution impact (352). A significant ($p = 0.01$) inverse relationship was demonstrated between annual radial increment and industrial production level. The eastern white pine stand previously studied (412) was reexamined for growth reduction in trees of differing classes of symptom versus pollutant sensitivity (353). Regression analysis revealed no significant differences in growth rate between symptom classes (ranging from asymptomatic to greater than 25 percent of the needles tipburned) and industrial production peaks; that is, the growth of asymptomatic trees was reduced as much as growth of trees with symptoms during the time of sampling (1935-74). Unfortunately, the researchers evaluated the trees at the end of each period, and did not document that the then asymptomatic trees were asymptomatic during previous periods of high pollution levels. Growth as measured by radial increment in this eastern white pine stand has continued to increase since 1972 as a result of reduced levels of industrial production and concurrent pollution-abatement efforts at the major sources of SO_2 and nitrogen oxides (331).

Eastern white pine in the field exhibited increased height growth after a power plant smokestack was made higher, which effectively removed the air pollutants from the immediate vicinity of the pines (120). The increase in height growth was detectable 2 years after construction of the taller stack and the amount of increase decreased with distance from the source.

Continuous exposures of Norway spruce (Picea abies) to 0.05, 0.10, and 0.20 ppm SO_2 from April through July 1976 caused significant depressions in carbon dioxide uptake long before visible symptoms occurred (225). Increasing SO_2 levels caused a decrease in width of annual rings with particular effects to summer wood formation following the springtime fumigation. Industries selling wood on a weight basis therefore may suffer additional losses through decreased production of the denser summer wood. Continuous exposure to 0.10 or 0.20 ppm SO_2 for 10 weeks caused significant depression in photosynthesis of silver fir (Abies alba) needles in the absence of foliar symptoms (223). Exposure of spruce to 0.05 ppm SO_2 for 9 months decreased the buffering capacity and increased the activity of peroxidase (222). Low SO_2 concentrations for several summer weeks significantly depressed photosynthesis in pine. The viability of fir pollen was reduced if the plants were exposed to SO_2 during the winter (222).

Wintertime exposures to SO_2 killed terminal buds of beech (Fagus sylvatica) and caused increases in sulfur compounds in leaf tissues flushed from surviving buds (224). Norway spruce, beech, and black pine were more sensitive to frost injury after continuous exposure to 0.05, 0.10, 0.15, and 0.20 ppm SO_2 for 2.5 to 4.0 months. These data help explain the more frequent occurrence of frost damage in polluted areas.

The effects of ambient levels of pollutant (mainly SO_2) on cone, seed, and pollen characteristics were examined on eastern white pine (*Pinus strobus*) and red pines (*P. resinosa*) growing in areas of high and low pollution (194). Significantly lower values were found for seeds per cone, 100-seed weight, and percent pollen germination for white pine in the high-pollution area. Significantly lower values for cone length, 100-seed weight, percent filled seed, percent seed germination, and pollen tube length were found in red pine. None of the trees exposed to SO_2 showed leaf injury symptoms.

Scotch pine, known to be relatively resistant to SO_2 damage following continuous long-term exposure (average 0.07 ppm, maximum 0.24 ppm), suffered decreases in cone yield, cone length, seed yield, and seed weight with an increase in field SO_2 concentrations (317). The germination rate of the seed and the growth and development of 1-year seedlings grown from the seeds were not significantly affected. The trees were also grouped by height classes. As the concentration decreased, the number of trees that bore fruit increased for all height classes.

Elevated SO_2 content in the atmosphere around the Urals significantly weakened Scotch pine stands, thereby lowering the reproductive capacity of the trees (287). The number of seeds per cone decreased, and the ratio of male to female cones changed in favor of the females. The cone size of the trees in the smoke-damaged areas also decreased. The quality of the seeds and pollen grains from trees growing in the smoke-damaged areas was significantly lower than that of pollen and seeds from trees in undamaged stands.

Exposures of cotyledon-stage red pine seedlings under continuous field fumigation adversely influenced seedling development and regeneration of pine communities. Somewhat high concentrations were used (0.5, 1.0, 3.0, and 4.0 ppm SO_2) for periods of 15, 30, 60, or 120 min. Visible injury occurred only with the high concentrations of SO_2 at longer exposure periods (78).

Research published in the early 1970s has demonstrated effects within plants of low continuous exposure to SO_2. Many of the effects occur in the absence of visible foliar injury, but can lead to reductions in growth and yield. The few studies that have associated decreased photosynthetic rates with yield reductions (225, 237, 272) support the contention that reduced photosynthetic rates lead to reduced growth. The demonstrated effects of SO_2 on reproductive systems (cone size and number, seed size and germination capacity, pollen germination and growth) (197, 222, 287, 317) could have an impact on the competitive ability of some species. The reported increases in susceptibility to biotic and abiotic (296) factors of the environment brought about by SO_2 may also be of importance to the growth and survival of plants. Metabolic changes may indicate not only growth losses but also losses in quality of the plant product. Many important economic and ecologic effects could therefore be occurring as a result of SO_2 that are not obvious even to the trained observer.

7.2.4 Chronic Injury Due to SO_2 Exposure

Plant injury that is visible but does not involve collapse and necrosis of tissues is termed chronic injury. This type of visible injury is usually the result of short-term, high-concentration or long-term low-concentration exposures to SO_2. It has also been referred to as being "sulfate injury" since a slow accumulation of sulfate is the end result of such exposures (97). As with most air pollutants, SO_2 enters plants primarily through stomata during normal gas exchange functions. Once within the substomatal cavities, SO_2 reacts with intercellular water to quickly form sulfite and bisulfite, which are slowly oxidized to sulfate which is approximately 30 times less toxic than sulfite and bisulfite (418). The capacity of the plant tissues to convert sulfite and bisulfite to sulfate may

never be exceeded and as such only latent injury may occur with no further expression of symptoms. In some studies sulfate levels in plants exposed to SO_2 have been demonstrated to be several times greater than those in controls (269). However, if sulfite and bisulfite ions are formed, and sulfate accumulates to phytotoxic levels, then chronic symptoms first appear as various forms of chlorotic (yellowing) patterns. As sulfite and bisulfite ions accumulate after exposure to high levels of SO_2, destruction of individual chloroplast membranes or a reduction of chlorophyll production ensues. Accumulation of toxic levels of sulfate induce reddening or bleaching of cells without causing death. Following such accumulations, there is a fine distinction between chronic and acute symptom expressions.

In broadleaf plants, chronic injury is usually expressed in tissues found between the veins, with various forms of chlorosis predominating. Chlorotic spots or chlorotic mottle may persist following exposure or may subside and disappear following removal of the pollutant or as a result of changing environmental conditions. A yellowing of lower leaf surfaces of cotton was found to follow exposure to SO_2; symptoms progressed to the upper leaf surface as exposure to low concentrations continued (57). Later the symptoms progressed to bleaching or a brownish-red coloration, but the tissues remained turgid.

The chronic effects of SO_2 in perennial conifers are generally first expressed on older needles (270). Chlorosis of tissues visible as spots or mottle progresses down the needle from the oldest to youngest tissues. Advanced symptoms may follow, involving reddening of affected tissues. Houston (193) found that symptoms were initiated in eastern white pine seedlings following a 6-hr fumigation with 0.05 ppm SO_2.

7.2.5 Acute Injury Due to SO_2 Exposure

Acute injury usually results from exposure to high concentrations of SO_2. Such symptoms are easily recognized in most plant species. Acute injury from rapid absorption of a toxic dose of SO_2 causes marginal and intercostal necrotic areas which at first have a dull dark-green, watersoaked appearance. After desiccation and bleaching of the tissues, the affected areas become light ivory to white in most broadleaf plants. However, some species show darker colors, brown or red, but there is characteristically an exact line of demarcation between symptomatic and asymptomatic portions of leaf tissues. Bifacial necrosis is common (444).

In conifers, acute symptoms are expressed as needle-tip necrosis that has progressed from banding (necrosis) of distinct areas of affected tissues. Recently incurred injury is light colored, but later, bright orange or red colors are typical for the banded areas and tips. As needle tips die, they become brittle and break or whole needles drop from the tree. Pine needles are most sensitive to SO_2 during the period of rapid needle elongation, but injury may also occur on mature needles (104).

In summary, the response of plants to sulfur dioxide may take the form of latent injury only, or of visible injury; the latter may take chronic or acute forms. The response of individual plants or plant communities may be governed by the dose of pollutant, the number of exposures, the season of exposure, or any one or a group of environmental and biological factors that influence basic physiological functions.

7.2.6 Classification of Plant Sensitivity

7.2.6.1 Introduction--Because of space limitation, it is not possible to list all plants that are known to be sensitive to various doses of SO_2. Further-

more, in a listing of sensitive plants, the evidence collected should also indicate the environmental, genetic, and cultural considerations that may in fact determine such sensitivities. It has also been demonstrated that plant response to air pollutants varies at the genus, species, variety, and cultivar levels.

Lists of plant sensitivities have been prepared on the basis of the expression of visible symptoms by any given plant. Injury expressed by growth or yield losses has not been considered in the preparation of such lists.

7.2.6.2 Plant Sensitivity to SO_2--Jacobson and Hill (202) included a listing of plants sensitive to the major phytotoxic air pollutants. Other compilations have been presented. The report of Davis and Wilhour (105) provides information on an international basis. Specific reports have been prepared for vegetation native to the south-western deserts of the United States (182). Table 7-2 provides a partial listing of more common plants found to be sensitive to SO_2.

Extensive efforts have been made to develop certain plant species as bioindicators. Perhaps the most extensively examined plants for this use are eastern white pine (*Pinus strobus*) and numerous species of lichens. The white pine literature has been reviewed (145, 330) and the most recent review of lichen bioindicators was prepared by LeBlanc and Rao (256).

Other recent reports have been prepared for various ornamentals (96, 177, 349), bluegrass cultivars (320), scotch pine (109), loblolly pine (236), hybrid poplar (113), and trembling aspen (218). These represent examples of the continued efforts to identify sensitive plants suitable for use as bioindicators.

TABLE 7-2. PARTIAL LIST OF PLANTS KNOWN TO BE SENSITIVE TO SO_2 UNDER FIELD EXPOSURE CONDITIONS

Cultivated Crops:

Alfalfa - *Medicago sativa* L.
Barley - *Hordeum vulgare* L.
Bean - *Phaseolus vulgaris* L.
Bluegrass - *Poa annua*L.
Cabbage - *Brassica oleracea* L.
Cucumber - *Cucumis sativus* L.
Oats - *Avena sativa* L.
Pea - *Pisum sativum* L.
Radish - *Raphanus sativus* L.
Rhubarb - *Rheum rhaporiticum* L.
Rye - *Secalecereale* L.
Soybean - *Glycine max* Merr.
Spinach - *Spinaciaoleracea* L.
Tobacco - *Nicotiana tobacum* L.

Weed Species:

Big-leaved aster - *Aster macrophyllum*
Bindweed - *Convolvulus arvensis*
Blueberry - *Vaccinium angustifolium*
Curly dock - *Rumex crispus*
Dandelion - *Taraxacum officinale*
Fleabane - *Erigeron canadensis*
Lambsquarter - *Chenopodium album*
Pigweek - *Amaranthus retroflexus*
Plantain - *Plantago major*
Ragweed - *Ambrosia* spp.
Raspberry - *Rubus* spp.
Smartweed - *Polygonum* spp.
Wildgrape - *Vitis* spp.

Forest Trees:

Ash, white - *Fraxinus americana*
Aspen, large tooth - *Populus grandidentata*
Birch - *Betula* spp.
Elm - *Ulmus* spp.
Fir, Douglas - *Pseudotsuga menziesii*
Hybrid poplar - *Populus*
Larch - *Larix* spp.
Maple - *Acer* spp.
Mountain ash - *Sorbus aucuparia*
Pine, jack - *Pinus banksiana*
Pine, ponderosa - *Pinus ponderosa*
Pine, eastern white - *Pinus strobus*
Willow - *Salix* spp.

Ornamentals and Flowers:

Aster - *Aster bigelovii*
Azalea - *Rhododendron* spp.
Bachelor's button - *Centarea cyanus*
Begonia - *Begonia* spp.
Cosmos - *Cosmos bipinnatus*
Four-o'clock - *Mirabilis jalapa*
Morning glory - *Piomoea purpurea*
Petunia - *Petunia hybrida*
Sweet pea - *Lathyrus odoratus*
Verbena - *Verbena canadensis*
Violet - *Viola* spp.
Zinnia - *Zinnea elegans*

Detection of symptoms similar to SO_2 injury on sensitive species will provide additional evidence in diagnostic procedures. However, other causes may induce injury symptoms that mimic those of SO_2, and several bioindicators are desirable for evaluation in any given area. In addition, individual species and more complicated plant bioindicator systems are not as effective for detecting SO_2 at low concentrations as are sophisticated instruments.

7.3 Dose-Response Relationships--SO_2

Dose may simply be defined as concentration of pollutant(s) times the duration of the exposure period without further consideration of any environmental or biological influences. The response of any individual plant may be evaluated in light of influencing physical and biotic factors. Dose-response, therefore, is a term used to define and characterize the reaction of any given plant to various doses and the specific reaction may be enhanced or mitigated by a complexity of factors within the exposure conditions.

Plant responses induced by low-dose exposures (as usually characterized by low concentrations over short or long periods of time) involve the expression of latent symptoms that may lead to growth and yield effects or overt symptoms that seldom become more serious than those associated with chronic injury.

Plant responses induced by high-dose exposures (as characterized by high concentrations for short or peak periods of time or longer periods) usually involve the expression of symptoms leading to the necrosis of cells, tissues, entire organs, or plants and plant communities. Such symptoms usually develop rapidly following high-dose exposures and are usually described as acute injury.

Response may be characterized by a measurable change in any parameter. Induced changes have been measured in biochemical pathways, gas exchange rates, photosynthetic rates, physiological functions, degree of

visibly recognizable leaf injury, or subsequent growth and yields. The latter two effects have most commonly been expressed as quantitative changes. Results such as those obtained by Horsman et al. (186) are not easily tabulated into dose-response tables. They provided strong evidence that high doses of SO_2 were responsible for a population differentiation within perennial ryegrass, favoring a few, more tolerant, clones within those receiving high doses.

Numerous physical and biotic factors must be considered in evaluating dose-response data. Changes in exposure conditions, differences in exposure methodology, efficiency of monitoring equipment, and consistency of measurements within a study and between studies on the same plant will directly influence results (Figure 7-2; Heck and Brandt, ref 173).

Several attempts have been made to characterize dose-response relationships in a mathematical sense using monitored concentrations, exposure times, and injury thresholds as modified by physical and biotic factors expressed as constants.

O'Gara (341) derived the following formula from short-term fumigations of alfalfa; $(C - C_t)\ t = K$. In this function, concentration (C) and exposure time (t) are directly proportional. The value C_t is the threshold concentration at which no injury occurs, even under long-term exposures. As C approaches C_t, t approaches infinity.

After extensive experimentation with SO_2, the equation has been modified so that the pollutant dose that causes a particular degree of injury can be predicted (422). For example, under conditions of extreme plant sensitivity,

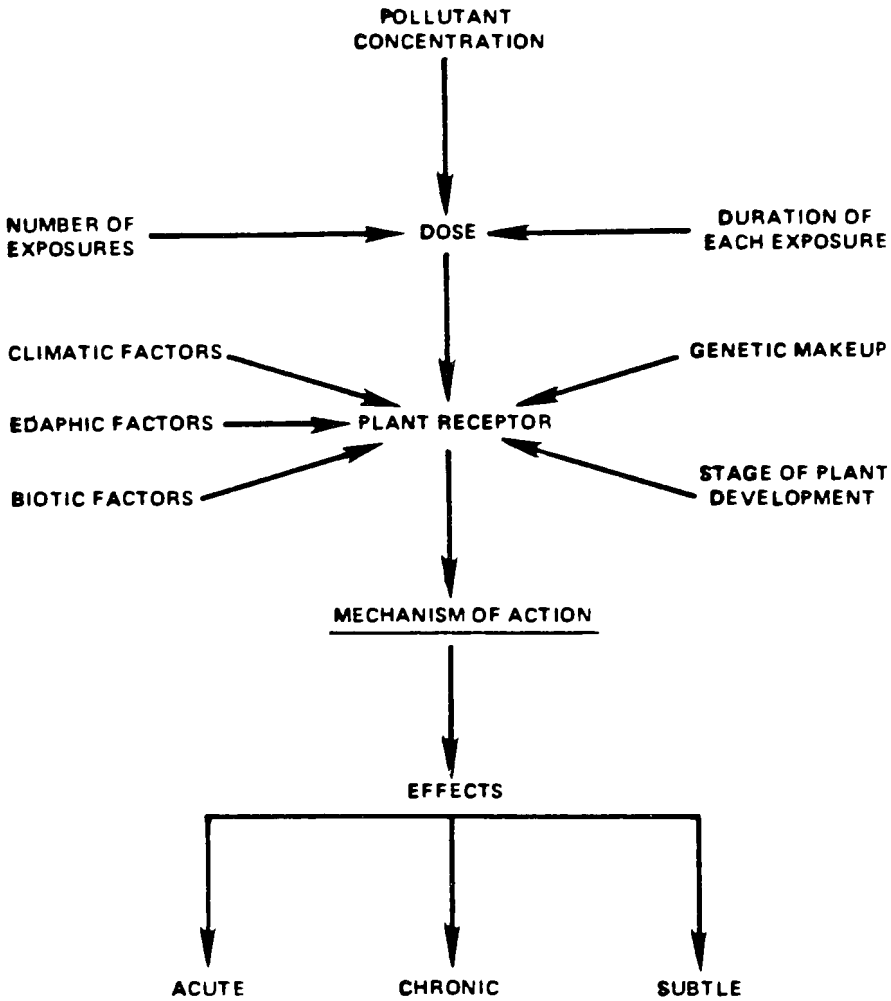

Figure 7-2. Conceptual model shows factors involved in air pollution effects (dose-response) on vegetation. Subtle effects are called "latent effects" in this chapter.

Source: Heck and Brandt (1977).

the following values are given:

$$(C - 0.24)t = 0.94, \text{ slight necrosis}$$

$$(C - 1.40)t = 2.10, \text{ 50 percent necrosis}$$

$$(C - 2.60)t = 100 \text{ percent necrosis}$$

Zahn (494) developed an equation for the function of the threshold concentration for short-term exposure to high SO_2 concentrations resulting in acute injury:

$$t = \frac{1 + 0.5c}{C(C - a)}$$

where a = threshold concentration, b = measurable resistance factor incorporating influences of environmental conditions, C = monitored concentration, and t = time of exposure.

However, studies on the influence of concentration (C) and exposure time (t) have shown that dose-response induced by SO_2 does not always conform to such simple computations. Van Haut (451) demonstrated that injury to radish increased progressively with increased SO_2 concentrations even though time was correspondingly reduced, that is, the product of concentration and time was held constant (Table 7-3).

According to Larsen and Heck (250): (1) a constant percentage of leaf surface will be injured by an air pollutant concentration that is inversely proportional to the exposure duration raised to an exponent, and (2) for a given exposure duration, the percent leaf injury as a function of pollutant concentration tends to fit a log-normal frequency distribution.

The following exponential function has been developed which takes into account the particular risks of high SO_2 concentrations (250):

$$t - t_r = (e^{-a(c - C)_r})K$$

where t is exposure time, t_r is the threshold time minus minimum exposure time required to cause injury, C = pollutant concentration, C_r is the threshold concentration minus the minimum concentration required to cause

TABLE 7-3 PROGRESSIVE INCREASE IN THE DEGREES OF INJURY OF RADISH WITH INCREASING SO_2 CONCENTRATIONS

SO_2 ppm concentration	Exposure time in hours		Area of leaf injury
C	C	Ct	%
1.15	12	36	2
2.3	6	36	20
3.4	4	36	40
4.6	3	36	77

[a] Converted from mg/m^3 to ppm ($2.62\ mg/m^3$ = 1 ppm) at 25° C, 760 mm Hg.

Source: Van Hart (451).

injury, a is an internal and external growth parameter, and K is growing time. Larsen and Heck used this approach to predict the dose-response relationship for SO_2 on Norway maple, gingko, pin oak, and Chinese elm. The latter species mentioned was the most sensitive, being injured by SO_2 doses of 3.5 ppm for 1 hr, 0.46 ppm for 3 hr, and 0.07 ppm for 8 hr. The authors used such data to develop an effects model.

Information on SO_2 doses causing acute injury on sensitive plant species is summarized in Table 7-4. When evaluating the material presented in the table, the reader must remember that demonstration of an effect in terms of injury does not necessarily indicate an effect in terms of damage. Damage always implies injury; injury may occur, however, without damage. (See section 7.2.1 for a further explanation of this consideration.)

Tables 7-5, 7-6, and 7-7 present salient information taken from numerous reports of SO_2-induced effects to field crops, forest trees, and other forms of vegetation, respectively. Many of these reports have been reviewed in more detail elsewhere in this chapter; several more have been added here to emphasize the total number of studies available for review. The tables have been arranged on the first-order basis of increasing concentrations of SO_2, and increasing lengths of exposure times have been used as a second-order breakdown under concentrations. For the sake of brevity, only common names of plants have been presented. Latin binomials of all plants used within this table may be found in the composite listing in appendix A of this chapter. The conditions of exposure refer to the location of the experiment as to field or indoor tests and the type of fumigation systems used. Effects examined are indicated by an (X) as the designation of foliar or yield effects being examined; the (X) does not indicate that such effects were found. The effects listed are those considered to be the most important findings from the research data presented in original articles. Each effect has been located

TABLE 7-4. SULFUR DIOXIDE CONCENTRATIONS CAUSING VISIBLE INJURY TO VARIOUS SENSITIVITY GROUPINGS OF VEGETATION[a] (ppm SO_2)

Maximum average concentration	Sensitivity grouping		
	Sensitive	Intermediate	Resistant
Peak	1.0-1.5	1.5-2.0	>2.0
1-hr	0.5-1.0	1.0-2.0	>2.0
3-hr	0.3-0.6	0.6-0.8	>0.8
	Ragweeds	Maples	White oaks
	Legumes	Locust	Potato
	Blackberry	Sweetgum	Upland cotton
	Southern pines	Cherry	Corn
	Red and black oaks	Elms	Dogwood
	White ash	Tuliptree	Peach
	Sumacs	Many crop and garden species	

[a]Based on observations over a 20-year period of visible injury occurring on over 120 species growing in the vicinities of coal-fired power plants in the southeastern United States.

Source: Jones et al. (213).

TABLE 7-5. DOSE-RESPONSE INFORMATION SUMMARIZED FROM LITERATURE PERTAINING TO CULTIVATED AGRONOMIC CROPS AS RELATED TO FOLILAR, YIELD, AND SPECIFIC EFFECTS INDUCED BY INCREASING SO_2 DOSE

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.01	10 min	EC	Corn			Stomata open wider	448
0.01	Growing season		Oats	X		Light leaf injury	159
0.015	Growing season		Wheat		X	15% decrease in grain weight yield	159
0.02	10 min	EC	Bean			Stomata open wider	448
0.035	3 hr for 8 exp, growing season	F/CC	Wheat			No effect on apparent photosynthesis, no effect on the average head length or number of grains per head	394
0.02 0.05 0.10	Growing season (2 year)	F-ZAP	Winter wheat Prairie June grass			S content increased with increase in SO_2 concentration; digestibility of dry matter was reduced by 2 years of treatment; crude protein content in winter wheat decreased significantly	473
0.03- 0.10	72 hr/wk for growing season	F/CC	Barley Durham wheat Spring wheat		X	No effect on yield	473
0.3- 0.06 0.10 0.15 0.20	24 hr/day for 30 days	F/CC	Winter wheat ev. Yamhill ev. Ilyslop		X X	0.03 ppm increased yield 27% 0.06-0.15 ppm, no effect 0.06 ppm decreased yield 22%) 0.20 ppm decreased yield 70%	473
0.035 1.75	8 hr	EC/SD	Broadbean			Depressed photosynthesis	40
0.05	10 min	EC	Broadbean			Stomata open wider; threshold 0.02 ppm for 10 min	37

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.05	5 hr/day; 5 day/wk for 4 wk	EC/SD	Alfalfa		X	26% decrease in foliage dry weight	430
					X	49% decrease in root dry weight	
			Tobacco		X	22% decrease in leaf dry weight	
0.05 0.10 0.25	4 hr	EC/SD	Oats Radish Soybean Tobacco	X		No foliar injury	431
0.05 0.20	8 hr/day 5 days/wk for 18 days	EC/SD	Soybean	X		No effect on top fresh or dry weight; root fresh or dry weight; plant height; shoot/root fresh or dry weight ratio	
0.06	68 days	EC/SD	Alfalfa		X	28% decrease in foliage stubble, 45% decrease root dry weight 21% decrease in total protein content, amino acid content, total nonstructured carbohydrates, symbiotically fixed nitrogen	327
0.065 0.13 0.26	1-55 days	GC	Cabbage Chinese cabbage Cucumber Eggplant Lettuce Spinach	X X X X X X		Foliage injury threshold 0.13x27 days Foliage injury threshold 0.26x55 days Foliage injury threshold 0.13x26 days Foliage injury threshold 0.13x11 days Foliage injury threshold 0.13x15 days Foliage injury threshold 0.13x1 day Other parameters measured such as plant height, number of leaves, top fresh weight, number of flowers, fresh weight vs. dry weight of roots were not found to be significantly different from controls	140
0.10	20 min	EC	Bean Corn			Stomata open wider, effect also shown to occur in dark	448
0.10	1 hr	EC	Bean			Stomata open wider, water-stressed plant had wider opening of stomata compared with controls	448
0.10	8 hr	GH	Tobacco	X		Foliar injury threshold for development of fleck-like lesions	283

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.10	6 hr/day for 133 days	F/CC	Soybean		X	No significant effect on growth or yield; 92nd-day defoliation was 12% greater; 135th-day seed weight was 1% reduced from control	169
0.10	18 days	GC	Pea		X X	3% decrease in fresh weight of shoot 5% decrease in dry weight of shoot 4% decrease in total nitrogen 30% decrease in H^+ (buffer capacity) 10% increase glutamate dehydrogenase activity 110% increase in inorganic sulfur content	204
0.10	6 hr/day 43 days 92 days 133 days	F/OT	Soybean			No significant effect on foliar injury, defoliation fresh weights, seeds/plant, or weight of seeds/plant	171
0.125-1.0	1-3 hr	EC/SD	Oats Radish Sweet pea Swiss chard	X		No foliar injury	32
0.15	18 days	GC	Pea		X X	3% decrease in fresh weight of shoot 8% decrease in dry weight of shoot 2% decrease in total nitrogen 35% decrease in H^+ (buffer capacity) 32% increase in glutamate dehydrogenase activity 140% increase in inorganic sulfur content	204
0.15	72 hr/wk for growing season	F/CC	Barley Durham wheat Spring wheat	X X	X	42% decreased yield in Durham wheat; 44% decreased yield in barley; no effect on spring wheat	473
0.25	18 days	GC	Pea		X X	32% decrease in fresh weight of shoot 26% decrease in dry weight of shoot 24% decrease in total nitrogen 42% decrease in H^+ (buffer capacity) 80% increase in glutamate dehydrogenase activity 150% increase in inorganic sulfur content	204
0.11	103.5 hr/wk for 20 wk	GC	Cocksfoot Meadowgrass Italian ryegrass Timothy		X X X X	40% decrease in total dry weight 28% decrease in total dry weight Nonsignificant 51% decrease in total dry weight (Yield reductions were related to decrease in leaf areas)	13,14

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.15	24 hr	EC/SD	Corn Rice			Absorbed SO_2 remained in water-soluble form and very difficult to assimilate to protein	490
0.15- 0.30	7 days	EC/SD	Barley Bean Corn	X X X		Severe foliar injury No injury Severe foliar injury	288
0.15	14 days	GH	Celery	X		Increased peroxidase activity, caused chlorosis of leaves	356
			Big plantain	X		Increased peroxidase activity, decreased buffering capacity of cells, caused necrotic leaf injury	
			Bean	X		Caused necrotic leaf injury	
			Big mallow	X		Caused necrotic leaf injury	
0.17	2 hr	EC/SD	Broadbean			Decreased photosynthetic rate, decreased stomatal resistance if RH > 40%, increased stomatal resistance if RH < 40%	39
0.20 0.25	I hr	EC/SD	Alfalfa			No effect on photosynthesis	471
0.25	2 hr	GC	Alfalfa Barley Oats			Threshold dose for inhibition of photosynthesis	30
0.20 0.30 0.40 0.50 0.60 0.70	2 hr		Alfalfa Barley			No effects at these doses	30
0.20	15 days	GC	Tomato	X		Threshold dose for initial symptom of tissue death, decrease or change in vitamin B_1, B_6, and nicotinic acid content	449
0.20	To maturation	EC/SD	Kidney bean		X	15% decrease in total yield	33
0.218	4.5 hr/day for 4 days	F-ZAP	Soybean	X		No visible damage	201
					X	20% decrease in yield	

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.23	14 days	GH	Buckwheat	X		Caused necrotic leaf injury	356
			Lucerne	X		Caused necrotic leaf injury	
			Red clover	X		Caused necrotic leaf injury	
			Little stinging nettle			Increased peroxidase activity	
			Ryegrass			Increased S content in leaves	
0.25	1 hr		Broadbean			Slight swelling of stroma thylakoids of chloroplast, effect reversible	464
0.25	2 hr		Broadbean			Stroma thylakoids spread to granum thylakoids, effect reversible	
0.25 0.40 0.80 1.20	Once every wk (3 hr) to once in 5 wk (3 hr)	F/CC	Alfalfa Barley Durham wheat Spring wheat		X	No effect on yield	473
0.25	4 hr	EC/SD	Broccoli	X		1% leaf injury	432
			Tobacco, Bel B,	X		6% leaf injury	
0.25	8 hr	EC/SD	Tobacco			Chlorophyll a decreased more sharply than chlorophyll b	40
0.25	24 hr	GC	Broadbean			Stomata opened faster and wider in light condition; stomata opened longer in darkness	286
0.25	1 hr	EC	Begonia	X		Foliar injury	431
0.25 0.40 0.80 1.20	3 hr every 2 wk for growing season	F/CC	Alfalfa Barley Durham wheat Spring wheat		X	No effect on yield	473
0.25	Unknown	EC	Pea			50% decrease in net photosynthesis	62
0.25	Unknown	EC	Sunflower			10% decrease in photosynthetic rate	450
			Morning glory			20-30% decrease in photosynthetic rate	
			Corn			No effect	
			Sorghum			No effect	
0.29	15 days	GC	Lettuce	X		Foliar injury, 30% decrease in thiamine content	449

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.30	5 hr/day	EC/SD	Barley			11% foliar injury; 38% decrease in dry weight shoot	292
	6 day/wk		Bean			1% foliar injury; 38% decrease in dry weight shoot	
	12 days		Sunflower			5% foliar injury; 41% decrease in dry weight shoot	
	26 days		Barley			21% foliar injury; 26% decrease in dry weight shoot 2% foliar injury; 15% decrease in dry weight shoot 16% foliar injury; 29% decrease in dry weight shoot	
0.35	1 hr	EC/SD	Alfalfa			80% decrease in apparent photosynthesis	472
0.35	21 days	EC/SD	Pea			Increase in glutamine content, decrease in glutamic acid and protein content inorganic S accumulated	205
				X	X	Necrosis and growth inhibition at 0.35 x 14 days	
0.38 1.15 1/90	14 days	0	Radish	X		Decrease injury at 0.38 and above, inhibited seed germination, formation of green leaflets of sprouts, and root growth	111
0.40	3 hr		Oats	X		Threshold for leaf injury	174
0.40 0.50 0.60	4 hr	EC/SD	Tomato			Increase accumulation total and soluble S content	29
0.40	6 hr	EC/SD	Apples			No effect	227
0.40	6 hr/2 wk (1-2 exposures)	EC/SD	Alfalfa Cotton Pecan Pepper			No difference found in total N, protein/total N ration, chlorophyll, all plants, all treatments	424
0.45	3 hr for 7 exposures for growing season	F/CC	Wheat		X	No accumulative effect on yield, no effect on average head length or number of grains/head	394
0.46	7 hr	EC	Buckwheat	X		Injury threshold	498
0.50-6.00	30 min	F/CC	Soybean	X	X	Very significant negative linear relationship between percent leaf area destroyed and percent crop loss; 0.66% yield loss for every 1% increase in foliar injury; asymtomatic plots increased yield by 6.02% over controls	102

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.50	1.5 hr	EC/SD	Soybean	X	X	7% decrease in short fresh weight; trace foliar injury	172
0.50	1.5 hr		Oats		X	Inition of leaf injury	174
0.50	2 hr	EC	Begonia			No effect	
			Petunia		X	30% decrease in flower number; 15% decrease in shoot weight	2
			Coleus			No effect; 12% decrease in shoot weight	
			Snapdragon		X	11% decrease in number of flowers; no effect	
0.50	2 hr	EC	Grape			190% increase in stomatal resistance	371
0.50	4 hr	EC/SD	Alfalfa	X		19% leaf injury	
			Broccoli	X		4% leaf injury	431
			Radish	X		1% leaf injury	
			Tobacco	X		1% leaf injury	
			Tomato	X		1% leaf injury	
0.50	4 hr	EC/SD	Oats	X		Foliar injury occurred to all crops	441
			Radish				
			Soybean				
			Tobacco				
0.50	4 hr/day for 14 days	EC/SD	Oats		X	32% decrease top dry weight; 13% decrease in root dry weight; number of heads unchanged	175
0.50	5 hr/day		Barley			24% foliar injury; 42% decrease in dry weight shoot	292
	6 days/wk		Bean			7% foliar injury; 31% decrease in dry weight shoot	
	for 12 days		Sunflower			18% foliar injury; 44% decrease in dry weight shoot	
	26 days		Barley			36% foliar injury; 45% decrease in dry weight shoot	
			Bean			12% foliar injury; 34% decrease in dry weight shoot	
			Sunflower			26% foliar injury; 35% decrease in dry weights shoot	

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.50 1.00 1.50	4 hr	GC/G	Red Clover			Increase in vitamin A, fat, protein content Significant change in plant nutritional components	196
0.50	5 hr/day 6 days/ week for 14 days	EC	Broadbean Sunflower Tobacco			Under drought conditions exposure caused wider opening of stomata, no effect on diffusive resistance	379
0.50	6 days	O	Pea			Increased glutamate dehydrogenase; increased peroxidase activity	465
0.56 0.77 0.92	4 hr	EC/SD	Cucumber			Accumulation of significant total and soluble sulfur	29
0.60	6 hr	EC/SD	Apples	X		7.3% increase in foliage injury; 5% increase leaf abscission	227
0.60	6 hr/day 5 days/week for 14 days	EC/SD	Soybean White bean	 X		No effects Bifacial necrotic lesion on mature leaves	183
0.70	8 hr/day for 3 days	EC/SD	Broadbean			20% decrease in photosynthesis after 2 hr fumigation; after 3-day fumigation, 1 hr to full recovery in light condition; no foliage injury	24
0.70	6/12, 24 hr/day 1-7 days	EC	Bean	X		Increase in total amino acids and ammonium, decrease in aspartic acid glutamic acid and protein synthesis, all before visible injury present	
0.75	3 hr	EC/SD	Alfalfa	X		No injury developed	192
0.80	2 hr		Alfalfa	X		Threshold dose for foliar necrosis; 25-50% decrease in net photosynthesis	30
0.80-2.00	4 hr, 20 min	F/ZAP	Soybean		X X X	4.5% decrease in yield at 1.4 ppm 11% decrease in yield at 1.7 ppm 15% decrease in yield at 2.0 ppm	310
0.80-2.00	4 hr, 20 min	F/ZAP	Soybean	X	 X	Epidermal and mesophyll cell death, the number of dead mesophyll cells highly correlated with increase in SO_2 Highest SO_2 concentration, significant decrease in seed yield	

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.90	2 hr	EC/SD	Broadbean			26% decrease in net photosynthesis under saturated light conditions; 52% decrease in net photosynthesis under nonsaturated light conditions	39
1.00	2 hr		Barley	X		Threshold dose for foliar necrosis; 30-60 decrease in net photosynthesis	30
1.00	3 hr	GC	Poinsettia eight cultivars			No effect	177
1.00	3 hr	EC/SD	Alfalfa	X		Leaf necrosis at 315 ppm CO_2 was 2.8x that induced under 645 ppm CO_2	192
1.00	2 hr	EC	Begonia			No effect	
			Petunia		X	30% decrease in flower number; 19% decrease in shoot weight	
			Coleus		X	27% decrease in flower number; 19% decrease in shoot weight	
			Snapdragon		X	14% decrease in flower number; 16% decrease in shoot weight	
1.00	4 hr	EC/SD	Broccoli	X		38% leaf injury	
			Bromegrass	X		65% leaf injury	431
			Cabbage	X		70% leaf injury	
			Lima bean	X		25% leaf injury	
			Radish	X		46% leaf injury	
			Spinach	X		49% leaf injury	
			Tomato	X		33% leaf injury	
1.0	1 hr/2 days for 4 days	EC/SD	Geranium			Rapid closing of stomata in low-RH air after exposure; slow closing in high-RH conditions, stomata remained open	47
1.0	6 hr/day for 3 days	EC/SD	Strawberry			No effect on growth and development	
				X		Necrotic lesions, lower leaf surface	358
1.00	1.5 hr	EC/SD	Soybean	X	X	9% decrease in shoot fresh weights, 4% leaf	
	3 hr				X	injury 21%-29% decrease in shoot fresh weight	172
1.50	0.75-3 hr	EC/SD	Soybean	X	X	24-94% decrease in shoot fresh weight; 63-93% foliar injury	172
1.50	3 hr	EC/SD	Alfalfa	X		Leaf necrosis at 315 ppm CO_2 was 2.5x that induced under 645 ppm CO_2	192

TABLE 7-5 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
1.50	To maturation	EC/SD	Kidney bean		X X	20% decrease in root dry weight; 14% decrease in legume dry weight; 17% decrease in seed dry weight; 10-30% decrease in apparent photosynthesis. Increase in chlorophyll a and b content	33
2.00	2 hr	EC	Begonia		X	14% decrease flower number; 22% decrease in shoot weight	2
			Petunia		X	32% decrease in flower number; 24% decrease in shoot weight	
			Coleus		X	30% decrease in flower number; 20% decrease in shoot weight	
			Snapdragon		X	15% decrease in flower number; 15% decrease in shoot weight	
2.0	3 hr	GC	Poinsettia eight cultivars	X		0-18.3% foliar injury	177
2.5	6 hr	EC/SD	Apples	X	X	17% increase in foliar injury; 62% increase in lead abscission; 19% decrease in shoot growth	227
3.0	1 hr	GC	Poinsettia eight cultivars	X		0.13.8% foliar injury	177
	2 hr	GC		X		1.8-26.8% foliar injury	
	3 hr	GC		X		18.8-96.5% foliar injury	
4.00	2 hr	EC	Begonia		X	27% decrease in flower number; 33% decrease in shoot weight	2
			Petunia		X	42% decrease in flower number; 32% decrease in shoot weight	
			Coleus		X	30% decrease in flower number, 21% decrease in shoot weight	
			Snapdragon		X	20% decrease in flower number; 19% decrease in shoot weight	

[a]Table arranged by increasing SO_2 concentration as first-order and exposure time as second-order divisions. Doses within a single study that did not induce specifically different effects are listed along with the lowest SO_2 concentration that induced said effect.

[b]F = field or forest surveys
F/CC = Field, closed chambers
D/OT = Field, open-top chambers
F/ZAP = Field, zonal air pollution system
G = Greenhouse
GC = Growth chambers
EC = Exposure chambers
EC/SD = Exposure chamber, special design
O = Other

[c]See Appendix A for most scientific latin binomials of plants.

TABLE 7-5 (continued)

[d]X Indicates study examined foliar and/or yield effects. The X does not necessarily imply that an effect was found.

[e]Most prominent or significant effect reported.

TABLE 7-6. DOSE-RESPONSE INFORMATION SUMMARIZED FROM LITERATURE PERTAINING TO FOREST TREE SPECIES AS RELATED TO FOLIAR, YIELD, AND SPECIFIC EFFECTS INDUCED BY INCREASING SO_2 DOSE

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.001	10 yr avg.	F	Forest trees	X	X	No injury	~~118~~ 272
0.003-0.09	Annual avg	F	Scotch pine	X	X	Decreased photosynthesis leading to the death of tree	355
0.09-0.12	Annual avg						
0.004 0.35	Annual avg Annual avg (exposed 5 mo)	F	Eastern white pine			No significant difference in S content of foliage	369
0.006	Growing season	F	White birch			No effect on foliar S content	273
0.007-0.01	Annual avg	F	Fir forests		X	20 ± 5% growth increase	297
0.007-0.01	Annual avg	F	Fir forests	X	X	20 ± 5% growth decrease Premature defoliation	296
0.008	10 yr avg	F	Forest trees	X	X	Very little chronic foliar injury	~~118~~ 272
0.011	Growing season	F	White birch	X		Increased foliar S content; trace to light foliar injury	273
0.017	10 yr avg	F	Forest trees	X	X	Mostly chronic foliar injury; some acute injury	~~118~~ 272
0.015	Annual avg	F	Conifers		X	30% decrease in growth	454
0.019	Annual avg	F	Conifers		X	52% decrease in growth	454
0.023	Annual avg	F	Conifers		X	54% decrease in growth	454
0.025	6 hr	EC/SD	Eastern white pine	X		Threshold dose for needle damage; most sensitive clones only	193

TABLE 7-6 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.025-0.037	Annual avg	F	Fir	X	X	Death of groups of trees	297
0.026	Growing season	F	White birch	X		Moderate to severe foliar injury	273
0.026-0.037	Annual avg	F	Fir	X	X	Rapid death of groups of trees	296
0.035	5 mo	F	Eastern white pine	X		Foliar injury	369
0.038-0.057	Annual avg	F	Scotch pine		X	Species occurrence negatively correlated with SO_2 ambient conc.; foliar S content positively correlated with SO_2 ambient conc.; foliar S content positively correlated with SO_2 ambient conc.; by distance from source	133
0.045	Growing season	F	Jack pine	X		Reduced chlorophyll content, tissue death	273
0.045	10 yr avg	F	Forest trees	X	X	Acute and chronic foliar injury	~~118~~ 272
0.048	Growing season	F	White birch	X		Severe foliar injury; foliar S concentration 3x normal	273
0.05 0.15	6 hr	EC/SD	Eastern white pine	X		60% of tolerant clones foliar injury developed	193
0.05	49 days		Norway spruce	X		Foliar injury	491
0.05	10 wk	F/CC	Spruce		X	No effects	224
0.05 0.10 0.20	5 mo	F/CC	Beech	X		Increase in S concentration proportional to increase in SO_2 exposure conc.; terminal bud death	223
0.05	9 mo	F/CC	Spruce			Decreased foliar buffering capacity; in-peroxidase activity	222
0.05-0.10	9 mo	F/CC	Scotch pine			Decreased photosynthesis	222
0.05 0.10 0.20	9 mo	F/CC	Fir			Decreased pollen viability	222

TABLE 7-6 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.069	Annual avg	F	Conifer		X	70% decrease in growth	454
0.07	3 days	EC	Eastern white pine	X		Chlorotic spotting and death of needle tips	19
0.10 0.20	10 wk	F/CC	Spruce		X	Decreased CO_2 uptake; positive correlation between CO_2 uptake and cambium growth; increase in conc. induced annual ring width	223
0.10	76 days		Black alder			Increase phenoloxidase activity	491
0.15 0.30	9 wk		Poplar		X	Decreased leaf area index and foliar growth	209
0.18- 0.20	24 hr		Jack pine			Inhibited foliar lipid synthesis, inhibition reversible; increase in dose = increase in recovery time	286
0.20- 1.00	1 hr		Azalea Firethorn White ash White birch			No appreciable effect on foliar sorption of SO_2	367
0.20	12 hr/day for 7 wk	EC/SD	Hybrid poplar		X	Slightly decreased height; decreased relative growth rate, relative leaf growth rate, and relative leaf area expansion rate	208
0.20	110 days		English birch			No effect on phenyloxidase activity	491
0.025	2 hr	EC/SD	Eastern white pine Jack pine Red pine	X X X		6.5% foliar injury 4.5% foliar injury 0.5% foliar injury	34
0.25	2 hr	EC/SD	Loblolly pine Shortleaf pine Slash pine Virginia pine	X X X X		All equally sensitive; most sensitive period 8-10 wk of age or older	35
0.27	3 mo	EC	Pin oak White birch		X X	45% decrease in height growth 107% increase in height growth	368
0.35	3 hr	EC/SD	Trembling aspen	X		2% foliar injury	217
0.40 0.50	74 hr	EC	Yellow pine Eastern white pine			Chlorophyll content varied inversely with concentration	100

TABLE 7-6 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.45	6 hr	EC/SD	Eastern white pine	X		All tolerant clones developed foliar injury	193
0.45	9 hr/day for 8 wk	EC	Ponderosa pine	X		Severe needle tip chlorosis and necrosis	128
0.5	15 min		Red pine			Decreased primary needle chlorophyll content.	78
	30 min					Decrease dry weight of primary needles and cotyledons	
	60 min						
	120 min					Further increase of all of above effects	
0.50	2 hr	EC/SD	Eastern white pine	X		12% foliar injury	34
			Jack pine	X		11% foliar injury	
			Red pine	X		2% foliar injury	
0.50	3 hr	EC/SD	Trembling aspen	X		11% foliar injury	217
0.50	5 hr	GC	Austrian, Ponderosa Scotch pine, Balsam, Fraser, White fir Blue, White spruce Douglas fir	X		No injury	399
0.50	30 day	GC	Chinese elm	X		Severe chlorosis and necrosis	416
			Gingko	X		Moderate marginal chlorosis	
			Norway maple	X		Moderate marginal chlorosis	
			Pin oak	X		Slight overall chlorosis	
0.65	3 hr	EC/SD	Trembling aspen	X		23% foliar injury	217
1.00	4 hr	GC	Austrian, Ponderosa, Scotch pine, Balsam, Fraser, White fir, White spruce, Douglas fir	X		Less than 4% foliar injury all species	399
1.00	8 hr	EC	American elm			Inhibition of stomatal closing	335
1.07-6.41	30 min to 6 hr	O	Scotch pine *P. pinea* *P. nigra*	X		Visible injury was proportional to foliage S content	65
1.83	50 min	O	Pine Spruce	X		SO_2 absorbed by exposed foliage in wintertime; S stored in new shoots	298

TABLE 7-6 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
2.00	2 hr	CG	Austrian, Ponderosa Scotch pine, Balsam, Fraser, White fir, Blue, white spruce, Douglas fir	X		No foliar injury on Douglas fir, firs, spruce Pine foliar injury threshold, necrotic tips	399
2.00	6 hr	GC	American elm	X	X	Induce severe foliar injury; defoliation in older leaves; significant reduced expansion of new leaves; number of emerging leaves and root dry weight reduced	76
2.00	6 hr	GC	American elm			No significant reduction in lipid content; significant decrease in new leaf protein content; significant decrease in leaf, stem, root carbohydrate content	79
2.00	6 hr	GC	Chinese elm	X		100% leaf necrosis	416
2.00	6.5 hr	O	Ginkgo			Water-stressed plant increased uptake of SO_2	335
2.00	12 hr	O	American elm			Induced stomatal closing; S content increased in plants fumigated in light	416
3.00	6 hr	GC	Ginkgo Norway maple	X		50% leaf necrosis	416

[a] Table arranged by increasing SO_2 concentration as first-order and exposure time as second-order divisions. Doses within a single study that did not induce specifically different effects are listed along with the lowest SO_2 concentration that induced said effect.

[b] F = field or forest surveys
F/CC = field, closed chambers
D/OT = field, open-top chambers
G/ZAP = field, zonal air pollution system
G = greenhouse
GC = growth chambers
EC = exposure chambers
EC/SD = exposure chamber, special design
O = other

[c] See Appendix A for most scientific latin binomials of plants

TABLE 7-7 DOSE-RESPONSE INFORMATION SUMMARIZED FROM LITERATURE PERTAINING TO NATIVE PLANTS AS RELATED TO FOLIAR, YIELD AND SPECIFIC EFFECTS INDUCED BY INCREASING SO_2 DOSE

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.006 0.018	6 mo	F	Lichens		X	Loss of chlorophyll, decreased growth	255
0.01- 0.02	Annual avg	F	Lichens			Elimination of many lichen species	256a
0.015	Annual avg	F	Bryophytes Lichens			Decreased lichen diversity	397
0.017	6 mo	F	Bryophytes			Elimination of species	147
0.02	29 days 22 days in 2 consecutive growing seasons	GC	Ryegrass		X	No effect on net photosynthesis, dark respiration, transpiration coefficients, number of tillers and yield	87
0.14	29 days 22 days in 2 consecutive growling seasons	GC	Ryegrass	X	X	As above effects except visible foliar injury and reduction of specific leaf area	
0.02	85 days	GC	Ryegrass			Increased organic S content	89
0.02	Growing season	GC	Ryegrass			Increased organic and inorganic S content	86
0.03	10 wk	GC	Ryegrass		X	Alleviated S deficiency	277
0.04					X	Alleviated S deficiency	
0.08					X	Alleviated S deficiency	
0.15					X	Reduction in yield without symptoms	
0.03 0.04	6 mo	F	Lichens	X		Tissue death	256a
0.04 0.15	51 days	GC	Ryegrass			Decreased concentration glycine and serine; inhibited photorespiration pathway	234
0.05	Growing season	GC	Ryegrass	X		Alleviated S deficiency symptoms	86

TABLE 7-7 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.06	Growing season	GC	Ryegrass		X	Increase in photosynthesis, respiration and chlorophyll content; light increase in productivity	135
0.067	26 wk	EC	Ryegrass		X	Increase in dry weight of leaves, number of tillers, dry weight of stubble and leaf area; 51% decrease in yield	24
0.073	26 wk	EC	Ryegrass			50% decrease in shoot dry weight 24% decrease in chlorophyll a content; 26% decrease in chlorophyll b content	25
0.074	18 hr	0	Spiderwort			Increase in chromosome aberration rate of germinating pollen	282
0.08	13 hr/day for 28 days	EC	Foxtail grass	X		Foliar injury as caused by heavy metals was increased by SO_2 exposure	236
0.09 (peak)	115 days	F/CC	Ryegrass	X		Decrease in weight; accelerated leaf senesence	42
0.11	4 wk	0	Cocksfoot		X	30% decrease in leaf area; 45% decrease in dry weight; decrease in number tillers; decrease in number of green leaves; decrease root/shoot ratios	12
0.11	4 wk	0	Ryegrass		X	20% decrease in leaf area; 40% decrease in dry weight; decreased root/shoot ratio	14
0.11	103 5 hr/wk for 20 wk		Grass		X	Significant decrease in leaf area and all dry weight fractions; decrease in number of leaves and tillers	13
0.12	9 wk	EC	Ryegrass			Decrease in dry weight of leaves, number of tillers, dry weights of stubble and leaf area; 46% decrease in yield	24
0.13 0.25 0.50 1.00	6 wk	EC/SD	Ryegrass	X	X	Foliar necrotic lesions and decrease in net primary productivity at 0.13 ppm and above	135
0.13	6 wk	EC/SD	Ryegrass	X	X	Decreased productivity	135

TABLE 7-7 (continued)

Conc, ppm	Exposure time	Exposure condition[b]	Plant[c]	Effects on Foliar	Effects on Yield	Species Effect[c]	Reference
0.15	6 wk		Duckweed		X	Decrease in starch content and size of fronds	131
0.15	51 days		Duckweed		X	Decrease in starch content and growth; decrease in surface area dry weight	131
0.15	Growing season	GC	Ryegrass			Alleviated S deficiency symptoms; increase in S content of foliage, free amino acid content, and N/S ratio	85
0.20	2 hr	GC	Kentucky bluegrass	X		Visible foliar injury	320
0.20 (peak)	55 days	F/CC	Ryegrass	X	X	Decrease in weight; accelerated leaf sensence	42
0.25	5 wk	EC/SD	Ryegrass		X	No effect on number of tillers; 17% decrease in yield	188
0.27	14 days	EC/SD	Ryegrass			Increase in free amino acid content	11
0.27	8 wk	EC/SD	Ryegrass		X	38% decrease in green weight; 30% decrease in total dry weight; no reduction in number of tillers; 2x senesence	188
0.38 (peak)	6-43 wk	EC/SD	Ryegrass		X	36% decrease in total dry weight	93
0.50-11.00	2 hr	F/CC	87 Desert species	X		Most plants required more than 2.00 ppm SO_2 to produce foliar injury	182
0.71	1 hr 2 hr 5 hr	EC/SD	Lily			Inhibited pollen tube elongation at all exposure durations	294
2.00-0.00	8 hr	EC/SD	Diplacus meteromeles			Increase in SO_2 dose induced a progressive decrease in photosynthesis and transpiration	478
3.50	1 hr	O	Acacia	X		Foliar injury	337

TABLE 7-7 (continued)

[a] Table arranged by increasing SO_2 concentration as first-order and exposure time as second-order divisions. Doses within a single study that did not induce specifically different effects are listed along with the lowest SO_2 concentration that induced said effect.

[b] F = field or forest surveys
F/CC = field, closed chambers
D/OT = field, open-top chambers
G/ZAP = field, zonal air pollution system
G = greenhouse
GC = growth chambers
EC = exposure chambers
EC/SD = exposure chamber, special design
O = other

[c] See Appendix A for most scientific latin binomials of plants.

spatially in reference to dose. However, if no difference in response was obtained within plant species or groups of plants exposed to a series of doses as reported in a single publication, then all effects data have been summarized at the point in the tables of lowest sequence in dose.

The concept of dose-response can be demonstrated by a synthesis of data presented in Tables 7-5, 7-6, 7-7. The following conclusions were developed by summarizing the dose-response data without regard to confounding environmental variables:

(1) Yield of economically important agricultural species can be significantly suppressed by SO_2 concentrations in the range of 0.05 to 0.06 ppm if the exposure period is sufficiently long, i.e., 2 weeks in length. Both crop quality and quantity can be negatively affected.

(2) Fluctuating, long-term (seasonal, annual) SO_2 exposures averaging 0.05 ppm or less can cause economically and ecologically undesirable effects to productivity and stability of range and forest ecosystems.

(3) As SO_2 concentrations increase to 0.25 ppm, a variety of agricultural crops such as alfalfa, timothy, range grasses, soybean, barley, wheat, cabbage, lettuce, spinach, tobacco, cucumber, eggplant, pea, and kidney bean responded with necrotic foliar injury or suppressed yield. Approximately 70% of the cultivated agronomic crop species exposed to 0.25 ppm or less SO_2 responded to the treatment with changes in stomatal aperture, foliar injury, or yield effects. Foliar injury on vegetables and yield suppression are directly related to economic value.

(4) Forest tree species representing coniferous and deciduous forest ecosystems such as pine, spruce, fir, beech, alder, and poplar responded to 0.25 ppm or less SO_2. Approximately 90% of the species tested in this range of SO_2 concentrations responded with physiological modifications, suppressed

photosynthesis, foliar injury, death of buds, or suppressed foliar or woody growth.

(5) Non-woody components of native ecosystems such as lichens and grasses also responded to SO_2 concentrations up to 0.025 ppm. Responses included suppressed growth, death, and reduced diversity in lichen populations, and suppressed photosynthesis and growth of leaves, tillers and stubble of grasses.

(6) At SO_2 concentrations between 0.25 and 0.50 ppm, less than 50% of the agronomic species tested responded negatively to the SO_2 treatments. A comparison of this 70% species response to the 90% response at SO_2 concentrations less than 0.25 ppm might be taken to suggest that plant response is not positively correlated with dose. This is not the case; exposure durations used at the higher range SO_2 studies generally ranged 1-8 hours while multiple day exposures were frequently at the lower SO_2 concentrations. Above 0.50 ppm SO_2 the expected trend is apparent--greater sensitivity at increased SO_2 concentrations. All agronomic species responded to SO_2 exposures at 0.50 ppm for exposure durations ranging from 1.5 to 5 hours. A variety of responses occurred, including physiological modifications, foliar injury, and suppressed growth.

These trends imply that as SO_2 concentrations are increased:

(1) shorter exposure duration is sufficient to elicit the same or greater plant response which occurred at a lower concentration;

(2) responses become more severe;

(3) plants tolerant at lower concentrations become sensitive.

For additional information on dose-response relationships the reader is referred to the sections in this document on the interactive effects of SO_2 and particulates with other air pollutants.

7.4 PLANT EXPOSURE TO SULFUR DIOXIDE

7.4.1 Deposition Rates of Sulfur Compounds

Deposition processes limit the lifetime of sulfur compounds in the atmosphere, control the distance traveled before deposition, and limit the atmospheric concentrations of the pollutant (142). As previously mentioned, sulfur dioxide and particulate sulfate are the predominant forms of sulfur in the atmosphere of developed countries.

7.4.1.1 Dry Deposition--There have been several studies of the deposition of particulate material to natural surfaces (68, 276a, 382). Very large particles are chiefly deposited by sedimentation. Particles in the range of 1-100 μm are also borne towards the surface by turbulence where sedimentation is supplemental to impaction on rough surfaces. Submicron particles (sulfuric acid aerosols) diffuse by Brownian motion through the thin laminar layers close to the surface elements. This may be followed by active uptake in the case of plant leaves. The mean SO_2 deposition velocities are surprisingly similar for a wide range of deposition surfaces (Table 7-8).

Dry deposition is capable of removing significant amounts of the larger particles from the atmosphere within 2 or 3 days but would require several weeks to remove the submicron fraction.

7.4.1.2 Wet Desposition--Both SO_2 and sulfate may contribute significantly to the amount of dissolved sulfur in rain. Hogstrom (184) found that sulfur emitted by a point source in Sweden was deposited during rain with a removal time of 1 to 2 hr. However, Granat and Rodhe (155) found that less than 6 percent of sulfur emitted from the tall stacks of a power-generating station was removed within 15 km of travel distance. Dissolved SO_2 in

TABLE 7-8. RESULTS OF SEVERAL EXPERIMENTAL INVESTIGATIONS OF SO_2 DEPOSITION BY VARIOUS SCIENTISTS[a]

Surface	Method, Conditions	Mean v_g' cm/sec	Mean r_g' sec/cm	Mean r_s' sec/cm
Calcareous soil	Laboratory, mass balance			0.24-0.39
Acid soil	Laboratory, mass balance			1.2-3.8
Calcareous soil	Gradient, field	1.2	0.83	0.01
Grass	Gradient, field			
	Summer	0.8		0.8
	Autumn	0.3		3.0
Grass	$^{35}SO_2$ tracer, field	0.8		
Short grass	Gradient, field	0.85	1.2	0.34
Medium grass	Gradient, field	0.89	0.46	0.66
Medium grass	Tracer, field	0.19	0.38	0.45
Cotton (sedgemoor)	Gradient, field	0.7	--	--
Wheat	Gradient, field	0.74	--	1-2.5
Wheat		0.44	0.28	2.0
Soybean		1.25	0.11	0.69
Pine forest	Tracer	0.1-0.6	0.1	1.5-5.0
Pine forest	Tracer	1.0		

[a] SO_2 deposition expressed in terms of deposition velocity relative to 1 m. r_g = gas plus resistance, r_x = surface resistance.

Source: Garland (1978) (143).

rainwater in England was about 3 mg/liter when the corresponding air concentration was about 100 ug/m^3(101).

Sulfur dioxide removal from the atmosphere may be characterized (142) as follows:

(1) SO_2 is removed by dry deposition with a deposition velocity of approximately 0.8 cm/sec for most surfaces.

(2) The deposition velocity of sulfate aerosol is no greater than 0.1 cm/sec.

(3) Sulfate is removed by rain with a time constant on the order of 10^{-4}/sec.

(4) SO_2 removal by rain is about an order of magnitude less efficient than that for sulfate.

7.4.2 Routes and Methods of Entry Into the Plant

The stomata of leaves have been demonstrated to be the major avenue of SO_2 entrance into plants. Although this is a widely accepted conclusion that has been presented in numerous reviews (159, 219, 420, 421, 442), there is still a controversy as to the role of stomata in plant sensitivity. Many factors that govern the mechanism of stomatal opening and closing have been determined to be independent of SO_2 concentrations. The physical factors such as light, leaf surface moisture, relative humidity, and soil moisture availability may actually play a major role in plant sensitivity as related to initial passive entry of SO_2 into the leaf (114, 307, 383, 405, 497).

There is reported to be no linear relationship between stomatal pore size and permeability of leaves to gases (427). The diffusion of a gas through the stomata is a dynamic process that depends upon the diffusion coefficient of the gas, the partial pressure difference between the atmosphere and the inside of the leaf, the leaf or stomatal resistance, and the boundary layer resistance (159). When the other factors are held constant or are of known predictable variations, then the importance of the stomatal resistance can be estimated in relation to the entry of pollutants. Although several methods of measuring stomatal resistance have been reported (91, 428), as have methods of determining the number and distribution of stomata (258), the influence of actual pore radius may also be of importance (159). The numerous independent physical factors that influence stomatal opening and closing must therefore be considered when determining plant sensitivity or tolerance to the entry of SO_2.

The absorption rate of SO_2 into plants varies not only with species, but also with previous exposure to SO_2. Bigtooth aspen (*Populus grandidentata*) had a higher SO_2 absorption rate during exposure to 2.75 ppm SO_2 for 2 hr than white ash (*Fraxinus americana*) or yellow birch (*Betula alleghaniensis*) when they were exposed to 0 to 6 hr of prefumigation with 0.75 ppm SO_2(210). However, after 20 to 36 hr of the prefumigation treatment, the rate of SO_2 absorption during the 2.75 ppm SO_2 exposure was greater for the birch and ash. The sulfur content of the foliage increased in all species. Eight days after fumigation with $^{35}SO_2$ varying amounts were translocated throughout the plants including roots (210).

Sulfur dioxide induced the closure of *Pelargonium hortorum* stomata especially when they had been fully opened before the exposure. However, large stomata still remained 50 percent open and necrosis was not averted (46). Kodata and Inoue (233) demonstrated that SO_2 entered leaves of *Pinus*

resinosa through stomata and that it accumulated in the cells around the stomata for some time before diffusing inward through the leaf. They reported that lateral diffusion was slower.

Once SO_2 has entered, it may itself induce stomata to remain open for longer periods of time or to open wider than before fumigation. Exposure to SO_2 when relative humidities were above 40 percent caused an increase in stomatal opening, but a depression of stomatal opening at lower relative humidities (285, 290). A 3-min fumigation with 2.5 ppm SO_2 increased carbon dioxide uptake and stomatal opening in Sinapsis alba plants. However, with the same concentration suppressed carbon dioxide uptake and stomatal closure were noted (63). Potted sunflower, broadbean, tobacco, bean, barley, and corn plants maintained under drought conditions and treated with 0.5 ppm SO_2 for 5 hr over several days showed a wider stomatal opening than plants supplied with adequate moisture (390).

Stomatal opening of the leaves of many crops may be increased by ambient SO_2 levels, possibly inducing two undesirable consequences (448). Increased transpiration rates would lead to earlier and more severe water stress in periods of prolonged drought and therefore restricted growth. Induced opening of stomata would also increase the access of other toxic gases or pathogens to the underlying susceptible mesophyll tissues. Increasing the SO_2 concentration evenly up from zero reduced stomatal resistance in beans (Vicia faba) and corn (Zea mays) at 0.02 and 0.01 ppm, respectively, with young leaves exhibiting the lowest resistances. The effect of SO_2 on stomatal resistance was greater on leaves of water-stressed plants (448).

The effects of low concentrations of SO_2 on Vicia faba include larger and more rapid stomatal opening in older leaves exposed to 290 $\mu g/m^3$ (37). Stomatal resistance of leaves exposed to up to 0.5 ppm SO_2 decreased by 20 percent, and it was estimated that response to SO_2 should increase the

transpiration rate by 32 percent for single leaves in a growth chamber and by 23 percent for a field situation (37).

Uptake of SO_2 through the cuticle of the leaf surface has been suggested. Sulfur could be washed from pine shoots shortly after exposure, and thus SO_2 uptake by the cuticle may be a reversible reaction (143). Uptake of SO_2 by wheat plants during periods of stomatal closure was considerably enhanced by dew since there was considerable surface resistance during periods of no dew (137).

It has been suggested by Keller (221) that pollutants such as SO_2 and hydrogen fluoride may enter through bud scales or lenticels of certain hardwood species. The percent bud kill in beech following winter fumigation with low increasing SO_2 concentration lends support to this avenue of ingress over long periods of exposure.

7.4.3 Beneficial Effects

Under certain conditions, atmospheric SO_2 can have beneficial effects on vegetation. This subject has been recently reviewed (334). Sulfur requirements to maintain high crop production range from 10 to 40 kg/ha per year. A decline in the use of sulfur-containing fertilizers in recent years has placed a greater dependency on the atmosphere as a source of supplemental sulfur to meet the needs of vegetation.

Cowling et al. (86) found beneficial effects of SO_2, such as increases in yield and sulfur content, in perennial ryegrass that was grown with an inadequate supply of sulfur to the roots.

Faller (129) conducted a series of experiments to determine the effects of varying atmospheric concentrations of SO_2 on sunflower, corn, and tobacco. In these studies, the plants were grown in nutrient media containing adequate supply of all essential elements, but no sulfur.

Plants grown in the atmosphere without SO_2 developed sulfur deficiency

symptoms within a few days. In other treatments, total plant yield increased to some extent with increasing concentrations of atmospheric SO_2. For tobacco, the total dry weight increased by up to 48 percent. The yield of leaves and stems alone increased by 80 percent, while increments in the dry weights of tobacco occurred even at the highest SO_2 concentration used (1.5 mg/m^3); sunflower and corn had their highest biomass at SO_2 concentrations of 1.0 and 0.5 mg/m^3, respectively. Beyond these concentrations, visible injury was observed. Additional studies by Faller (129) with ^{35}S suggest that up to 90 percent of the plant sulfur can originate from the atmosphere under the specific experimental conditions.

Recently, Noggle and Jones (334) conducted a 2-year study using ^{35}S to determine the contributions of soil and atmospheric sulfur to the sulfur requirements in cotton and fescue. Cotton was more efficient than fescue in accumulating sulfur from the atmosphere. The amount of sulfur accumulated from the atmosphere was apparently influenced by the amount of sulfur supply in the soil relative to the sulfur requirements of the plant. A crop grown in a sulfur-deficient soil will accumulate more sulfur from the atmosphere than the same crop grown in a soil that has an adequate supply of sulfur. Noggle and Jones (334) showed that cotton grown in the vicinity of certain coal-fired power plants accumulated significant amounts of atmospheric sulfur (as SO_2) and produced significantly more biomass than that grown at a location remote to the industrial source of sulfur. Thus, under appropriate conditions, such as with sulfur-deficient soils, the atmosphere can be an important source of sulfur for plant requirements.

7.4.4 Tissue Concentration

Studies of sulfur accumulation after exposure to a constant dose consisting of different concentrations and exposure times have shown that after short-term exposures to SO_2 concentrations sufficient to cause injury,

sulfur content of exposed tissue is relatively low. In this case, it is not the amount of sulfur absorbed but the rate of absorption that is the deciding factor. High concentrations of SO_2 can cause acute necrosis on fast-growing plants under conditions of high light and humidity and favorable temperature at levels of absorbed sulfur that are difficult to detect (59). In polluted areas, high concentrations of atmospheric SO_2 occur in combination with low concentrations. Because of the comparatively high contribution of low SO_2 concentrations to the total frequency of occurrence, chemical analysis of leaves for the detection of sulfur accumulation is less problematic at higher pollutant loads. Sulfur content in plant organs, therefore, can be used as a diagnostic tool to determine the effects of atmospheric SO_2 on vegetation, but is not useful to establish air quality criteria.

Several reports in the literature show that plants resistant to SO_2 injury can accumulate more sulfur than sensitive plant species growing under the same conditions. In interpreting the sulfur analysis of foliage for diagnostic purposes, consideration should be given to the geographic location, the state of plant growth, the relationship between visible injury and pollutant or biological causes, the sulfur content of the soil, and atmospheric SO_2 concentrations.

7.5 INTERACTIVE EFFECTS ON PLANTS WITH THE ENVIRONMENT--SO_2

7.5.1 Physical Factors

Environmental factors are unstable and highly variable, and therefore no generalized statements can be made about long-term effects over large geographic areas. However, environment plays an extremely important role in plant response to SO_2.

7.5.1.1 Temperature--Temperature plays an important part not only in determining the metabolic rate of the plant, but in determining (with moisture, fertility, and light) the species diversity and richness of a given ecosystem

(325). The primary path of entry of SO_2 into the leaf is through the stomata. Temperature exerts an effect on the guard cells that control the stomatal opening and closing and thus the entry of SO_2. Temperature regimes that increase the physiological activity of the plant also increase the plant response to SO_2 (363). It is generally believed that plant sensitivity increases with temperature over a wide range, from about 4 to 35°C (159). Several studies suggest greater resistance of conifers to SO_2 in the winter, attributed to lower rate of physiological activity (325). However, there is some conflicting evidence. According to Guderian and Stratmann (161), in areas with SO_2 emissions, winter wheat and winter rye are more severely injured than the summer varieties. Guderian (159) interpreted this to be due to gas exchange taking place through the stomata at temperatures as low as -2°C.

7.5.1.2 Relative Humidity--Relative humidity is another factor that controls stomatal opening and thus plant sensitivity to SO_2. Although plant sensitivity increases with relative humidity, once above a relative humidity of 40 percent, changes of 20 percent or more are required to cause changes in plant sensitivity (383). According to Zimmerman and Crocker (498), although relative humidity is important in governing sensitivity and consequently the susceptible population, it is not as important as the tissue turgidity. Based on the water relation in trees, Halbwachs (163) has rated plants as sensitive, intermediate, and tolerant at relative humidities of over 75 percent, 50 to 75 percent, and below 50 percent, respectively.

7.5.1.3 Light--Light also controls stomatal opening and thus the plant sensitivity. Plants are more tolerant when fumigated in darkness with SO_2 or when held in the dark for a few hours before exposure (498). This relationship is complex, since injury is greater if the night exposure follows daylight (325).

Setterstrom and Zimmerman (383) observed that buckwheat grown at a light intensity of 35 percent or less of full sunlight was more sensitive to

SO_2 than when grown under full sunlight. Other investigators have found that injury was more severe when tomato stems and foliage were fumigated on clear days than it was on cloudy days (325).

Plants seem to be more sensitive from midmorning to midafternoon, in spite of a high light intensity that might continue after midafternoon (363, 421). At the same time, plants may be more sensitive in the morning during good weather, but may become more sensitive if temperature and light increase in late afternoon (452).

7.5.1.4 Edaphic Factors--Soil factors influence directly and indirectly the responses of plants to SO_2. Soil fertility, moisture, and soil physics directly influence plant sensitivity to SO_2 (325). Adequate soil moisture and the resultant stomatal opening result in plant sensitivity, whereas wilting conditions confer tolerance (383, 493, 498). As long as plants are grown with an adequate supply of water, they are much more sensitive to SO_2 than are plants grown with an inadequate supply, even though the moisture content of the soil is the same at the time of fumigation (383). Therefore, sudden changes in soil moisture at particular growth stages will probably have little influence on sensitivity to SO_2 injury (325), although withholding water from some crops during periods of high pollution risk has been suggested (56). According to Brandt and Heck (56), sensitivity is less for plants grown in heavy soils than it is for those grown in sandy soils. Obviously, heavy soils have better water retention capacity than sandy soils. This may also be related to differences between the two soils in the oxygen tension.

Soil fertility has a significant influence on plant response to SO_2. Some plants become more tolerant to SO_2 upon its application (126, 493). On the contrary, with eastern white pine, increased nitrogen, phosphorus, and potassium concentrations in the greenhouse raised tolerance (decreased needle necrosis) in sensitive clones, but did not prevent chlorotic banding in the field (81). Nitrogen and sulfur deficiencies were correlated with decreased

tolerance to SO_2 in tobacco and tomato (262). Conversely, nutrient deficiencies increased SO_2 sensitivity in alfalfa (383). Fertilization of several dicotyledons with a complete fertilizer has been effective in decreasing their sensitivity to SO_2, but similar treatment of monocotyledons like oats and barley have been ineffective (452, 493).

7.5.2 Biotic Factors

Plant disease is caused by the interaction of a plant and a pathogen acting under suitable environmental conditions. The influence of SO_2 directly on any given plant and pathogen has been difficult to investigate. Whenever the variables of the physical environment are added to such experimental sequences, the subject becomes even more difficult to examine. Heagle (170) has provided the most recent review of the interaction between air pollutants and plant parasites (Table 7-9).

The powdery mildew fungus (*Microsphaera alni*) is often sparse in sites exposed to urban air pollutants. Although the fungus is tolerant of ozone, infection was reduced by acute and chronic doses of SO_2. Previously fumigated leaves became infected, which indicated that SO_2 was directly fungicidal to *M. alni* rather than being toxic to the plant and thereby making it less susceptible to infection (180). Such interactions do not always take place, as was reported by Majernik (284) in studies of barley and the powdery mildew fungus *Erysiphe graminis*. He could show no relationship between SO_2 fumigation and disease development even though infection by *E. graminis* enhanced stomatal closing and SO_2 stimulated stomatal opening. Fumigation with sulfur dioxide is a well-known treatment to prevent mold and rot of grapes during storage and shipment (328, 329, 375).

Relatively low concentrations of SO_2 (0.20 ppm) reduced the germination of uredospores and thereby reduced the incidence and severity of bean rust caused by *Uromyces phaseoli* (463). Exposure of the bean plants to sulfur dioxide

TABLE 7-9. EFFECTS OF SULFUR DIOXIDE ON PLANT DISEASES.

Pollutant and disease affected	Effects	Pollutant dose	Location
Wheat stem rust	Decreased incidence	Ambient	Sweden
Tree rusts	Decreased incidence	Ambient	Canada
Wood rots	Decreased incidence	Ambient	Czechoslovakia
Needle cast on juniper	Decreased incidence	Ambient	England
Needle cast on larch and pine	Decreased incidence	Ambient	Canada
Rhytisma on maple	Decreased incidence	Ambient	England
Hysterium on alder and birch	Decreased incidence	Ambient	Sweden
Apple scab	Decreased incidence	Ambient	Poland
Oak powdery mildew	Decreased incidence	Ambient	Austria
Lilac powdery mildew	Decreased incidence	Ambient	U.S.A.
Rose black spot	Decreased incidence	Ambient	England
Rose black spot	Smaller lesion	0.04 ppm for 48 hr	England
Dwarf mistletoe on larch and pine	Decreased incidence	Ambient	Canada
Armillaria in trees	Increased incidence	Ambient	Canada Czechoslovakia, Poland, Germany
Wood rots	Increased incidence	Ambient	Czechoslovakia
Needle cast on spruce	Increased incidence	Ambient	Poland

Source: Heagle (170).

before inoculation was most effective in reducing disease.

Concentrations of 0.01 ppm SO_2 for 2 days after inoculation slightly favored disease development on roses inoculated with Diplocarpon rosae, but 0.04 ppm SO_2 reduced the disease (375).

Decreased parasitism by several pathogenic fungi has been noted on trees injured by SO_2 (377). Smelter emissions decreased the incidence of rust (caused by Cronartium ribicola); less heart rot was found in white pines located close to a source of SO_2 (269).

Sulfur dioxide, like other harmful agents, weakens plants and permits many organisms to invade. Such is the suspected reason for increased incidence and severity of attack by Armillaria mellea in trees weakened by SO_2 (116, 206, 245).

The effects of SO_2 on infection by organisms other than fungi have also been studied. Abies concolor and A. vertchi were severely attacked by plant lice in an environment of high SO_2, but Pinus strobus was attacked less and P. griffithi and P. sylvestris were not attacked at all (409).

The sensitivity of plant nematodes to SO_2 and ozone varies with species and feeding habits (461). When plants were exposed to 0.25 ppm ozone and SO_2 singly and in combination for 4-hr periods three times per week, the ozone and the mixture of ozone and sulfur dioxide inhibited the development of Heterodera glycines and the reproduction of Trichodoris christiei. Sulfur dioxide treatment alone increased the reproduction of Pratylenchus penetrans.

No direct effects of SO_2 on plant pathogenic bacteria have been reported, but Heagle (170) presented a brief review of the indirect effects of SO_2 in relation to the acidity of soil and nutrient exchange. Table 7-10 groups a number of microorganisms, most of which are known to be pathogenic, according to their sensitivity to SO_2.

As with higher plants, a direct influence of SO_2 on plant pathogenic

TABLE 7-10. RELATIVE SENSITIVITIES OF SOME MICROORGANISMS TO GASEOUS SULFUR DIOXIDE

Group[a]	Organism
Extremely sensitive	Some yeasts, *Displocarpon rosae*, *Sclerotinia delphinii*, *Rhizoctonia tuliparum*, *Venturia inaequalis*
Very sensitive	*Phytophthora infestans*, *Rhytisma acerinum*, *Botrytis cinerea*, *Botrytis* sp., *Sphaerotheca pannosa*, *Melampsora cerastii*, *Didymellina macrospora*, *Alternaria* sp., *Microsphaera alphitoides*
Sensitive	*Sclerotinia fructicola*, *Pestalotia stellata*, *Glomeralla cinguluta*, *Macrosporium sarcinaeforme*, *Puccinia graminis*, *Puccinia striiformis*, *Pucciniastrum* sp., *Coleosporium* sp., *Cronartium* sp., *Phragmidium* sp., *Alternaria brassicicola*
Less sensitive	*Ceratostomella ulmi*, anaerobic yeasts, *Aspergillus niger*, *Penicillium* sp.

[a]These are arbitrary ratings based on field surveys (presence or absence of organism) and supported by extrapolations from fumigation trials and germination tests (inhibition > 76 percent).

Source: Saunders (1973) (376)

organisms has been demonstrated. In addition, the indirect influence of SO_2 on the process of pathogenesis through increasing the host's susceptibility to attack by biotic pathogens has also been shown to occur. The frequency of these events under natural conditions has been difficult to study, and therefore estimates of the importance of such occurrences are lacking.

7.6 INTERACTIVE EFFECTS OF SO_2 WITH OTHER POLLUTANTS INCLUDING PARTICULATE MATTER

7.6.1 Introduction

Ambient atmospheres usually contain more than one specific air pollutant. Long-distance transport of photochemical oxidants and oxidant precursors (200, 441), the demonstration of acidic rainfall over large areas of the eastern United States (74), and atmospheric monitoring suggest that emissions from specific sources are mixed with ambient concentrations of one or more associated pollutants. Extrapolation from results of single pollutant effects on vegetation under ambient field conditions must be approached with caution. Reactions to pollutant combinations may be additive, less than additive, more than additive, or antagonistic. Reinert (360) and Reinert et al. (362) have prepared the most recent reviews of this area of investigation. In addition, a compilation of studies using $\leq$0.50 ppm SO_2 in combination with other pollutants is presented in Table 7-11.

7.6.1.1 Sulfur Dioxide and Ozone--A more than additive reaction on vegetation was first noted with ozone and SO_2 (308). Tobacco was severely injured by 0.03 ppm ozone and 0.24 ppm SO_2 when the pollutants were combined for either 2 or 4 hr, whereas when used alone, neither pollutant produced foliar symptoms.

Since that first report, the interactive effects of ozone and SO_2 have been studied using a variety of plant species. Radish and alfalfa plants showed more than additive foliar injury from a 4-hr exposure to a mix of

TABLE 7-11. EFFECTS OF SULFUR DIOXIDE ALONE AND IN COMBINATION WITH OTHER POLLUTANTS ON SELECTED PLANTS AT 0.50 PPM OR LESS

Species	Exposure	Duration	Result
Pea	0.05 ppm S_s + 0.05 ppm NO_2	1 hr	Significantly decreased net photosynthesis.
Alfalfa	0.15 ppm SO_2 + 0.15 ppm NO_2	1 hr	Inhibited photosynthesis; percent of reduction not stated, but authors state synergistic effect most marked at this concentration.
Alfalfa	0.15 ppm SO_2 + 0.15 ppm NO_2	1 hr	Greater than additive inhibition (7%) of photosynthesis (as measured by CO_2 uptake). Similar results at 0.25 ppm for both gases.
Alfalfa	0.30 ppm SO_2 + 0.10 ppm O_3 (O_3)	1 hr	Additive inhibition of photosynthesis (11% $\pm$ 3%) measured by CO_2 uptake. Some tissue damage.
Alfalfa	0.15 ppm SO_2 + 0.15 ppm NO_2	2 hr	7% reduction in apparent photosynthesis. Some tissue death.
Radish	0.15 ppm SO_2 + 0.10 ppm NO_2	4 hr	17% leaf injury, lower leaf surface. 0.5 ppm SO_2 alone = threshold; 2 ppm O_3 alone = threshold.
Pinto bean	0.05 ppm SO_2 + 0.05 ppm NO_2	4 hr	2% leaf injury measured as pigmented lesion, tissue death, loss of chlorophyll.
Radish	0.05 ppm SO_2 + 0.05 ppm NO_2	4 hr	Tissue death and loss of chlorophyll.
Oats	0.05 ppm SO_2 + 0.05 ppm NO_2	4 hr	Tissue death and loss of chlorophyll.

TABLE 7-11 (continued).

Species	Exposure	Duration	Result
Eastern white pine	0.05 ppm SO_2 + 0.05 ppm $)_3$	4 hr	Severe needle injury (2-3 cm leaf tip injured) on new needles, expressed most vividly 72 hr after exposure
Radish	0.10 ppm SO_2 + 0.10 ppm O_3	4 hr	50% leaf injury
Cabbage	0.10 ppm SO_2 + 0.10 ppm O_3	4 hr	22% leaf injury. 0.10-0.5 ppm SO_2 alone = no foliar injury; 0.05 ppm O_3 alone = 1% foliar injury.
Broccoli	0.10 ppm SO_2 + 0.10 ppm O_3	4 hr	34% leaf injury. 0.05 ppm SO_2 alone = 4% leaf injury; 0.10 ppm O_3 alone = 1% leaf injury.
Tomato	0.10 ppm SO_2 + 0.10 ppm O_3	4 hr	50% leaf injury.
Radish	0.10 ppm SO_2 + 0.10 ppm O_3	4 hr	50% leaf injury.
Alfalfa	0.10 ppm 2 + 0.10 ppm 0	4 hr	24% leaf injury.
Cabbage	0.50 ppm SO_2 + 0.05 ppm O_3	4 hr	4% leaf injury. 0.10-0.05 ppm SO_2 alone = no leaf injury; 0.05 O_3 alone = no leaf injury.
Broccoli	0.05 ppm SO_2 + 0.05 ppm O_3	4 hr	17% leaf injury. 0.5 ppm SO_2 alone = 4% leaf injury; 0.10 ppm O_3 alone = 1% leaf injury.

TABLE 7-11 (continued).

Species	Exposure	Duration	Result
Radish	0.50 ppm SO_2 + 0.05 ppm O_3	4 hr	7% leaf injury.
Peas	0.10 ppm SO_2 + 0.10 ppm O_3	5 hr	14.6% damage. Leaf surface destruction more severe on lower leaves. Ash-colored spots on intermediate leaves and veins.
Peas	0.05 ppm SO_2 + 0.10 ppm O_3	5 hr	9% visible injury. Upper leaves showed ozone injury; lower leaves showed ozone leaf surface destruction. Author calls this response synergy.
	0.10 ppm SO_2 + 0.10 ppm O_3	5 hr	14.6% leaf tissue death
Peas	0.15 ppm SO_2 + 0.10 NO_2	6 days 24 hr/day (144 hr)	15% reduction in RDP enzymes. Snyergism at metabolic levels.
Loblolly pine (2 wk old) Sycamore (1 wk old) seedlings	0.14 ppm SO_2 + 0.05 ppm O_3 + 0.10 ppm NO_2	6 hr/day for 23 days (168 hr)	Significant growth reduction (measured as height) compared to either ozone alone or ozone and sulfur dioxide combined. Needles were significantly shorter than for any other exposure. This study is an example of growth reduction with slight leaf symptoms. Leaf symptoms most sensitive in early July.
Scotch pine Norway spruce Douglas fir Frazier fir	less than 0.01 ppm SO_2 0.01 ppm NO_2 0.07 ppm HF^2 0.05 ppm O_3 4-month average during growing season	Growing season	Growth abnormalities, needle loss, and tissue death.

TABLE 7-11 (continued).

Species	Exposure	Duration	Result
Lichens	0.041 ppm plus dust at g/m^3 ambient	Monthly	Lichens completely absent.

Source: Montana Air Quality Bureau (1978).

0.10 ppm O_3 + 0.10 ppm SO_2 (432), but less than additive growth reduction (top and root weights) from an 8 hr per day, 5-week exposure to a mix of 0.05 ppm O_3 + 0.05 ppm SO_2 (429, 430). Greater than additive foliar injury effects have also been reported for broccoli and tobacco, while additive or less than additive effects have been noted for cabbage, tomato, lima bean, bromegrass, spinach, onion, and soybean (432). Soybean has exhibited less than additive foliar injury effects (432) while exhibiting greater than additive growth effects (433).

As can be seen from the preceding research, plant species vary in their expression of interactive effects, and the type of interactive effect (additive, less than additive, greater than additive) may depend on the parameter measured.

Field-grown soybeans (cv. Dare) exposed to 0.10 ppm O_3 alone or 0.10 ppm O_3 + 0.10 ppm SO_2 for 6 hr/day for 133 days in field chambers exhibited injury and defoliation. Increased injury and decreased yield due to the mixture was evident but not significantly different from the ozone treatment (171). Two cultivars of bean exposed to sulfur dioxide and ozone showed interactive effects between these two gases, but the magnitude and direction of the effects depended on the cultivar and on the pollutant concentrations (203).

Alfalfa exposed in closed field chambers to low levels of ozone and sulfur dioxide singly and in combination for varying periods of time exhibited significant reductions in yield, quality, and nitrogen fixation compared with the control plants, but there were no significant interactive effects (327).

Many studies have been conducted on the interactive effects of sulfur dioxide and ozone on eastern white pine (*Pinus strobus* L.) (19, 80, 112, 193, 195). Genetic control of sulfur dioxide and ozone tolerance in this species has been demonstrated for low concentrations of SO_2 (0.25 ppm) and O_3 (0.05 ppm) for only 6 hr with consistent injury to the exposed sensitive clones (195). Houston (193) later used mixtures of sulfur dioxide and ozone and doses to

simulate actual field conditions and reported that even the lowest concentrations of O_3 (0.05 ppm) and SO_2 (0.025 ppm) in mixture caused more serious damage than that resulting from either pollutant alone at similar concentrations. Loblolly pine and American sycamore exposed to 0.05 ppm O_3 and 0.14 ppm SO_2, 6 hr/day for 28 consecutive days, showed more than additive foliar injury in the mixture (239, 240). Height growth reductions were greatest with the mixture, but not significantly greater than with SO_2 alone. A less than additive effect on foliar injury was noted when Scotch pine trees were exposed to 0.25 ppm SO_2 and/or 0.14 ppm or 0.29 ppm O_3, 6 hr/day for varying time periods (332).

Histological examination of ponderosa pine needles injured by 3 weeks of exposure to 0.45 ppm O_3 and/or 0.45 ppm SO_2 for 9 hr/day revealed some differences in the tissues injured (128). Different parts of the needles were affected (the tip for SO_2, the middle for ozone) initially, so the potential for interactive effects may exist.

Exposure of aspen clones to 0.05 ppm O_3 and/or 0.20 ppm SO_2 for 3 hr resulted in a more than additive number of plants in the mix exhibiting foliar injury (217).

7.6.1.2 Sulfur Dioxide and Nitrogen Dioxide--The occurrence of sulfur dioxide and nitrogen dioxide has been associated with power-plant plumes as well as mobile sources. However, ambient concentrations of nitrogen dioxide seldom reach the injury threshold, and the literature for that pollutant suggests that any injury associated with nitrogen dioxide results from interactions with other pollutants.

No injury occurred to oats, beans, soybeans, radish, tomato, or tobacco following exposure for 4 hr to up to 2 ppm NO_2 or 0.50 ppm SO_2 (431). However, at 0.10 ppm of each gas, injury was noted on all species; at 0.05 ppm of each gas, injury was noted on all species except tomato. A greater than additive suppression of the apparent photosynthetic rate of alfalfa was obvious when

exposed to 0.25 ppm of SO_2 and/or NO_2 for 2 hr (472). At 0.15 ppm of each gas singly, there were no measurable effects, but a 7 percent suppression of apparent photosynthetic rate was noted in the mixture (472).

Field exposure of seven different species of plants indigenous to the cold desert areas of the Southwestern United States to 0.50-11.0 ppm SO_2 or 0.10-5.00 ppm NO_2 and combinations thereof in 2 hr fumigations resulted in no evidence of more than additive foliar injury (182).

More than additive foliar injury was noted on radish leaves exposed for 1 hr to 0.50 ppm SO_2 and/or 0.50 ppm NO_2. No interactive effects were found for other plants tested (oats, Swiss chard, and pea). More than additive effects have been noted for the enzyme activity in pea plants exposed to 0-0.20 ppm SO_2 and/or 0-0.10 ppm NO_2 for 6 days. Peroxidase activity was increased and ribulose-1,5-diphosphate carboxylase activity was decreased (189).

7.6.1.3 Sulfur Dioxide and Hydrogen Fluoride--Linear growth and leaf area suppressions (in the absence of foliar injury) of Koethen orange plants exposed to SO_2 (0.80 ppm) and/or hydrogen fluoride (2.3-19.4 ppb) for 23 days were no greater than additive. Satsuma mandarin plants exposed to the same conditions for 15 days exhibited only additive foliar injury effects, and no growth suppressions at all (299). Greater than additive foliar injury was exhibited by barley and sweet corn exposed to 0.06-0.08 ppm SO_2 and/or 0.60-0.90 ppb hydrogen fluoride for 27 days (288). Using higher concentrations of SO_2 for only 7 days resulted in simply additive foliar injury effects. Pinto beans were not injured in any of the treatments.

7.6.1.4 Sulfur Dioxide, Nitrogen Dioxide, and Ozone--Fujiwara et al. (140) combined SO_2, NO_2, and O_3 at concentrations ranging from 0 to 0.2 ppm in an artificially controlled environment and exposed peas and spinach for 5 hr. Ozone was the most injurious, SO_2 was next, and NO_2 elicited only minor injury.

More than additive foliar injury followed exposure to $SO_2 + O_3$, but only additive effects were observed with $SO_2 + NO_2$ or $NO_2 + O_3$. The addition of NO_2 to the $O_3 + SO_2$ had little effect on foliar injury. Reinert (361) exposed two cultivars of cotton and one cultivar each of radish, snap bean, tomato, pepper, soybean, and tobacco to pollutant mixtures of $NO_2 + SO_2 + O_3$, $NO_2 + SO_2$, and $SO_2 + O_3$ and each single gas for 3 or 6 hr. Gas concentrations varied from 0.10 to 0.60 ppm. Injury from the $NO_2 + SO_2$ mixture was greater than that induced by either pollutant alone, and except for snap bean, injury from the $SO_2 + O_3$ and $NO_2 + SO_2 + O_3$ exposures was greater than injury from O_3 alone. All plant species were injured by the $NO_2 + SO_2 + O_3$ mixture at 0.25 ppm.

Loblolly pine and American sycamore exposed to 0.14 ppm SO_2, 0.10 ppm NO_2, and 0.05 ppm O_3 singly and in combination for 6 hr/day for 28 consecutive days exhibited significant height growth suppressions when exposed to $O_3 + SO_2$ compared to O_3 alone (239, 240). Growth reductions of 21 and 26 percent were observed in the $O_3 + SO_2$ and $SO_2 + NO_2 + O_3$ treatments, respectively, for loblolly pine. American sycamore height growth was suppressed 32 and 45 percent, respectively, for the $O_3 + SO_2$ and $O_3 + SO_2 + NO_2$ treatments. A slight stimulatory effect on growth was noted with NO_2 alone. There was no foliar injury on sycamore and less than 1 percent foliar injury on pine in any of the treatments.

In addition to pollutant combinations under controlled conditions as presented in the above-cited reports, the interaction of constantly changing environmental factors and fluctuating pollutant doses must be further evaluated before a conclusive statement of the importance of such interactions can be made. Further research is needed in order to determine the influence of pollutant sequencing during combination exposures, meteorological influences, the effect of various cultural practices, and many other variables in relation to vegetation

effects induced by SO_2 combined with other pollutants.

7.6.2 Particles in Combination with Other Pollutants

Few investigations have attempted to relate particulate depositions and accumulations on and within plants in combination with gaseous air pollutants to a specific response in plants.

Ricks and Williams (365) presented evidence obtained with the scanning electron microscope that partial occlusion of stomata by particles was responsible for decreased diffusion resistance of oak leaves at night. They further reported that overall water loss rates were not seriously increased by the reduction in stomatal diffusion resistance at night, but uptake of gases such as SO_2 appeared to be enhanced. This fact may explain the increased sulfur level in tissues of oak leaves collected in polluted areas. Sprugel et al. (407) suggested that SO_2 fumigations influenced the accumulation of elements from the soil (increased zinc, copper, manganese, and calcium; decreased magnesium and boron) in field-exposed soybean. Evidence of direct relationships between lowered pH of soil and elevated levels of foliar manganese in lodgepole x jack pine trees has been reported (261). Foliar manganese was found to decrease dramatically with increasing distance from the source and the known transmission corridor. Site variability did not modify the observed effect. Other elements that did not follow this same trend (i.e., they were site related) were phosphorus, potassium, iron, magnesium, zinc, calcium, and aluminum. Similarly, Krause (235) showed that exposure to low concentrations of SO_2 increased zinc and cadmium phytotoxicity to bean plants.

More recently, evaluations of the combined effects of several heavy metals and sulfur dioxide have been made in relation to ion uptake through leaves, yield, and foliar injury (236). *Lactuca sativa* L, *Raphanus sativus oleifera* L., *Raphanus sativus radicula* L., *Setaria italica* L., and *Tagetus*

spp. were dusted with a mixture of cadmium oxide, lead dioxide, cupric oxide, and manganese dioxide once a week for 4 weeks while being exposed over the 28 days to 0.21 mg/m^3 of SO_2 (approximately 0.08 ppm). Exposure to SO_2 did not influence the uptake or translocation of the heavy metals. The heavy metal treatment reduced yield in all plant species, and this was not influenced by the SO_2 exposure. However, SO_2 exposure resulted in a more than additive increase in the amount of foliar injury.

Guderian et al. (160) investigated the phytotoxic effects of complex pollutant conditions consisting of combined gaseous and particulate components under experimental conditions similar to an actual field situation in West Germany. There was a general yield reduction with all the plant species used, and this reduction in yield increased progressively as the number of chemical components used in the treatments increased. Maximum yield loss from the interactive effects of SO_2 and multiple particulates was 30 percent of the control.

7.7 SYMPTOMATOLOGY OF PARTICLE-INDUCED INJURY

Particulate-induced injury to plants has most often been associated with sustained accumulation of particles such as dust or fly ash. Few investigations have dealt with direct or indirect chemical interactions at the plant surface or subsequent effects. The toxicity of accumulated heavy metals in soils has been established for several plant species.

The various forms of particulates and their associated impacts on plants have been reviewed (99, 263, 440, 445). Krupa et al. (243) have also prepared an extensive review of various forms of heavy metal depositions and impact. Tolerance of plants for heavy metals has been reviewed, and fine particles of 0.01 to 2.0 μm and their bioenvironmental impacts have also been reviewed (443).

7.7.1 Dusts

The chemistry of this form of particulate matter has been poorly defined

in relation to plant effects, and therefore indirect effects have been considered to occur primarily from a mechanical basis. Heavy metals, arsenic, and boron have been identified as constituents of various kinds of particles and, as such, have become of interest to the understanding of subsequent plant effects following dust deposition.

Dusts directly affect plants by coating all exposed plant parts, including leaves, stems, flowers, and fruits (207, 220, 271). Depending on the chemical nature of the particles and environmental conditions, deposits may accumulate as dry dusts, as encrustations in the presence of free moisture, or as greasy films or tars. Encrustations on leaves result in reduced gas exchange, increased temperatures, reduced photosynthesis, and eventual yellowing and tissue desiccation (94, 346).

Terminal growth is greatly reduced in length in hemlocks with heavy dust deposits. Chlorosis of 2-year-old needles is also reported. In addition, changes in microflora of needles compared with control plants has been reported, with fungal propagules increasing and bacterial numbers decreasing (289). Brandt and Rhoades (54) reported long-term changes in plant community structure and species composition, and later indicated that radial growth rates were reduced in the species involved (55). On the exposed site they demonstrated a 19 percent reduction in radial growth of red maple, chesnut oak, and red oak but a 76 percent increase in radial growth of tulip poplars as compared with representatives of these species growing on a similar but nonexposed site. Deposition rates averaged 824 $\mu g/m^3$ of suspended particulates during a February-March (1970) monitoring period. The deposition of limestone dusts has caused substrate pH changes followed by lichen community changes namely replacement of acid-loving communities of lichens by more alkaline-loving species. A reversal of this trend occurred in areas where SO_2 was of importance prior to limestone dust emission. No exact pollutant doses of

either limestone dusts or SO_2 were reported. Winter SO_2 levels were estimated to average 65 $\mu g/m^3$.

Cement kiln dusts have been collected from precipitators and applied to vegetation. Visible effects were demonstrated on beans following application of particles of >10 μm at rates of 0.05 mg/cm^2/day to 0.38 mg/cm^2/day for 2-3 days. The lower dose induced a slight reduction in carbon dioxide exchange, and the two higher doses reduced carbon dioxide uptake by 16-32 percent (99).

The accumulation of dust caused increased reflection of solar radiation in wavelengths of 400 to 750 nm and has been demonstrated to reduce photosynthesis (365). Conversely, increased absorption of solar radiation by dusted leaves at wavelengths 750-1350 nm has been demonstrated to lead to heat stresses within the leaf tissues (406).

Growth and yield effects induced by the accumulation of dust have recently been reviewed (443). Conflicting reports of yield increases and decreases from such accumulation appear to be caused by variations in doses applied, substrate nutrient balances and pH, and other specific physiological interferences with processes such as pollination of fruit trees (7).

Dusts, therefore, have only been considered of importance to vegetation growing near emission sources. Accumulation of dusts has been demonstrated to reduce photosynthesis and radial-increment growth of some forest tree species but has increased them in other species.

7.7.2 Heavy Metals, Arsenic, and Boron

The phytotoxicity of these elements has been demonstrated after accumulations in soils and subsequent uptake by plants. Table 7-12 presents a summation of toxic effects of individual elements (246). Published reports of direct effects on plants from specific sources are discussed in the following paragraphs.

7.7.2.1 Arsenic--No evidence is available to show foliar uptake of airborne arsenic. Arsenic sprays have been applied to the foliage of many plants to

TABLE 7-12 SOME REPORTED TOXIC EFFECTS (VISUAL SYMPTOMS) OF HEAVY METALS, ARSENIC, AND BORON FOLLOWING ACCUMULATIONS IN SOILS

Element	Symptoms	Reference
Arsenic	Reduced germination of seeds, rotting of roots, leaf wilt, brown to red coloration of leaves, reduced yield in fruit trees, death.	Liebig (265)
Boron	Yellowing of leaf tips, necrosis between lateral veins and midrib of monocotyledons, marginal leaf scorch, downward cupping of leaves, reduced flowering, fruit lesions.	Bradford (52) Krupa and Kohut (244) Yopp et al. (492)
Cadmium	Reduced root elongation, general growth retardation.	Yopp et al. (492)
Copper	Stunted root development, chlorotic leaves, reduced vegetative growth.	Reuther and Labanauskas (346)
Lead	Stunted root growth, shoot retardation, increased leaf abscission, reduced yields.	Yopp et al. (42) (492)
Magnesium	Leaf rolling, spiraling inhibition of leaf emergence. Narrow leaf development	Embleton (125)
Manganese	Necrotic spots on leaves, necrosis of internal bark, marginal leaf yellowing, incurling of leaf margins	Yopp et al. (492) Labanauskas
Mercury	Possible reduced growth	Lagerwerff, (249)
Nickel	Repression of vegetative growth, leaf chlorosis, white or light yellow and green striping.	Vanselow (453)
Potassium	Fruit coarseness and leaf necrosis, leaves curl downward, marginal leaf necrosis, intervenal chlorosis, plant dieback.	Ulrich and Ohki
Zinc	Uniform chlorosis, reduced terminal growth, twig dieback, chlorotic striping of leaves, stems stiff and erect.	Chapman (69)

Source: Adapted from Krupa et al. (ref 246).

hasten fruit maturation by causing premature defoliation and chemical changes in the fruit. For example, lead arsenate sprayed on grapefruit trees caused a "fruit gumming" reminiscent of boron deficiency (265). Boertitz (44) reported that arsenic deposited at 22 mg/kg soil reduced the yield of wheat, rye, winter rape, and red clover by 25, 8, 0, and 6 percent respectively.

7.7.2.2 Cadmium--Most of the biologically active cadmium enters plants through root uptake (214). Small oxide particles (0.01 to 0.03 μm) may enter leaves through stomata, but it is thought that the oxides remain largely inert. Cadmium accumulated by apple leaves may be translocated and incorporated into fruit as they develop (492).

7.7.2.3 Copper--Wu and Bradshaw (489) demonstrated a selection of individual plants of *Agrostis stolonifer* growing near metal smelters, thus indicating an indirect effect of within-species simplification within a population through selection.

7.7.2.4 Lead--Davis and Barnes (107) reported reduced growth of loblolly pine and red maple seedlings in pots of two forest soils treated with 2×10^{-4} to 2×10^{-2} M lead chloride. Lead toxicity symptoms may include fewer and smaller leaves, reduced plant size, leaf yellowing, and necrosis of elder, sugar beet, squash, and bush bean (378a). Plants growing in soils already high in these metals tended to be more sensitive to the addition of metals by air pollution.

7.7.2.5 Nickel--The phytotoxic effects of nickel may be insignificant even though plants can absorb and translocate airborne nickel salts (324). Once inside the plant, nickel affects photosynthesis and other processes such as stomatal function (23). In cases of incipient nickel toxicity to vegetation, no definite symptoms have been observed other than the repression of growth. In cases of moderate or acute nickel toxicity, chlorosis resembling symptoms of iron deficiency is common (6, 9).

7.7.3 Classification of Plant Sensitivity--Particles

Coarse particulates have not been shown to elicit responses in plants in a manner to allow plants to be placed into sensitivity classes similar to those developed for gaseous pollutants. Accumulations of particulate matter such as roadside dusts, cement, quarry particle emissions, or other forms of deposits such as fly ash, are deposited on all surfaces and induce responses discussed under the symptom portion of this chapter. However, heavy metals do elicit differential responses in plants, and therefore it is possible to develop lists of particularly sensitive plants.

Heavy metals are constituents of many coarse particles emitted from various sources. To our knowledge, there has not been an organized effort to establish under field conditions the toxicity of specific chemical constituents of particulates in relation to sensitivity groupings of vegetation. Table 7-13 lists plants that may be sensitive to component heavy metals following deposition.

TABLE 7-13. PLANTS SENSITIVE TO HEAVY METALS, ARSENIC, AND BORON AS ACCUMULATED IN SOILS FOLLOWING POTENTIAL ATMOSPHERIC DEPOSITIONS

Metal	Plant
Arsenic	Snap bean, lima bean, onion, pea, cucumber, alfalfa, legumes, sweet corn, strawberry (on light and sandy soils) (246)
Boron	Barley, var. Atlas 46; lima bean, var. Henderson; kidney bean, var. Navel; oats, var. Riverside; onion, var. Cabot; pea, var Alaska; peach, var. J.H. Hale; persimmon, var. Kaki; rose, var. Snow White; soybean, var. Wilson, var O'Tootan; wheat, var. Opal; yellow zinnia (406)
Cadmium	Red oak, birch, trembling aspen (Jordan, 1975); beet, carrot, celery, green pepper, lettuce, radish, soybean, Swiss chard, tomato, winter wheat (406)
Copper	Bean, citrus fruits, corn, mustard (291)
Lead	Bean dwarf French, var. Carters, beet, corn, fescue, lettuce, lupine, loblolly pine, red maple (406)
Magnesium	Orange (only case known from published literature) (214)
Manganese	Alfalfa, broadbean, cabbage, cauliflower, cereals, citrus, clover, lespedeza, pineapple, potato, tobacco, tung (243); Barley, var. Atlas 46, var. Herta; yellow birch, cranberry, peanut, potato, var. Kesweck (406); alfalfa, apple, apricot, barley, bean, brussels sprout, carrot, clover, cotton, lettuce, medic, orange, peas, potato, sugar beet, vetch, wheat (265)
Mercury	Broadbean, oxalis, sunflower (406), bean, butterfly weed, cinquefoil, fern, Hydrangea, Mimosa, Oxalis, privet, sunflower, willow (99)
Nickel	Citrus fruits (378a), alfalfa, oats, var. Victory; pear (406)
Potassium	Orange, tung (only case known from published literature) (346)
Zinc	Oats, orange, tung (6); barley, var. Trail; corn, var. Whatley's Prolific, var. Ida Hybrid 330; cowpea, var. Suwannee; wheat, var. Gaines (406); barley, citrus, oats, sugarbeet (6)

7.8 DOSE-RESPONSE RELATIONSHIPS--PARTICULATE MATTER

Review of the published literature suggests that it is not possible at present to give even generalized dose-response relationships for the effects of particulate air pollutants on plants. Many reports deal only with gross visible effects or tissue accumulation of one or more constituents of the particulates. The emphasis of research has been on settleable coarse particles. Since these are conglomerates of several pollutants, their chemical constitution is frequently not defined properly; however, their source is often identified. Little information could be found on the effects of fine particles on vegetation. Most of the sulfate and about half of the nitrate, metals, and metalloids are found in fine particles.

Where cause-and-effect relationships have been established, generally no information is presented on the actual concentration, particle size, and frequency distributions. Deposition rates and plant effects vary significantly with particle size. Few studies are available where two independent scientists have evaluated the effects of particles on vegetation with closely comparable physical and chemical properties under reproducible conditions.

Much of the literature refers to particulates from point and line sources, and their accumulation in or on soils and vegetation. Tissue accumulation of a given element or elements must be considered as a plant response. Soil scientists have contributed much of the information on plant toxicity symptoms that has been obtained under laboratory conditions. Since many of the plant effects observed are due to the accumulation of elements up to toxic concentrations the prior tissue concentrations will affect the amount and elemental composition of particulates that plants can tolerate, that is, the dose-response relationship. The dose-response relationship is therefore conditioned by the back-ground concentrations of various elements in the soil where the plant is growing.

The effects of surface accumulation of cement kiln dust on bean leaves have been investigated by Darley (99). Doses of 0.6-3.8 g/m^2 per day were applied for 2 or 3 days, and foliar injury and reductions in carbon dioxide exchange were observed. Reductions in carbon dioxide exchange of up to 33 percent were noted in the absence of foliar injury (Table 7-14). Bean leaves dusted with cement kiln dust at the rate of 4.7 g/m^2 per day for 2 days and then exposed to dew developed leaf rolling and interveinal necrosis (263). Leaves not exposed to dew following the dust treatments remained asymptomatic.

Reduced yields and injury to leaves and flowers of several plant species were observed when the plants were exposed once a week for 4 weeks to a dust containing cadmium, lead, copper, and manganese (236). Yield reductions of up to 36 percent were noted (Table 7-15).

Plants accumulate different elements at differing rates. Tissue concentrations of some elements (particles) are known to be significantly higher in the vicinity of a source for those elements (particles) in comparison with background or baseline concentrations. This elevated tissue concentration may be due to direct foliar uptake or uptake from the pollutant accumulations in the soil. In many of these cases, elevated tissue concentrations of a given metal or metalloid are not paralleled by visible injury.

Demonstration of injury symptoms on vegetation under field conditions as a result of accumulation of metals or metalloids is rare. These demonstrated cases are for such cases as strip mine wastes. Predicted effects from atmospheric deposition include plant community changes, chronic long-term physiological changes, and indirect effects through modification of response to other types of stress. Thus, the state of our knowledge concerning the effects of particles on vegetation is inadequate at this time and does not allow the development of accurate dose-response curves.

TABLE 7-14. EFFECT OF CEMENT KILN DUST ON BEAN LEAVES AS DETERMINED BY OBVIOUS TISSUE DAMAGE AND CO_2 EXCHANGE

Dust no.	Dosage, $g/m^2/day$	No. of days dusted	Water added to leaves	Tissue damage	Average CO_2 exchange, ppm/cm^2 Control	Damage	Percent difference
1	1.5 est.	2	X	None	0.225	0.189	-16
	1.5 est.	2	X	None	0.221	0.170	-23
	1.5 est.	2	--	None	--	--	--
			Dry plants	None	0.196	0.196	0
			Wet plants	None	0.181	0.181	0
	Pretreatment	--	--	--	0.189	0.205	+9
	3.0 est.	3	X	Margins necrotic	0.213 (Lowest value for single leaf)	0.114	16
					0.200	0.053	-73
	0.6	2	X	None	0.238	0.221	-7
	1.0	3	-	None	0.236	0.157	-32
			Wet all plants	None	0.229	0.161	-33
2	1.5	3	X	None	0.216	0.146	-32
	1.8	2	X	Necrosis, leaf roll	0.714[a] (Single dusted leaves)	0.160[a]	-8
				3%	--	0.204	+17
				5%	--	0.160	-8
				13%	--	0.138	-21
				26%	--	0.140	-20
	3.8	2	X	Necrosis, leaf roll	0.157 (Single dusted leaves)	0.085	-46
				13%	--	0.091	-42
				16%	--	0.097	-38
				20%	--	0.072	-54
				29%	--	0.083	-47
3	2.2	2	X	None	0.196	0.142	-27

[a]Carbon dioxide exchange measured on third day after end of dusting.

Source: Darley (99).

TABLE 7-15. EFFECT OF A DUST CONTAINING CADMIUM (5.2 mg/m^2), LEAD (488 mg/m^2), COPPER (20.8 mg/m^2), AND MANGANESE (72.8 mg/m^2) (TOTAL APPLICATION) ON YIELD (DRY WEIGHT) AND FOLIAR FLOWER INJURY AFTER APPLICATION ONCE A WEEK FOR 4 WEEKS

Plant species	Treatment	Relative yield depression and % injured leaves/flowers	
		Total, yield, %	Injured leaves/flowers, %
Lactuca sativa L., leaf	Control	100.0	0.0
	Dust	94.4	20.2
Raphanus sativus oleifera L., leaf	Control	100.0	0.0
	Dust	86.4	54.3
Setaria italica L., leaf	Control	100.0	1.0
	Dust	63.8	32.9
Raphanus sativus radicula L., root	Control	100.0	--
	Dust	85.3	--
Tagetus spp., flowers	Control	--	0.0
	Dust	--	18.4

Source: Adapted from Krause and Kaiser (1977) (236).

7.9 PLANT EXPOSURE TO PARTICULATE MATTER

7.9.1 Deposition Rates

Deposition of particles is strongly dependent on particle size. Most sulfates and nitrates are found in the size range of 0.1 to 1.0 μm, and very little information is available on the deposition rate for these particles. Shinn (387) divided particulate deposition into three categories based on particle size:

CATEGORY 1. Particles more than 10 μm in diameter; includes dust and spores.

CATEGORY 2. Particles between 1 μm and 10 μm in diameter where the collection efficiency is highly dependent on the particle diameter.

CATEGORY 3. Submicron particles between 0.1 and 1.0 μm in diameter, which have a nearly constant collection efficiency.

Current experimental data suggest that collection efficiencies in category 3 are at least 10 times less than in category 2 (387). The collective data indicate that the efficiency of collection increases as the particle size increases. According to Clough (72a), in the range of wind speeds normally encountered, the larger particles in the atmosphere are much more efficiently collected than the smaller fraction.

Little (276) evaluated the effect of leaf surface texture on the deposition of monodisperse polystyrene aerosols on the leaf surfaces. Rough and hairy leaf discs collected 5.0 μm particles up to seven times more efficiently than did smooth leaves. Very large differences in particle deposition velocities were observed between the laminas, petioles, and stems of each species. The velocity of deposition of particles to plant surfaces was proportional to both wind speed and particle size.

7.9.2 Routes and Methods of Entry Into Plants

7.9.2.1 Direct Entry Through Foliage--Foliage is continuously subjected to natural and manmade coarse particles that are insoluble or sparingly soluble in

water. Coarse particles in general are too large to enter leaves through stomata. In certain cases, such as with cement kiln dusts (263) and other types of aggregate particles (401), a limited amount of stomatal clogging can occur. This is apparently dependent on the statistical probability of the particulate matter falling on the stomata, the size of the particle, and the stomatal aperture. In many plants, the stomatal opening is on the lower surface. Cement kiln dust forms a crust on leaves, twigs, and flowers. According to Czaja (94), crusts of this type form because some portion of the settling dust consists of calcium aluminosilicates typical of the clinker from which cement is made. Hydration of the dust on the leaf surface results in the formation of a gelatinous calcium aluminosilicate hydrate which later crystallizes and solidifies to a hard crust.

When coarse particles are water soluble or have some water-soluble components, plant uptake of ions from the leaf surface does occur. Because of analytical difficulties, the exact magnitude of the uptake is difficult to measure. Since it is not possible to predict the efficiency of any washing procedure used to remove particles from the leaf surface, it is difficult to separate the concentration of a given element on the leaf surface from its concentration inside the tissue. In addition, leaching of elements from within the tissue is known to occur during the washing (275).

Smith (399b) evaluated metal contamination of urban woody plants by using a variety of washing procedures. Indirect evidence from all these studies strongly suggests that a variable concentration of metals originating from coarse particulates can accumulate in plant foliar tissue through direct uptake.

At this time, one of the significant problems in deriving conclusions concerning the magnitude of direct foliar deposition and uptake of atmospheric particulates is the lack of coordinated data on size and frequency distribution

of the particles and their chemistry, rates of deposition, and dose in conjunction with changes in tissue concentrations over time relative to background conditions. This is an area of research where there is definite need for further information.

7.9.2.2 Indirect Entry Through Roots--Many of the inorganic constituents of particulate air pollutants occur naturally in the soil. Deposition of these pollutants may increase the soil concentrations of the chemical species in question. Some of the chronic effects caused by particulate air pollutants may result from changes in soil physics and chemistry and from increased plant uptake of either the added particles themselves or some other soil-borne elements made more available by the influence of the deposited particles.

It should be recognized that only a portion of the total elemental content of the soil is available at a given time for plant absorption (53). As uptake of elements proceeds, there may be a redistribution of nutrients or toxicants in the soil. Excess magnesium and potassium are the only macronutrients from particles that are considered phytotoxic.

The availability of nutrients or other chemical elements from the soil is strongly influenced by type, chemical composition, and acidity of the soils. Plant nutrients, when present in optimal amounts, are usually available at a neutral pH; however, when the soil becomes acidic, toxic elements such as aluminum become available.

7.10 INTERACTIVE EFFECTS ON PLANTS WITH THE ENVIRONMENT--PARTICULATE MATTER

7.10.1 Biotic Interactions

Few studies have examined the influence of dusts or heavy-metal-containing particles on the interactions between organisms capable of causing disease and the predisposition of the host plant to the disease process.

Infection due to *Cercospora* spp. increased on sugar beet leaves exposed to cement dust of 36 percent calcium oxide and 15 percent silica (378). Increased

occurrence of fungus-induced leaf spots on wild grape and sassafras have been observed near a source of heavy emissions of limestone dust (289). After examining 40 leaves in each of five locations exposed and not exposed to the dust accumulations, disease development was two to three and six to seven times greater, respectively, for the two diseases in the exposed areas.

Natural exposure to combustion nuclei from automobile exhaust which supplied increased levels of Aitken nuclei and atmospheric lead reduced germination of uredospores of Puccinia striiformis (stripe rust of wheat); in situ development of disease was prolonged about 4 days. Similar studies at a nonexposed site did not result in decreased spore germination (384,385).

The influence of heavy metals on microbes has been investigated; some studies deal with toxicity effects related to pesticides (373), and others deal with the ability of microbes to accumulate metals and serve as potential bioindicators (1).

7.11 EFFECTS OF SULFUR DIOXIDE AND PARTICULATE MATTER ON NATURAL ECOSYSTEMS

7.11.1 Introduction

The ecosystem is the basic functional unit of ecology since it includes both the living organism (biotic) and the non-living (abiotic) environment in which these organisms live. Odum (379) has defined an ecosystem as

> ...any unit that includes all of the organisms in a given area interacting with the physical environment so that a flow of energy leads to clearly defined trophic structure, biotic diversity, and material cycling witin the system.

Due to the inseparable nature and interdependence of the components of ecosystems, any change that occurs in one component of the system potentially affects all the components of that ecosystem. Generally, the higher the diversity, the more numerous the interrelationships within the ecosystem, and therefore, the more stable it is (Jernelov & Rosenberg, ref 211). As a result,

agricultural ecosystems are considered very susceptible to any external stresses; the diversity of the producers in the ecosystem is reduced to one or two species and thus restricts the other trophic levels of the system.

Agricultural ecosystems, or agro-ecosystems, have been extensively studied because of their great economic importance to man, and, as a result, can be managed. Natural ecosystems have also been studied but are not fully understood, primarily because of their extremely complex nature.

It is, therefore, not possible to predict exactly how a natural ecosystem will react to a pollutant stress. In addition, it must be remembered that very little is known about the effects of atmospheric pollutants such as SO_2, NO_x, O_3, and PAN on natural vegetation and wild animals, since most of the work has been performed on crops and domestic species.

In an ecosystem the flow of energy and the cycling of nutrients are of paramount importance because they link the biotic and abiotic components. Energy flow and nutrient cycling are closely interrelated. Energy flow, however, is unidirectional. Light energy from the sun is converted by producers (green plants) through the process of photosynthesis to chemical energy. Chemical energy moves to herbivores when they consume vegetation and to carnivores when they eat herbivores. Further transfer of energy occurs when producer-decomposer organisms feed on the remains of plants and animals to obtain their energy (see Figure 7-3). Energy flow through an ecosystem is mediated at the level of the individual organism. At each trophic (feeding) level some energy is lost in respiration so that less energy is available to the organsims at each trophic level. Interference with or removal of a particular trophic level in one part of an ecosystem will potentially affect the movement of energy elsewhere.

Nutrients are cycled from living organisms to the non-living environment

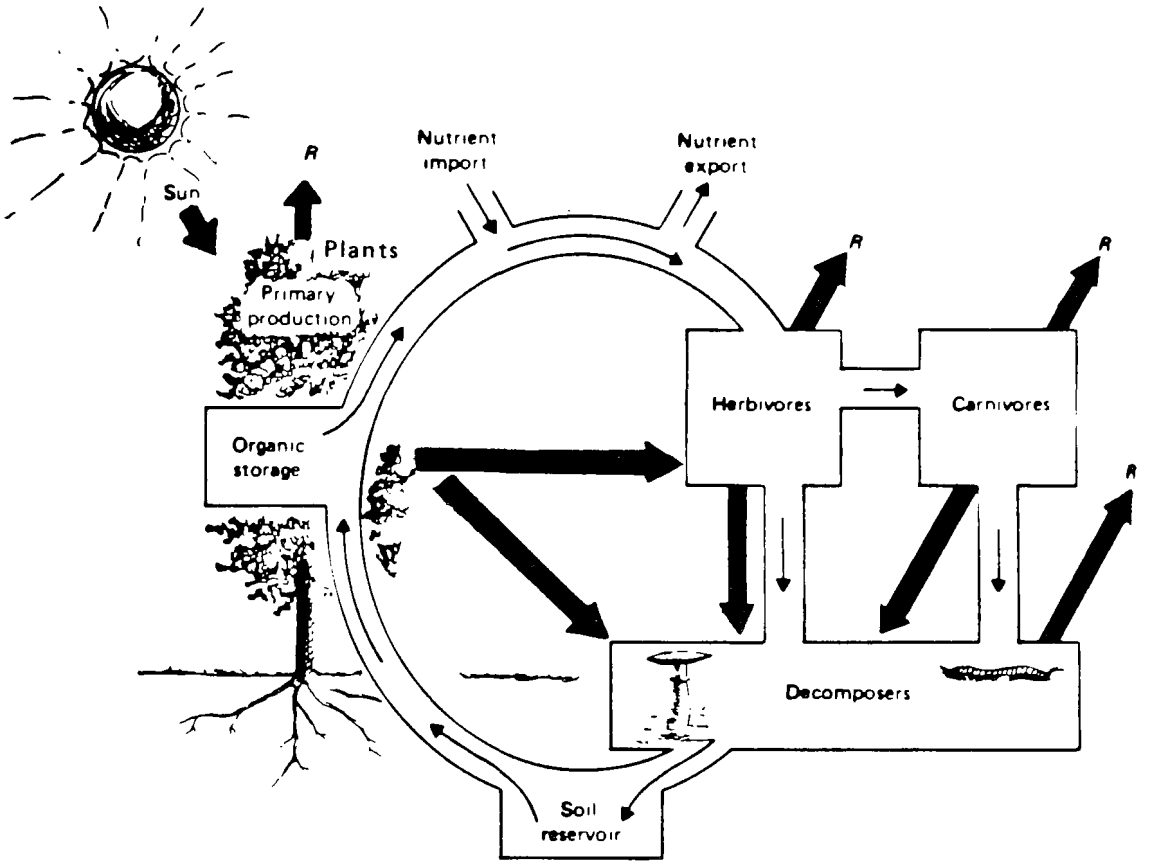

FIGURE 7-3. Nutrient cycles and energy are closely interrelated, as this model indicates. It also stresses the face that energy flow is unidirectional, whereas nutrient flow is cyclic. (R-Respiration)

Source: Adapted from Smith (399a).

and back to living components of the ecosystem. In this way, plants and animals obtain the nutrients mecessary to their well-being. Some of the elements, the macro-elements, are required by plants and animals in relatively large quantities. Micronutrients, or trace elements, are required in smaller or minute amounts. Though required in minute amounts, the micronutrients are just as essential as macro-nutrients. Neither plants nor animals can exist without them. Micronutrients, however, in too large an amount are toxic. Many of the pathways followed by nutrients parallel those of energy flow and this reflects the interrelatedness of energy utilization and materials cycling.

This network of interactions, which dictates an ecosystem structure and function, determines how the ecosystem responds to stress. A perturbation at one site not only affects proximal structures and functions but also induces effects elsewhere in the system. The complexity of ecosystems coupled with the attribute of self-maintenance makes specific predictions of reversible and irreversible effects difficult. This is particularly so for stresses of varying intensity and stressors capable of being assimilated by the ecosystem. Chronic stress may result in significant ecosystem responses due to the slow accumulation over time of many small alterations. Consequently, visible modifications in the functioning of the ecosystem may not be apparent until a long time after the stress was initiated.

Natural ecosystems are integral to the maintenance of the biosphere. They are the support system of all life on earth. The most obvious ecosystem benefits derived by man are recreational (e.g., hunting, fishing, hiking) and economic (e.g., forest products); however, a variety of more subtle benefits are important for human welfare (Table 7-16). These include regional and local control of ambient air temperature, prevention of erosion, recharging of groundwater supplies, modulation of stream flow, and cleansing of water and

TABLE 7-16. EXAMPLES OF ECOSYSTEM BENEFITS THAT EITHER DIRECTLY AFFECT HUMAN WELFARE OR UNDERLIE THE MORE DEMONSTRABLE ECONOMIC AND ESTHETIC PRODUCTS DERIVED FROM NATURAL ECOSYSTEMS

Benefit of ecosystem function	Source of benefit	Consequency
Temperature control of local and regional climate	Light-reflective capacity of foliage	Moderation of temperature via removal or actual or potential heat energy
Control of hydrological cycle	Transpiration	Reduced stream flow
	Water retention capacity of soils	Reduced erosion
		Recharged groundwater supplies
Control of atmospheric chemistry	Filtration of soil water (upper soil horizons)	Temperal stability of water chemistry leaving ecosystem despite variable chemistry of incident precipitation
Control of water chemistry	Deposition (wet and dry) of particles and gaseous materials	Clearer air

Source: Bormann (ref. 48).

air resources (48). The net effect of summing these subtle benefits is a predictable environment that is pleasing to man and accommodating to his culture and technology. Furthermore, these benefits are provided cost-free to man since natural ecosystems are self-maintaining units.

The following discussion addresses the response of terrestrial ecosystems to sulfur dioxide and particulate matter. Although the focus is on natural ecosystems, managed ecosystems are also mentioned. The importance of acidic and acidifying precipitation is acknowledged, but discussion of effects of acidic precipitation on ecosystems is found in Chapter 8.

For simplification, the discussion that follows has been divided into a number of separate categories. These categories are related to the function and trophic level of the organisms in the ecosystem. All organisms referred to as producers, consumers, and decomposers perform the same basic functions in an ecosystem. Due to the inseparability and the interdependence of the components of an ecosystem, any change that takes place in the producer, consumer, or decomposer categories will result in a change in the other categories and therefore, in the processes of energy flow and mineral nutrient cycling.

7.11.2 Sulfur in Natural Ecosystems

7.11.2.1 The Sulfur Cycle in Natural Ecosystems--Sulfur is an element that is essential for the normal growth and development of plants. It is a basic constituent of protein and is required in large amounts by some plants. Under normal circumstances sulfur in rainwater and in soil organic matter is sufficient to meet the plant requirements. Excessive sulfur in the form of sulfur dioxide can be toxic to plants. The phytotoxic forms of sulfur, routes of entry into plants, and the symptomatology of SO_2 injury to plants have been discussed in the preceding sections.

Within any ecosystem, nutrients occur in the atmosphere in living and dead

organisms, and as available and unavailable salts in the soil and rocks. Air pollution, however, can influence nutrient cycling by altering the amounts in, and the rate of flow among, ecosystem compartments (400).

The biogeochemical cycle of sulfur is both sedimentary and gaseous. Sulfur in the longterm sedimentary phase is tied up in organic and inorganic deposits in the soil. Weathering and decomposition permit sulfur to enter into solution and to be carried into aquatic and terrestrial ecosystems. In its gaseous state, sulfur is circulated on a global scale (Figure 7-4).

Although major sources, sinks, and pathways of sulfur flux are accurate, estimates of the relative importance of the various cycle components vary (359). Estimates of the manmade contribution to the atmosphere (versus that released naturally by microbial activity) in the early 1970s ranged from 50 percent (226) to 70-90 percent (336, 359). Kellogg et al. (226) conclude that manmade sulfur emissions will actually exceed natural emissions in the northern hemisphere by the year 2000.

The influence of man on the sulfur cycle is best seen when studied on a regional basis (154) as Shinn and Lynn (388) have done for the northeastern United States. Atmospheric sulfur is not deposited equally over the global land areas (Table 7-17). The emission of sulfur from manmade sources results in greater deposition occurring on and adjacent to industrialized areas. In the northeastern United States, the deposition of atmospheric sulfur is 28.4 times greater than would be expected if emissions were uniformly distributed on a global basis. Globally, natural processes far exceed human contributions.

7.11.3 Ecosystem Responses to Sulfur Dioxide

7.11.3.1 Kaybob I and II Gas Plants, Fox Creek, Alberta, Canada (475,476,477)--The Kaybob gas plants, which emit SO_2 during the removal of hydrogen sulfide from natural gas, are located within transition montane-boreal forest dominated by a mixed assemblage of deciduous and coniferous trees. White spruce (*Picea glauca*) stands predominant in successional areas on well drained soils.

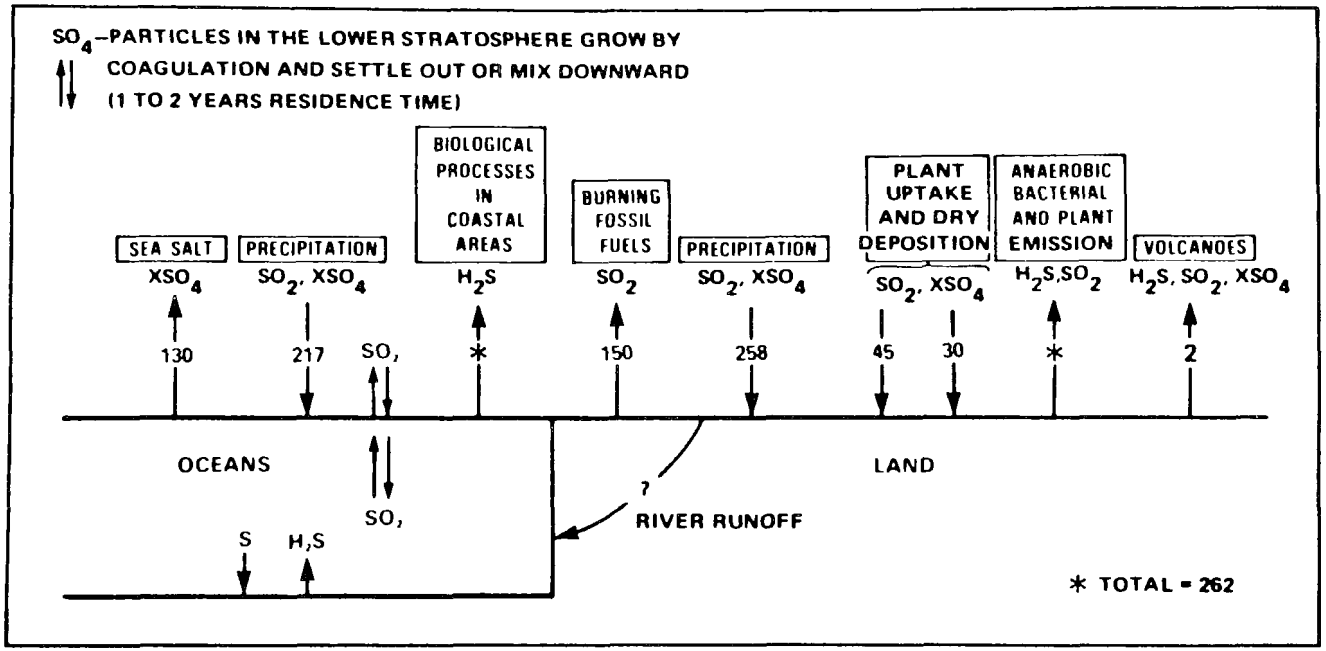

Figure 7-4. Schematic diagram shows sources and sinks of atmospheric sulfur compounds. Units are 10^6 metric tons (10^9 kg) per year calculated as sulfate.

Source: Adapted from Kellogg (1972).

TABLE 7-17. COMPARISON OF GLOBAL LAND SULFUR CYCLE WITH REGIONAL SULFUR CYCLE OF NORTHEASTERN UNITED STATES (10^6 tons of SO_4/year)

Cycle component	Global	Northeastern United States	
		By land area[a]	Experimental Data
(A) Atmospheric inputs			
Manmade SO_2	150	0.88	2.5
Microbial sulfur	210	1.23	2.0
(B) Terrestrial inputs			
Deposition (wet and dry)	360	2.11	13.0
Fertilizer	33	0.19	1.0
Weathering	42	0.25	1.0
(C) Terrestrial export			
Stream	250	1.32	15.0
Air	0	0	10.0

[a]Figures for "By land area" were calculated to illustrate what the various component figures would be regionally if sulfur inputs and outputs were distributed evenly over all global land areas.

Source: Adapted from Shinn and Lynn (ref. 388).

Since these P. glauca forests have less species variation than other sites, they were selected for analysis along a transect showing decreasing SO_2 stress and ranging in elevation from 600 to 1075 m. Since edaphic factors were responsible, in part, for the observed differences in plant communities, they were considered to be unimportant (475). The facility began operation in 1968, and the field study was completed in 1976. Field measurements of ambient atmospheric conditions were not made although the nature of the technological process would necessitate SO_2 emission products (260). From 1973 to 1975, it is estimated that the Kaybob facility emitted approximately 71,000 kg/day of SO_2.

Relative species diversity showed no gradient pattern of response to SO_2; however, percent coverage for all understory plants, including vascular species and mosses, showed a marked increase with distance from the source (476). A comparable pattern for the canopy was not recorded even though reproductive effort represented by seedling number in white spruce populations close to the refinery was reduced. Changes in moss communities were conspicuous and included decreasing values for moss canopy coverage, moss carpet depth, dry weight, capsule number, and frequency of physiologically active versus inactive moss plants. Close to the source, there were no mosses at all (475). These results suggest that species diversity, particularly in the mosses, has changed as a consequence of sulfur gas emissions. As noted by the authors, the decreased coverage of producer species close to the source was associated with an actual increase in species diversity (Shannon Weaver Index). The significance of this phenomenon is that qualitative changes in species composition have occurred as a consequence of sulfur emissions, and this has important ramifications for functional processes of energy flow and nutrient cycling.

In a subsequent study of the ecological fate of sulfur emissions in the same white spruce forests, Winner et al. (477) found an association between sulfur accumulation in foliage and the vertical location of the organism in the forest's stratification. Specifically, the sensitivity of mosses versus understory and canopy species was attributed to the greater sulfur accumulation derived solely from sulfur emitted from the Kaybob facility. This conclusion was based on tracer experiments (^{34}S:^{36}S) which unequivocally assessed the fate of emitted sulfur (41). This condition of enhanced moss sensitivity has ecological consequences since mosses serve several unique functions within a forest. These include water storage, soil formation, erosion prevention, and nutrient cycling; therefore, any stress (e.g., light, temperature, SO_2) that affects the performance of mosses is likely to induce changes throughout the ecosystem. This research is of particular relevance since it shows that species biomass is not necessarily a good indicator of ecological importance.

7.11.3.2 West Whitecourt Gas Plant, Whitecourt, Alberta, Canada (260)--The effects of chronic sulfur gas emissions in a forested ecosystem were investigated in a region experiencing effluents from a natural gas-processing facility. Ecological observations were coupled with physiological investigations, the goal being to explain changes in ecosystem structure and function by alterations in physiology. The processing plant began operation in 1961, and field studies were conducted in 1975 within a 120-year-old lodgepole x jackpine forest (*P. contorta* x *banksiania*) characterized by a bearberry-blueberry understory. Results of an air-monitoring program in 1975 within the pine forest showed SO_2 levels to be variable but not exceeding the Alberta air quality criteria standard of 0.2ppm/0.5 hr/24 hr. Measurable quantities of SO_2 (0.01 ppm detection level of the instrument) were recorded on 40 out of 46 days. On an average day detectable levels of SO_2 remained in the forest for four hours; however, over 46 percent of all hours monitored were characterized by pollutant levels below 0.05

ppm. The highest instantaneous level was 0.45 ppm. In general, pollution levels in the forest were greater during daylight hours. These data depicting the ambient SO_2 exposure for the forest are specific for 1975. Differences in exposure are documented for different years, although the general trends are consistent.

Two locations were selected based upon their similarity in many edaphic, climatic, and biological indices, but differing in their proximity to the source. Studies of structural changes induced by SO_2 at the ecosystem level were limited to studies of basal-area increments and biomass of the dominant pines in both the reference and SO_2-stressed location. Using basal-area increments as an example (Legge et al., ref 260), differences between sites were dramatic, with trees nearer the source showing smaller incremental additions, beginning in 1971 and continuing through 1975. Statistically significant differences were obtained in 1964 through 1975. In addition to these data, tracer techniques (^{34}S:^{36}S) coupled with atmospheric profile, micrometeorological studies showed that the pine canopy was acting as a sink for the sulfur emitted from the processing facility.

This evidence of changes induced by SO_2 in the dominant producer species led to physiological and biochemical experiments designed to investigate the mechanisms of growth inhibition. Controlled field exposures revealed no effect of SO_2 on photosynthesis of lodgepole/jackpine; however, laboratory studies indicated that the pine population inhabiting the stressed site had a lower rate of photosynthesis than that from the "reference" location. Other physiological investigations showed increased sulfate levels in pine needles throughout the growing season, decreased foliar retention of potassium and phosphorus, and lower soil pH.

Further evidence at the biochemical level pointed to SO_2 effects. These results included changes in plant pigment level, phenolic content, and adenosine

triphosphate (165). The authors remarked that "vegetation along the downwind path of SO_2 emissions is adversely affected on a molecular level," and this may be one of the causes underlying decreased basal-area increments.

The movement of materials within the forest also showed signs of SO_2-induced modification (260). This phase of the study compared indices of changes in a series of sites selected for their similarity in vegetation and in soil properties but varying in their exposure to SO_2. As expected, sulfur distribution in the soils and vegetation varied with distance and direction from the source. In lodgepole x jackpines sulfate levels in leaves in three successive years decreased with increasing distance along the corridor of SO_2 stress. Seasonal variation in sulfate in the leaves of tamarisk (Larix larincinia), aspen (Populus tremuloides), and lodgepole x jackpine was recorded, with progressive sulfur loading from June through September annually. Among the dominant producer species, foliar sulfate levels were higher in the deciduous forest trees than in the pine. Finally, sulfate in the leaves of forest canopy near the source decreased downward through the canopy.

The status of soil sulfur also reflected the direction and distance of the sample site from the source. Total soil sulfur generally decreased with distance along the downwind corridor of SO_2 stress. Along the corridor, consistently higher sulfur levels were found in the upper 2 cm of the soil, which also had the highest organic content. These data support the hypothesis that humus material is a major reservoir of soil sulfur. Finally, the acidity of the top 2 cm of soil varied as a function of SO_2 stress; higher acidity was recorded proximal to the source of SO_2.

Pollutant-induced modifications of the biogeochemical cycles were not restricted to sulfur alone but were also evident in a variety of other inorganic elements. The most striking and consistent pattern was recorded with manganese

distribution. Over 4 successive years, the manganese content of lodgepole x jackpine needles decreased with increasing distance away from the source. The authors noted the concordant changes in soil pH, a factor known to affect the availability of soil ions to plants. The potential importance of this effect lies in the fact that elevated manganese levels elicit iron deficiencies which, in turn, are known to affect the regeneration of pine forests. In addition, the recorded iron deficiency might explain, in part, the pattern of chlorosis observed in pines as well as the depressed photosynthetic rates. The distribution of other elements along the corridor also exhibited patterns associated with the level of SO_2 exposure: lodgepole x jackpine foliar concentrations of potassium, zinc, phosphorus, and iron were consistently lower in SO_2-exposed versus "reference" locations.

In summary, atmospheric emissions of SO_2 modified the forest ecosystem in an area of approximately 454 km^2, principally along a downwind corridor of decreasing SO_2 exposure. The atmospheric level of SO_2 is described as producing chronic injury to sensitive producer species. However, the authors contend that in terms of forest ecology, SO_2 foliar uptake and subsequent injury are less important as a mechanism responsible for ecological modification than deposition on the ground. Numerous SO_2-associated changes are recorded, and collectively they represent pollutant-induced modification of the rates and pathways traveled by nutrients moving among the atmosphere, soil, water, and vegetation components of the ecosystem. These modifications occur through direct and indirect pollutant effects, and collectively they interfere with physiological activities in producer organisms. These changes, however, are not viewed as being ecologically irreversible.

7.11.3.3 Montana Grasslands--In the near future, the grasslands of the upper plains will be subject to SO_2 emissions from the new coal-burning power facilities

that are being constructed in areas rich in coal reserves (122). There are insufficient data to evaluate accurately the ecological consequences of elevated atmospheric sulfur levels in grasslands, and the uniqueness of grass-dominated systems precludes extrapolating freely from results in forested or agricultural ecosystems impacted by SO_2 (485). To address this problem, plots of Montana grasslands were exposed to SO_2 during growing seasons of successive years. The exposure levels averaged 0, 0.02 (52 $\mu g/m^3$), 0.05 (105$\mu g/m^3$), and 0.15 ppm (183 $\mu g/m^3$) SO_2 and were delivered by a zonal air pollution system, or ZAPS (257). Field observations over 3 years verified that these concentrations were not sufficient to elicit any leaf lesions characteristic of acute SO_2 injury (253). Ambient pollutant concentrations were typically greater at night, and the concentration decreased rapidly from the interface of turbulent air and grass canopy downward to the soil (357). This pattern of decreasing pollutant concentration within a canopy is common for any gas being deposited on or assimilated by a surface.

The most prevalent producer species within the grassland is a perennial, Agrypyron smithii. In populations sampled over the growing season in each of the exposure regimes, SO_2 induced a variety of changes in biochemical indices of plant performance. Monthly samples of tillers and leaves showed a positive correlation of foliar sulfur (as sulfate) with time of exposure and canopy-level SO_2 concentrations (251). This relationship was most conspicuous with the two higher exposure regimens, and total foliar sulfate in the highest exposure plot was three times greater than that in vegetation sampled from control locations (253). As the sulfur content of leaf tissue increased, the ratio of nitrogen to sulfur decreased (178), as did the levels of crude protein and digestability (380).

This array of biogeochemical changes in the major producer species was mirrored by other modifications in plant performance. In A. smithii populations

exposed to 52 $\mu g/m^3$ SO_2 over the growing season the functional leaf life (the period of active photosynthesis) was increased by several weeks while the same index of plant performance was shortened by 2 weeks at 105 and 183 $\mu g/m^3$ SO_2. Parallel increases and decreases in chlorophyll content at the low and high SO_2 levels, respectively, were also recorded. Finally, with increasing SO_2 exposure plants stored less photosynthate in rhizome tissue (178).

Dominant producers were not the only flora exhibiting sensitivity to SO_2. In simulated pollutant exposure using a bisulfate solution, Sheridan (386) showed that nitrogenase activity in a major component of the lichen flora (*Collema tenex*) was reduced. Although the applicability of the data must be validated through field studies, the potential for such an effect must be recognized, particularly in light of the importance of soil lichens in regulating nitrogen fixation in the grasslands (386).

The significance of pollutant-induced changes in producers lies with the importance of these organisms in defining the structure and function of the grasslands. For example, a decrease in herbage quality (e.g., crude protein or digestibility) of a dominant grass may alter the potential of the grasslands for cattle grazing. In terms of the flux of energy and nutrients within the system, any factor affecting the rate at which consumers devour producers will have repercussions throughout the ecosystem (380).

Further evidence of SO_2-associated effects on the grasslands is recorded in both consumer and decomposer populations. The density of grasshoppers, a major consumer of *A. smithii* foliage, decreased with increasing SO_2 stress in two successive seasons (Laurenroth and Heasley, ref 253). Decomposition rates were also altered with less decomposition in SO_2-exposed plots. The mechanism involves a direct pollutant effect on decomposer activity rather than an indirect effect, such as elevated sulfur levels in the litter (253).

Larger consumers also exhibited responses reflecting the presence of SO_2 in the atmosphere; however, the responses were not dose dependent (71). Peromyscus maniculatus, prairie deer mouse, is a common and active vertebrate in grassland communities. Over one exposure season, the frequency of P. maniculatus in control plots increased, implicating an SO_2-induced behavioral response (habitat preference) whereby individuals seek habitats free of the pollutant. The speed of the response (within one season) suggests a direct, adverse effect of SO_2 on the animal's health.

Any summary of SO_2 effects on grasslands must be tentative since the research effort is not completed. At the reported exposure levels, SO_2 does induce changes in the performance of producers, consumers, and decomposers. Many of the responses are individually small, but collectively over time they are gradually modifying the structure and function of the grasslands (357).

The results of these studies, particularly the West Whitecourt and Montana grasslands studies, document the usefulness of addressing ecosystem-level responses to SO_2 from a multidisciplinary approach incorporating investigations of physiology, autecology, synecology, geology, meteorology, and modeling. The results confirm that producers are sensitive to direct SO_2 effects as evidenced by SO_2-associated changes in cell biochemistry, physiology, growth, development, survival, fecundity, and community composition. Such responses are not unexpected. An equally important point of agreement among the different research efforts is the potential for ecological modification resulting from either direct SO_2 effects on nonproducer species or direct changes in habitat parameters, which in turn affect an organism's performance. Changes in biogeochemistry, particularly in the soil compartment, are notably responsive to chronic SO_2 exposure.

7.11.4 Response of Producers, Consumers, and Decomposers to Sulfur Dioxide

7.11.4.1 Response of Producers to Sulfur Dioxide--In both natural and agroecosystems, producers are indispensable. They alone are capable of converting solar energy into a chemical form that is subsequently the energy source for the remainder of the ecosystem's organisms. Secondly, this flow of energy originating in producers and continuing throughout the ecosystem provides the pathway and driving force for the ecosystem's other major function--the cycling of materials. Finally, producers are commonly integral to the system's physical structure, providing a framework in the soil and above the ground. In so doing, producers collectively modify the environment, and create a variety of habitats for other producers, consumers, and decomposers. Thus, the interest in producers and their response to SO_2 are justified.

Vegetation is notably responsive to most environmental stimuli, including SO_2. This responsiveness is a consequence, in part, of the gas-exchange process in leaves whereby any gas in ambient air (e.g., CO_2, SO_2, ozone) exhibiting a concentration gradient will diffuse into the leaf interior. However, this predisposition to absorb pollutants is not the sole factor governing plant susceptibility; internal biochemical factors are also important. Sulfur is an element required for normal growth and development; however, in excessive amounts it is detrimental. Therefore, the concept of "cardinal points" (20) applies: a range of sulfur levels in plants is considered essential for optimal physiological activity, but either deficient or toxic levels reduce growth to levels below optimal. The interplay between differential pollutant uptake (gas-exchange process) and variation in sulfur metabolism underlies the great and confusing variation in plant response to SO_2.

In the literature there are many examples of producer responses to SO_2, and most describe how individual plants respond to artificially elevated SO_2 levels in controlled exposures. Seldom have in situ field studies been reported in which atmospheric pollutant levels are monitored throughout the course of study; thus the results must be interpreted with caution. From an ecological perspective, each report is of limited value, but collectively they are a valuable source of information on (1) SO_2 levels at which responses occur and (2) potential mechanisms underlying ecosystem-level modifications (436).

At the individual plant level, SO_2 has pronounced effects on a variety of vegetative and reproductive characters ranging from alterations in a cell's biochemical status to responses at the whole-plant level. Examples of these responses for species occurring in agricultural and natural ecosystems were outlined in Tables 7-5 and 7-6, respectively. The range of SO_2 doses at which changes are detected indicates that the lack of necrosis or chlorosis does not indicate absence of injury. Furthermore, even though the site of SO_2 toxicity is the leaf, pollutant-induced perturbation of physiological processes in the leaf can affect vegetative and reproductive activities that depend on the assimilatory capacity of the leaf.

In reviewing Tables 7-5 and 7-6 from an ecological perspective, the responses may be grouped according to how SO_2 affects the organism's ability to survive and reproduce as well as the importance of the response from the point of view of nutrient cycling (Table 7-18). Survival depends on the plant's autotrophic output remaining higher than its maintenance expenditures, hence the category entitled "net productivity." In this respect, two processes of obvious importance are the rate of photosynthesis and respiration, the difference being net photosynthesis.

TABLE 7-18. DOCUMENTED DIRECT SO_2 EFFECTS ON INDIVIDUAL PLANTS.[a]

Survival and reproduction	Nutrient cycling
A. Net productivity	A. Sulfur in vegetation
1. Photosynthesis	Dry deposition
CO_2 assimilation rate	Plant sulfur levels (root, stem, and leaf)
Chlorophyll content	Organic to inorganic sulfur ratio
Photosynthetically active tissue	Sulfur metabolism
2. Respiration	B. Nitrogen
3. Cell maintenance	Nitrogen: sulfur ratio
Buffer capacity	NO_2 emissions
pH	Nitrogen fixation
Lipid synthesis	C. Water
Membrane permeability	Transpiration
ATP levels	D. Carbon
B. Growth and development	Digestability
1. Vegetative processes	E. Miscellaneous
Terminal buds	Plant levels of potassium magnesium, phosphorus, calcium
Carbon allocation	Production of leaf litter
Senescence	
Shoot biomass	
Root biomass	
2. Reproductive processes	
Flower number	
Pollen germination	
Fertilization	
Seed quantity	
Seed quality	

[a]Effects are generalized from those summarized in Tables 7-5, 7-6, and 7-7. Their relevancy to ecosystem-level processes is indicated according to their impact on survival and reproduction or the cycling of nutrients.

As an example of the response of these three categories to SO_2, the effects of the pollutant on net photosynthesis are discussed.

The rate of carbon dioxide assimilation by foliage in controlled environments is responsive within minutes to elevated SO_2 levels. In barley (Medicago sativa), exposure to 0.25 and 0.40 ppm SO_2 reduced carbon dioxide uptake within 15 min to levels of 98 and 93 percent of the controls, respectively (29). Within 20 min the corresponding rates were 94 and 86 percent, and remained unchanged for the remainder of the 2-hr exposure. Once SO_2 was removed, CO_2 uptake rate returned gradually within 2 hrs to that exhibited by "control" plants. A similar pattern of photosynthetic depression at elevated SO_2 levels (1.0 ppm) is reported for Phaseolus vulgaris (21). In both high (84 percent) and low humidity (44 percent), CO_2 uptake was reduced within 10 min and, at the higher humidity, was completely suppressed. In a comparison of the response of photosynthesis to SO_2 in a deciduous (Diplacus aurantiacus) and an evergreen (Heteromeles arbutifolia) shrub, Winner and Mooney (479) found that the magnitude of depression depended strongly on concentration. Using a range of SO_2 concentrations from 0.25 to 1.71 ppm for 8 hr, net photosynthesis (as a percentage of the controls) decreased linearly with time, and the slope became more negative with increasing concentration. In both species and at all concentrations, photosynthetic rates returned to normal within 3 to 7 days after SO_2 exposure ceased.

The SO_2 response of net photosynthesis in three evergreen forest species (Abies alba, Picea abies, and Pinus sylvestris) was investigated at SO_2 concentrations of 0.0, 0.05, 0.1, and 0.2 ppm delivered continuously over a 10-week period (223). Exposures were conducted in either the spring, summer, or fall. Regardless of the species or season, increased SO_2 concentration and duration led to progressive reduction in photosynthesis. This response occurred even in the absence of visible needle injury and was common for all three seasons.

These studies highlight the sensitivity and responsiveness of photosynthesis to SO_2; however, the implications of the results for an assemblage of plants (e.g., crop canopy or forest stand) is difficult to assess, as was demonstrated by Black and Unsworth (39). Vicia faba plants were individually exposed to a range of low SO_2 concentrations (0-0.175 ppm) in a controlled environment designed to mimic conditions characteristic of agroecosystems in Great Britain. The levels of SO_2 used in the study were common ambient concentrations in that country. Whenever SO_2 levels exceeded 0.035 ppm, net photosynthesis of individual leaves decreased according to the amount of light irradiance. In light-saturated leaves (upper canopy), photosynthetic response was concentration-dependent, whereas the corresponding response with lower light irradiance was depressed equally whenever SO_2 levels exceeded 0.035 ppm. When SO_2 exposure ceased, photosynthesis rapidly returned to control levels within 1 to 12 hr. Dark respiration was notably increased (71 percent with low SO_2 levels), and this may explain the decrease in net photosynthesis.

The implications of these results for crop physiology and yield were discussed using a model of crop photosynthesis (39). The study indicates that the experimental results derived from individual plants studies are valuable in assessing crop-level response, but that direct extrapolation may not be accurate. This conclusion is derived from the understanding that physical associations among plants (in agricultural and natural ecosystems) create canopies that modify an array of habitat factors, including SO_2 levels (28). For example, light levels are attenuated vertically through the canopy so that lower leaves are not light saturated, and, as demonstrated by the authors (39), this factor modified the photosynthetic response. In a similar analytical fashion, Black and Unsworth showed that crop net photosynthesis is inhibited at a given low SO_2 concentration, but the response for the entire crop is not concentration-dependent since the majority of canopy foliage experiences less

than light-saturated irradiance levels. Model calculations (39) of dry matter accumulation (grams of dry matter per square meter ground) for a hypothetical crop of *V. faba* were as follows:

	Sulfur dioxide concentration (ppm)			
	0	0.035	0.088	0.175
Day (14 hr)	27.9	17.4	16.4	15.4
Night (10 hr)	-5.6	-9.5	-9.5	-9.5
Net total production (24 hr)	22.3	7.9	6.9	5.9

At SO_2 levels exceeding 0.035 ppm, net dry matter accumulation during daylight hours decreased only slightly, which reflects the fact that most foliage was below light saturation. During the evening, some of the photosynthate was consumed in dark respiration, which increased uniformly at SO_2 levels above 0.035 ppm. As a consequence, net accumulation of dry matter per day for a given area of ground decreased 65, 69, and 74 percent with increasing SO_2 levels. Therefore, dry matter production in this hypothetical crop does not respond to SO_2 in a concentration-dependent manner but rather is uniformly depressed above SO_2 levels of 0.035 ppm. These results are relevant to understanding the manner in which SO_2 impacts agricultural and natural ecosystems, and further experimental study is warranted.

The open system of plant growth and development suggests that changes in productivity should affect vegetative and reproductive processes. Furthermore, the concept of "cardinal points" dictates that the SO_2 response be a function of the plant's sulfur requirement and its ability to assimilate the SO_2 derived from the atmosphere. Results from a variety of research efforts support this assessment.

The response of plants to SO_2 may be interpreted as positive ("beneficial"), negative ("detrimental"), or undetectable. When sulfur levels in the plant are suboptimal, sulfur derived from SO_2 can remedy the deficiency, and thus enhance growth and yield (4, 138, 417). In a variety of plant species found in intensely managed agroecosystems (e.g., pastures, monocultured forests, croplands) such beneficial responses are reported (88, 130, 264, 334).

Conversely, elevated SO_2 levels may reduce growth and development. Exposure of poplar clones (Populus deltoides x P. trichocarpa) to 0.25 ppm SO_2 for 6 weeks caused leaf injury which was, in time, associated with reduced growth in height (113). Pinus sylvestris seedlings were exposed to 0.06 ppm SO_2 for 25 weeks in both summer and winter (132). Measures of growth (including stem and root dry weight) were reduced in both seasons, and the response was attributed to reduced CO_2 assimilation and subsequent effects on photosynthate allocation. Similar SO_2-associated growth effects are reported in the Biersdorf area of Germany, which experienced chronic SO_2 levels (161). In the first 10 years of elevated SO_2 levels, several indices of growth in beech (Fagus sylvatica), pine (Pinus sylvestris), and larch (Larix europaea) showed reductions associated with the level of SO_2 stress. Although several growth indices were studied, the most reliable were the ratio of thickness growth to shoot length, and new shoot number and length.

Keller (224) documented changes in shoot growth of two deciduous tree species (Ulmus scrabra and Robinia pseudoacacia) and attributed the response to SO_2 inhibition of terminal bud growth. Furthermore, the response was recorded after wintertime exposures when foliage was absent. Following controlled exposures to SO_2 concentrations ranging from 0.01 to 0.2 ppm, the number of buds failing to renew growth the following spring increased with SO_2 concentration.

Similar SO_2-induced changes in growth of meristematic tissue are reported for reproduction. In red (Pinus resinosa) and white (P. strobus) pines growing in a region experiencing elevated SO_2 levels emitted from a coal-burning power plant, several indices of impaired reproductive success (e.g., number seeds per cone, seed weight, and percent pollen germination) were associated with increasing sulfur levels in the atmosphere (194).

Evidence that SO_2 modifies the distribution of elements in individual plants may have implications for ecosystem-level nutrient cycles. With increasing atmospheric concentrations of SO_2, sulfur levels in vegetation rise accordingly; the significance of this for the ecosystem's sulfur cycle is discussed elsewhere (section 7.11.2). Concomitant effects of SO_2 on other elements are also observed. Materna (295) found that the concentrations of potassium, calcium, magnesium, and phosphorus increased in fir needles following controlled exposures to SO_2 over several consecutive growing seasons. The pollutant concentrations never exceeded 0.38 ppm and were routinely less than 0.19 ppm. Water-use efficiency in producers is also responsive to SO_2. In Vicia faba, an agriculturally important crop, exposure to 0.11 ppm SO_2 for a full day reduced stomatal resistance to water vapor flux by 25 percent (37); the authors estimate that an equivalent response in the field would increase the amount of water transpired by 23 percent. Finally, many reports describe pollutant-induced changes in a variety of proteins. Recently, Klepper (232) found that hydrated SO_2 derivatives were responsible for NO_2 emissions from foliage.

The response of plant populations and communities to elevated SO_2 levels is not documented as well as that for individuals. From an ecological perspective

this is unfortunate because single plant responses under controlled conditions may not necessarily be the same as a population or community-level effect. The response of populations is particularly relevant to intensely managed ecosystems (e.g., pastures, croplands, forests) in which a single or a few species dominate. Discussion of community responses is more appropriate to natural ecosystems.

The dilemma of extrapolating from SO_2 effects on individual plants to higher levels of organization is less difficult for populations than for communities, especially intensely managed agroecosystems. Typically, producers are genetically similar and experience comparable environments. The resulting physiological uniformity requires that most individuals respond to environmental stress in a comparable manner.

Managed agroecosystems are potentially very susceptible to SO_2 stress for several reasons. First, plants exhibiting distinctly seasonal growth and thriving in well-watered habitats maintain extremely high rates of gaseous exchange, which encourages SO_2 influx. Some evidence indicates that rapidly growing foliage (i.e., foliage with high intrinsic photosynthetic rates) is very sensitive to SO_2, gauged according to leaf injury (466) and reduced carbon dioxide assimilation (478). Furthermore, crops are commonly harvested for their reproductive effort, a process notably responsive to SO_2 (via altered photosynthate allocation). Finally, the developmental uniformity of single-species crops means that elevated SO_2 levels during a particularly sensitive stage of growth (e.g., flowering) will affect most individuals in the population with concomitant effects on yield. A more detailed discussion of stress response in managed agroecosystems is provided by Loucks (280).

From another perspective, agricultural ecosystems in sulfur-deficient areas (e.g., southeastern United States) may benefit from elevated SO_2 levels (334) if the exposure does not exceed the crop's ability to assimilate the pollutant. This assumes that the level of sulfur in the plant is suboptimal. This situation is strictly applicable to agricultural areas where soil sulfur retention is extremely poor because of the depletion of litter, which is the soil component most responsible for controlling the release of plant-available sulfur (176, 216, 301).

In 1950, Dunn hypothesized that elevated atmospheric levels of smog in the Los Angeles Basin were differentially affecting individuals in populations of native plants and that differential selection was gradually changing the genetic structure of the populations toward greater smog resistance. In recent years, this population phenomenon has been documented in many native species thriving in areas impacted by SO_2 (24, 187, 191). One example is the evolution of SO_2 resistance in populations of Lolium perenne in grasslands of Great Britain (187). These results indicate that at least some populations are experiencing gene pool shifts as a consequence of prolonged exposure to low-level SO_2 stress. The capacity to evolve resistance, which would ameliorate some of the adverse pollutant effects, is likely to be more common in naturally occurring species than in crop plants since the latter lack the inherent intraspecific variation upon which selection can act (187).

The significance of the induction of gene pool shifts by SO_2 is difficult to assess from an ecological perspective. Greater resistance may be beneficial to sensitive populations. Conversely, if increased resistance is associated with lower photosynthetic rates (478), slower intrinsic growth (466), or decreased water-use efficiency (182), selection of SO_2 resistance would lead to populations possessing a new set of ecologically important traits that might, in turn, redefine the species' niche (325).

Community-level responses resulting from prolonged exposures to SO_2 are not well documented; however, a theoretical basis from which to evaluate effects is emerging. This conceptual effort is exemplified by the development of a generalized forest growth model (50) that was designed to assess the consequences of perturbation on plant communities (49, 392). This model has been applied to the response of a mixed-species, deciduous forest in the southeastern United States to differential levels of growth reduction (0, 10, and 20 percent) following air pollution stress (468). Over several decades, simulated pollution stress altered dramatically the relative biomass importance of the major tree species within the forest; some species populations increased while others decreased in importance. This suggests that the qualitative composition of producer species changes in response to pollution stress, and since community structure is coupled to the flow of energy and materials, dependent processes within the ecosystem will necessarily be modified. The mechanism underlying community-level changes is twofold. First, the growth and reproduction of populations of sensitive species is impaired as a direct consequence of SO_2 toxicity. Second, since community composition is determined in part by species interactions (e.g., competition, symbiosis), the ecological importance of resistant species whose prominence in the community is determined by an interaction with sensitive species will be altered (468). The direction of this indirect response depends on the nature and extent of the interaction. An understanding of this governing role of species interactions is essential to predicting how ecosystems respond to low levels of pollution (49). This is also the justification for not extrapolating freely the results from intensely managed forest and agroecosystems to predict how a mixed-species community (e.g., natural forests or grasslands) will respond to a comparable perturbation (229, 313).

Modeling predicts that SO_2 affects species' performance directly through inhibition of growth and reproduction or indirectly by changing a population's relationship to other species. How does this conclusion compare with empirical data?

The results from community-level studies in acutely stressed areas such as Trail, British Columbia (326), lend credence to the modeling effort. Regardless of the region and intensity of SO_2 stress, patterns of plant community response are repeated. These include: (1) the species number decreasing toward the source, (2) a parallel pattern of decreasing importance of canopy species, (3) increasing prominence of ground vegetation toward the source, and (4) profusion of opportunistic SO_2-resistant species in areas vacated by SO_2-sensitive plants (483). The most likely explanation for these patterns is that SO_2 directly inhibits either growth or reproduction of many species populations. Following the decline of these SO_2-sensitive plants, SO_2-resistant species flourish as they invade areas previously occupied by competitors (483). The results from these acutely stressed locations indicate that the SO_2-susceptibility of individual species populations plays a greater role in determining community response than does species interaction.

This conclusion is not appropriate to regions experiencing lower levels of SO_2. Guderian (158), using communities consisting of only two or three different species, analyzed community-level responses to SO_2 and their underlying causes. Each community, which was typical of those purposely planted for fodder, was exposed to graduated levels of SO_2 for varying periods of time. Several key observations were reported. First, changes in community composition following exposure were a function of SO_2 dose, so that the higher the dose, the greater the community change. Second, altered community composition was attributed to both direct SO_2 effects on sensitive species populations and

indirect changes in species interactions. This is exemplified by the increased prominence of SO_2-resistant populations which outcompeted the SO_2-affected plants. Community biomass exhibited little quantitative change despite striking differences in species composition. The same conclusion was reached by another researcher in a similar study of artificial exposure to SO_2 in an old field in New England (73); it is also comparable to the conclusion achieved through the modeling effort (468).

This understanding of community-level responses was achieved through modeling and controlled exposures of intensely managed ecosystems. The results, however, are applicable to field studies of regions experiencing prolonged SO_2 stress (161, 372). As an example, Rosenberg et al. (372) assessed the species composition in 27 stands of natural regrowth northern hardwood forest dominated by oaks (*Quercus* spp.), white pine (*Pinus strobus*), and hemlock (*Tsuga canadensis*). The stands, which varied in their distance from a 25-year-old coal-burning power plant, exhibited no obvious *a priori* compositional differences. Atmospheric pollutant levels were not reported, although foliar symptoms typical of SO_2 toxicity were recorded on several occasions. In both upwind and downwind directions, the number of vascular plant species (canopy, understory, and ground) per unit area (species richness) increased with distance from the source. A similar distance-dependent response was recorded for species diversity using the Shannon-Weiner index. Both indices of plant community response approached asymptotic values with increasing distance, which implicates the facility as the cause of the response pattern. The more rapid approach to the asymptote in the upwind direction supports the hypothesis of an atmospheric pollutant affecting vegetation.

In spite of these SO_2-induced changes in community composition, an index of above ground biomass (basal area of overstory species) showed no variation among stands (372). Among the vascular plants, shrub and ground vegetation was more responsive (in diversity and richness) than the overstory to SO_2 stress,

and this enhanced susceptibility of the lower strata was attributed to the intense competition, unique population biology attributes, and microhabitat factors that tend to increase SO_2 levels close to the ground.

Among the most notable examples of SO_2 affecting plant communities is the response of cryptogamic flora (lichens and mosses); several reviews are available (110, 167). A map of epiphytic lichen communities for England and Wales has been devised that associates progressive shifts in species composition with SO_2 levels (168). In general, the higher ambient SO_2 levels were consistently associated with fewer species and an increasing relative frequency of crustose versus foliose or fruticose forms. The fidelity with which community composition changes in accordance with SO_2 has led to the suggestion that analyses of lichen communities be used as a natural bioassay to estimate ambient SO_2 levels (168).

Similar mapping efforts are reported for several regions of North America. In a rural area of Ohio surrounding a coal-burning power station (emitting 1025 tons SO_2/day), the distribution of two corticolose lichens, Parmelia caperata and P. ruderta, was markedly affected by elevated SO_2 levels (389). Both species were absent from regions experiencing an annual average SO_2 level exceeding 0.020 ppm. The distribution of more resistant lichens was not noticeably affected until SO_2 levels exceeded 0.025 ppm (annual average). Somewhat lower levels were projected by LeBlanc and Rao (255) to affect the ability of sensitive lichen species to survive and reproduce. Using lichen transplants along a gradient of decreasing SO_2 levels in the Sudbury region of Canada, they estimated that acute and chronic symptoms of SO_2 toxicity in epiphytic lichens occur when annual averages of SO_2 exceed 0.03 and 0.006-0.03 ppm, respectively.

The depauperate nature of cryptogamic flora in urban areas is well documented (254, 480), and SO_2 is implicated most often as the principal abiotic factor responsible for the change in species composition. Mosses and lichens have a predisposition to altered growth and reproduction in polluted atmospheres (146, 321, 322, 437).

The decline of cryptogamic flora in atmospheres containing elevated SO_2 levels is typically rapid. For example, LeBlanc and Rao (255) reported impaired growth in several transplanted lichens within 6 months. This rapid decline is in sharp contrast to the time required for lichen recolonization in the event of a restoration of clean air. Using simulation modeling to project reinvasion time by a common urban lichen (*Lecanora muralis*), Henderson-Sellers and Seaward (179) reported a minimum of 5 years. In addition, even though the rate of decline was a function of SO_2 concentration, cleaner air was only partly responsible for the recolonization rate.

In addition to their importance in energy flow and material cycling in ecosystems, producers also serve as hosts for a variety of microflora and fauna. The nature of these interactions, which commonly involve fungi, bacteria and viruses, ranges from being mutually beneficial (e.g. mycorhizae) to antagonistic. It is the latter interactions, principally parasitic diseases, that we know to be affected by elevated SO_2 levels. The mechanism of sulfur dioxide's effect is either a modification of the virulence of the parasite or the susceptibility of the host (435). Modification of the virulence of microorganisms by SO_2 is well documented, for example, in the development of pollutant susceptibility rankings for many common microflora (376). In general, spore germination is the most sensitive stage of development. In light of the extensive interspecific variation among microflora in response to SO_2, Saunders (376) hypothesized that prolonged exposure would lead to the selective elimination of SO_2-sensitive species.

Evidence in nature that virulence is modified by SO_2 is provided by the study of the distribution of Rhytisima acerinium, a leaf fungus responsible for tar spot disease in sycamore trees (36). Along a gradient of decreasing atmospheric SO_2 levels in Great Britain, the frequency of tar spot disease increased. Whenever SO_2 levels exceeded 0.034 ppm (annual average), the fungus was absent from sycamore foliage. This indicates that SO_2 prevented the spread of the fungus and, as a consequence, the disease. In a review of this subject, Heagle (170) concluded that documented cases of SO_2 inhibition of parasitic infestations are more common than the converse.

In a review of parasites in European pine forest experiencing chronic exposure to atmospheric pollutants, Sierpinski (393) found that infestations, particularly of beetles, were more prevalent in chronically impacted forests than elsewhere. The author hypothesized that the initial decline of producers was attributable to the pollutants but that subsequent infestation of "weakened" trees resulted in death. A comparable interaction between polluted air and beetle infestations is offered to explain the loss of pines in the San Bernardino National Forest, which has experienced chronic and acute pollution stress for several decades (312). The consensus of these studies is that pollutant-parasite interactions are principally governed by changes in the susceptibility of the host rather than the virulence of the microbe. Donnabauer (115) and Treshow (435) arrived at similar conclusions, and the former extends his analysis by highlighting the potential consequences for forest growth. He concluded that emissions may "...act as a stimulus for the development of parasites and thus lead to subsequent damage that is entirely disproportionate to the intensity of the emissions" (translated from the German).

7.11.4.2 Response of Consumers and Decomposers to Sulfur Dioxide--The network of biotic-abiotic interactions characteristic of managed and natural ecosystems leads to the hypothesis that SO_2 effects on producers must have repercussions at other trophic levels. Analysis of such responses, however, is difficult experimentally, and an accurate assessment of the importance of SO_2 in eliciting the response is plagued by the often complex relationships among producers, consumers, and decomposers.

This mechanism of response of consumers and decomposers to SO_2 via producers does not preclude a direct, adverse effect of the pollutant in a manner analogous to physiological injury in plants. Elevated atmospheric levels of SO_2 are particularly harmful to soil organisms (16) since soils are preferential sulfur accumulation sites. This focus on soil organisms takes on even more relevance since the rhizosphere is not only biologically active but also responsible for selectively fractionating sulfur derivatives (82, 260).

In forested areas experiencing prolonged elevations of atmospheric SO_2 levels, the species composition of soil microflora shifted toward a greater number and frequency of species capable of utilizing the sulfur additions (457). Specifically, the levels of thiobacilli and sulfur-oxidizing fungi were positively correlated with levels of SO_2 stress, soil depth (Wainwright, ref 457) and extent of tree canopy. In areas impacted by SO_2, the greatest concentration of thiobacilli and sulfur-oxidizing fungi were isolated from the upper 0 to 20 mm of soil. The importance of canopy was most conspicuous, for the absence of a litter on the forest floor reduced dramatically the number of "sulfur-loving" microflora. Comparable results were reported for an area in which the annual average SO_2 level exceeded 0.048 ppm (458). This study confirmed

the dual importance of litter layer and upper soil profiles in determining the microfloral distribution in SO_2-polluted areas and, in addition, documented an apparent SO_2- induced decrease and increase in the total numbers of heterotrophic bacteria and fungi, respectively.

Since prolonged SO_2 exposure tends to increase soil acidity concentration, acidification may be the predominant change in soil chemistry that elicits a response in the microfloral community. In native soils of Canada acidified to a pH of 3.0 due to their proximity to a sulfur-emitting "sour gas" processing facility, bacterial numbers (particularly heterotrophic forms) were reduced (59). Artificially acidified soils in "reference" locations responded in an analogous manner. Since the activity of heterotrophs contributes to nutrient cycling, this pollutant-induced modification could have adverse ecological consequences (59).

There is further evidence of SO_2 effects on soil nutrient levels as a consequence of pollutant-induced changes in soil microflora for nitrogen, although the applicability of the data to natural soils needs to be assessed. Soil exposed continuously to atmospheric SO_2 levels at 5-10 ppm showed changes in levels of ammonia, nitrate, and nitrite (247). Blue-green algae were found to be extremely sensitive to bisulfite (482), and since these organisms are the principal nitrogen fixers in several agricultural and natural ecosystems, their susceptibility warrants further study (16, 150, 247). Finally, the ability of heterotrophic bacteria to decompose organic substrate was inhibited during exposures to high SO_2 levels (156). The authors conclude that this response may be appropriate to acutely stressed areas but not to regions experiencing prolonged exposure at low SO_2 levels.

These experimental studies coupled with the understanding that SO_2 derivatives have pronounced effects on soil chemistry (268, 456) suggest that the rhizosphere is a potential site for pollutant-induced modifications that have far reaching ecological consequences. Nutrient cycling appears to be notably responsive. Unfortunately, few research efforts have focused on soil-pollutant interactions, particularly as regards the selective accumulation over time of pollutant derivatives in the rhizosphere and its influence of soil microbiota. Coleman et al. (75) postulated that root exudation of organics during active root growth is a bacterial stimulant. This response in turn elicits feeding by a variety of soil microfauna including nematodes and amoebae. This sequence of events is tightly linked to the mobilization of carbon, nitrogen, and phosphorus. Since SO_2 is known to affect root growth at levels that do not induce foliar injury, this may be a mechanism whereby SO_2 indirectly modifies nutrient cycling events in the soil even though pollutant derivatives do not accumulate.

7.11.4.3 Response of Natural Ecosystems to the Interaction of SO_2 with Other Pollutants--Sulfur dioxide is commonly associated with many other stresses, principally gaseous pollutants (including ozone, nitrogen oxides, PAN, hydrogen sulfide, and fluoride) and particulates.

The Copper Basin of Tennessee has received an array of stresses since the initiation of smelting operations in the 1850s, and foremost among these have been logging, fire, and acute levels of SO_2. The effect is dramatically evident over 6.2×10^6 ha, of which 1.8×10^6 ha are devoid of vegetation, and the remainder are covered by a grass region merging into forest (198). Prior to the stresses, the area was a natural mixed-species forest consisting of oak, white pine, sourwood, tupelo, and dogwood.

Even though the peak of logging and SO_2 emissions was around 1900, the vegetational component of the ecosystem continued to show pronounced effects in

the 1940s (198). In comparison to the surrounding forests, the soil and atmospheric environment of the grasslands and inner barren zone was different in air and soil temperature, evaporation, wind velocity, and rainfall. Furthermore, the denuded zone was continuing to increase in area as erosion gullies cut deeper into the sparsely vegetated terrain. Additional evidence of the lingering impact of the multiple stresses was exemplified by the study of factors limiting revegetation (481). Isolated plots of kudzu have been established successfully; however, expansion of the vegetation islands was limited to several meters since nutrients, particularly phosphorus and nitrogen, became limiting.

Several studies in regions surrounding zinc and copper smelters have reported effects attributed to the combined toxicity of heavy metals and SO_2. The pattern of community response in a desert ecosystem receiving episodic emissions of copper and sulfur dioxide over a 47-year period did not differ from that observed in areas stressed acutely by SO_2 alone (484). Along a gradient originating at the source, gradual increases in species number, vegetation density, species diversity, and percentage cover were recorded (484). Similar results are reported from Trail, British Columbia (326), WaWa (152) and Sudbury (153), Ontario, Canada.

Research addressing the effects of gaseous pollutant interactions on an individual's performance is receiving increased attention; however, comparable emphasis at the community and ecosystem level are wanting. Sulfur dioxide, nitrogen dioxide, and a combination of the two decreased the expansion rate of new leaves in American elm (*Ulmus americana*). The combined exposure caused the greatest suppression of growth (76). In intensely managed pastures dominated by several competing grasses, a combination of sulfur dioxide and nitrogen dioxide caused a much greater loss in dry weight and leaf area than did either pollutant alone (14). Predicting the effects of prolonged exposure of the grasslands to these mixtures

is further complicated by the interspecific and intraspecific variation in response to SO_2 and NO_2 alone and in combination. "Final" community composition will likely reflect competitive interactions between species and the respective levels of each pollutant in the atmosphere (14).

7.11.5 Response of Natural Ecosystems to Particulate Matter

The atmosphere contains a great variety of particulate matter, both natural and manmade (415). As discussed in Section 7.7, the heterogeneous physical and chemical nature of particulates presents problems in addressing the significance of elevated atmospheric particulate levels for natural and agroecosystems. From an ecological perspective this hindrance is particularly acute since terrestrial ecosystems are major sites for deposition and accumulation of many elements associated with manmade particles.

Wet and dry deposition are the two processes by which particulates are transferred from the atmosphere to the landscape. In wet deposition, water solubility of the particulate is of paramount importance since precipitation scavenging is the flux vector. In contrast, dry depositional flux is controlled by wind speed, particle size, and the physical properties of the receptor. In terrestrial ecosystems, the receptor is typically foliage since it provides an extensive, multi-tiered array of surfaces extending from the uppermost parts of the canopy down to the forest floor. However, the capacity of foliage to serve as a receptor varies with surface area (67, 462), location in the canopy (276), concentration of particulate matter in the atmosphere (460), and leaf pubescence (276, 462). The importance of pubescence is illustrated by the sevenfold greater flux of aerosols to a heavily pubescent (*Helianthus annus*) versus a smooth (*Liriodendron tulipifera*) leaf (462). This difference indicates that deposition rates will differ for different plant communities experiencing equivalent particulate exposure.

The fate of particles deposited on foliar surfaces depends on the solubility of the chemical in constituents, the occurence of precipitation, and the sorptive capacity of the leaf (275). Furthermore, many elements commonly associated with particulates are essential for plant metabolism (e.g., zinc and phosphorus) and, as a consequence, absorption may be a means by which the plant can supplement its nutrient supply (231,305). Some elements, once deposited, are tightly bound to the surface through chemical interactions; even rainfall may not be effective in removing all of the material. A good example is lead, which can be absorbed into the leaf tissue, sequestered in cellular organelles (496), held to the leaf surface by electrostatic charges (276), or washed off by rain. Since the leaf retains approximately 30-70 percent of the deposited lead, the element accumulates in vegetation to levels that far exceed those in the atmosphere or soil (72). This fate and distribution pattern is unique for lead; other elements associated with particulates may behave differently (231,275).

Vegetation may be only a transitory site for particulate matter and its associated constituents. If not retained by the leaf, material is washed off by rain or removed by litterfall and ultimately transferred to the forest floor. The net effect of these processes is to funnel leaf surface deposits to the litter-soil complex. This conclusion is verified for many atmospherically derived elements deposited in natural ecosystems: fluoride in a coniferous forest (423); cadmium, zinc, and copper in a deciduous forest (333); lead along a roadway (460); mercury in an urban ecosystem (278); and lead, zinc, cadmium, and copper in diverse hardwood forest (84). The tendency for the forest floor to serve as a sink for these atmospherically derived elements is further accentuated in the tendency of most heavy metals to remain solely in the upper soil profiles rather than being leached.

This retention of heavy metals in upper soil horizons is of potential ecological significance, particularly in areas near sources of emissions contaminated with heavy metals. The accumulation has not been fully explained, although several key factors have been identified (340, 431). First, if litter decomposition occurs faster in uncontaminated than in contaminated plant remains, then the heavy metal concentration will rise. Second, detritus is an effective sink for a variety of cations, and heavy metals are easily bonded to the negatively charged organic groups in detritus. The capacity of these processes to cause an accumulation of heavy metals is remarkably great. In a nonpolluted location, lead levels in detritus were four to five times higher than those in the living plant canopy; the corresponding value for comparable detritus sampled from a heavily polluted environment was 20 to 25 (340). The point at which equilibrium is attained between heavy metal inputs and outputs for the detritus is not known (340, 438).

These results, showing preferential retention of heavy metals in the soil-litter layer, follow a general characteristic of element cycling in ecosystems: even though most elements move throughout the entire system, the distribution of each is not uniform. Specific components (e.g., atmosphere, soil, plants) tend to serve as pools or reservoirs for individual elements, and as a consequence a disproportionate fraction of elemental inputs will be sequestered in one or several components of the ecosystem. Some of the best evidence supporting this observation is from regions acutely stressed by particulates containing high levels of heavy metals. Given the regional character of low-level particulate emissions, particularly along the east coast (446), the applicability of this conclusion to more moderate pollution levels needs to be assessed.

This concern has been addressed for a deciduous forest in the southeastern United States (267). Wet and dry deposition of aerosols, gases, precipitation, and

large particles were major sources of trace element input to the forest floor, including 99 percent for lead, 44 percent for zinc, 42 percent for cadmium, 39 percent for sulfate, and 14 percent for manganese. These seemingly large percentages are typical for rural or remote areas even though three major coal-burning power plants (total coal consumption of 7×10^6 tons/year) were within 20 km of the forest. The deposition patterns throughout the year indicate that the atmospheric chemistry is determined by regional source and transport phenomena rather than local emission sources, except during air stagnation.

Regardless of the source of particulates deposited in the forest, the atmosphere contributed a major portion of the trace element inputs (267). Water solubility was critical since insoluble constituents associated with the particles were not readily mobilized within the forest. Any event promoting solubilization (e.g., aerosol formation, rainfall scavenging, moisture formulation on leaves) enhanced an element's mobility. One example of the potential ecological significance of solubilization is the nontoxic accumulation of dry-deposited material on a leaf surface followed by a brief shower, a common summer condition. Following the rain, surface droplets of water should exhibit high concentrations of solutes resulting from rainfall scavenging and from solubilization of the dry deposits. Evaporation further enriches the concentration of these solutes, yielding concentrations from 100 to 1000 times greater than that in incident precipitation. Calculations using typical rainfall data and dry deposition rates for a Tennessee forest indicate that pH values of droplets on the leaf surface may often drop below 2.0.

This study confirms the hypothesis that regardless of the deposition rates, elements tend to become enriched in certain components. The behavior

of each element within a given ecosystem is unique, so specific accumulation sites and enrichment dynamics may not be comparable.

The consequences of particle deposition for natural ecosystems and agroecosystems are not simply identified. This dilemma results from the complex chemical variability of the particulate matter (88, 263), mobilization capacity of the associated constituents (267), size of accumulation, inherent response variation of the bioreceptor (303), and the importance of the receptor in ecosystem structure and function (263,303, 496).

The hypothesis that deposition of particles alone, regardless of the toxicity of its constituents, can adversely affect an ecosystem when deposition rates are high is well documented (408) and intuitively obvious, given the diversity of plant physiological responses elicited by particle deposits (see section 7.7).

A mixed hardwood-conifer forest of southwestern Virginia has been impacted by limestone dust for a maximum of 25 years, and pronounced structural changes in the producer community are evident. Crust formation on foliage of both deciduous hardwoods and conifers was reported to be responsible for the 18 percent reduction in lateral stem growth of Acer rubrum, Quercus prunus, and Q. rubra (54). The reduction was not clearly associated with the initiation of quarry activities but rather increased progressively with time as if the effects were cumulative. Not all trees were affected adversely; Liriodendron tulipifera increased its lateral growth by 76 percent indicating that local inhabitant conditions became more favorable for growth of this species. This growth stimulation is attributed to either a change in species interaction favoring the growth of L. tulipifera or a "fertilizer effect," that is, emissions provided

some element that was in limited supply (305). In hemlock populations within the same region, Manning (289) noted a striking reduction in terminal growth and increasing needle chlorosis of pines. Brandt and Rhoades (55) maintained that all acidophilic species (including conifers) were the least resistant of the producers to the emissions. A similar hypothesis is offered to explain the replacement of conifers by deciduous tree species in a region experiencing heavy deposition of particulate matter (high fluoride levels) in Newfoundland (423). The effect of limestone dust on species survival was also responsible for changes in leaf microflora where some species declined while others increased in prominence (289).

The deposition of material on leaf surfaces can have ecological effects in addition to producer-level responses. In particular, organisms that inhabit the leaf surface or consume the foliage may be affected (185), and the magnitude of the response is correlated with the toxicity of the soluble constituents. Smith (402) hypothesized that the accumulation of metallic elements on leaf surfaces results in toxicity to the leaf surface microbial community. To support his contention, he reported growth inhibition of the phylloplane fungus *Platanus acerifolia* by several common cations (including nickel, zinc, lead, aluminum, iron, and manganese) that are associated with particles. Since deposition of these constituents on the leaf surface in a water-soluble form constitutes a pronounced habitat change for the microbes, competitive interactions will be affected and result in community composition shifts. This same rationale is reported to be responsible for outbreaks of black pineleaf scale in pine and Douglas fir forests (124). The mechanism whereby emissions affect scale frequency

is complex and involves the particle-induced extinction of a parasitic species that regulates the size of the scale population. In forests exposed to dust emissions, the parasite's decline effectively modifies the "predator-prey" relationships between these two species. Other examples of pollution-induced habitat changes that in turn affect insects are reported to be responsible for the distribution pattern of ladyspot, Adalia bipunctata, in Great Britain (92) and atypical behavioral activity of two moths, Biston betularia and Gonodontis bidentata (38).

The implications for herbivores of particle deposition on plant surfaces in natural ecosystems is not well documented, even though food chain pathways suggest concern particularly for constituents that can be assimilated and concentrated in body tissues (231,340). In a study of this exposure pathway, Chamberlain (66) calculated that in comparison with inhalation of airborne particulates, ingestion of contaminated foliage by herbivores can be 350 times more effective as an exposure pathway. Evidence in support of this mechanism for livestock is reviewed by Chamberlain (66), Daessler (95), and Philips (351). Comparable results from natural ecosystems are only scattered (139, 281).

The leaf surface is not the only accumulation site for particles and their associated constituents. Through precipitation scavenging of particles in air, washoff of surface deposits, or litterfall, particulate material is transferred to the soil, where it is tightly bound to decaying organic matter. For producers, this retention of toxic substances in the upper soil horizons may explain in part the differences in zinc tissue levels in shallow-rooting versus deep-rooting species in an area near a smelter (275). Because of their surface-rooting characteristics, herbs may experience greater soil levels of soluble particulate materials than do deep-rooting trees (275).

The upper soil horizon, including decaying organic material, is a region of intense biological activity as a result of the degradation of litter, remineralization of the bound materials and root uptake of the nutrients available to plants. These processes are mediated by a variety of decomposers (bacteria, fungi, detritovores), and their presence fosters a hierarchy of primary, secondary, and tertiary consumers. Consequently, particulate emissions that interfere with microbial activity can have delayed effects on primary producers (438) and soil consumers. Evidence supporting decreasing decomposition rates with increasing emission levels are most demonstrable in acutely stressed regions. In woodlands near a lead-zinc-cadmium smelter, Coughtrey et al. (84) reported that 90 percent of the heavy metal burden in the environment was in the soil-litter component and that this accumulation was responsible for consistently greater amounts of standing litter. The authors attributed this increase to sustained leaf fall together with impaired decomposition rates. Toxic effects of heavy metals in soils on fungi and bacteria involved in decomposition are reported (374) and this effect may be propagated to other soil organisms (22,413).

In summary, particulate matter emissions, by influencing atmospheric chemistry, impact on terrestrial ecosystems. These effects are most apparent near large emission sources, but ecosystems within the same geographic region may also be the site of deposition. Foliar surfaces are the most probable site for initial dry and wet deposition; however, most material is eventually transferred to the soil Particulate matter alone constitutes an ecological problem only where deposition rates are high. Conversely, since many toxic elements (e.g., heavy metals, polycyclic aromatic hydrocarbons) are commonly associated with particles,

ecological modifications may arise even if deposition rates are not high. In this regard, regional atmospheric chemistry is important. Solubility of particulate constituents is a critical factor, since water-insoluble elements are not mobile within the ecosystem. One common characteristic of particulates is their tendency to accumulate selectively within a given environmental component. One transitional site of accumulation is foliage where wet- and dry-deposited material becomes highly concentrated during brief precipitation events. Unfortunately, the physiological effects of concentrated solubles is not fully resolved. Soils are long-term sites for the retention of may constituents found in particles. This accumulation in the soil-litter layer has demonstrated consequences for ecological processes, notably decomposition, mineralization, nutrient cycling, and primary production.

7.11.6 DISCUSSION AND CONCLUSIONS

In spite of their overt differences in biota, most terrestrial ecosystems are driven by comparable processes that control energy flow and nutrient cycling. These similarities have fostered the development of conceptual models to explain the movement of energy and materials in ecosystems.

One example of ecosystem performance supporting this conclusion is the common pattern of response in different ecosystems to acute and prolonged abiotic stress (486) such as ionizing radiation (487) and multiple perturbations near smelter operations (152,153). Woodwell (486) argued that regardless of the stress and the successional trends of the ecosystem, changes imposed by the stress were broadly predictable and included biotic simplification, reordering of energy flow, and modification of nutrient cycles. This simplification is characterized by the initial loss of stress-sensitive species followed by the progressive loss of vegetational strata in the sequence of canopy > subcanopy > understory > forest floor. With increasing stress, energy utilization is altered,

with a greater amount diverted to maintenance and less allocated to net photosynthate. This shift in net productivity decreases standing crop biomass which, in turn, reduces the capacity of vegetation and soils to store nutrients. As a consequence, nutrient cycles that develop during succession toward efficient redistribution of essential nutrients are broken, leading to a net export of materials in streamflow. In general, the inventory of organisms, energy, and nutrients is reduced, and this simplification effectively inhibits restoration.

This analysis of ecosystem response is applicable to systems experiencing prolonged exposure to acute levels of atmospheric pollutants. Wolak (483) predicted four disclimax communities in order of decreasing stress intensity: biological desert, grasslands, shrubs, and forest. Since the interplay of successional processes and stress intensity determines which zone will prevail, Wolak designated the equilibrium community as the "industrioclimax."

In contrast to responses to acute stress, patterns of ecosystem modification following low-level or chronic exposures are not easily identified. Table 7-19 outlines some examples of ecosystem response to an array of abiotic stresses, including radiation, nutrient subsidies, gaseous pollutants, pesticides, and species removal. The most common response is a change in species composition of the community. Initially, stress-sensitive species decline, followed by a corresponding increase in competitor species. This consequence of species interaction is not restricted to populations within one trophic level, but may be propagated between and among producers, consumers, and decomposers. Finally, in an analogous fashion, the fate and distribution of nutrients is also modified.

In ecosystems experiencing a prolonged stress (e.g., oxidants) or the lingering effects of a stress (e.g., species removal or radiation), a unique

TABLE 7-19. SUMMARY OF THE EFFECTS OF SELECTED ABIOTIC STRESSES ON NATURAL ECOSYSTEMS

Stress	Community	Effect	Mechanism	Reference
	Old field	Change in community composition: Loss of some species, increased importance of others	Radiation sensitivity Species interaction	98
Radiation	Old field	Establishment of a new equilibrium		10
Oxidant	Forest	Change in community composition: Demise of ponderosa pine, increased importance of others	Oxidant sensitivity Species interactions	312
Nutrients	Old field Grasslands	Change in community composition: Demise of some species, increased importance of others	Nutrient sensitivity Species interactions	17, 252
	Old field	Change propagated to other trophic levels	Species interactions	197
		Primary production increased	Species interactions	17
Herbicide	Old field	Change in community composition: Increased diversity and species richness Primary production unchanged	Species interactions	459
Fire	Forest	Interrupts and renews succession	Fire sensitivity plus species interactions	488
Species removal	Old field	Composition altered, primary production recovered	Species interactions	3
	Forest	Change in water cycling rates		

response emerges: as a consequence of succession, a new equilibrium between the stress and the ecosystem is achieved. However, in the process the ecosystem develops a new biotic diversity and concordant functional attributes unlike those of its predecessor. This is well documented in the response of old fields to ionizing radiation (10), projected successional changes for the San Bernardino National Forest experiencing elevated oxidant levels for several decades (312), and the modified water cycle that developed in 15 years following the conversion of a southeast watershed from a canopy of deciduous hardwoods to conifers (414).

What factors influence the response of ecosystems to chronic and low levels of abiotic stress? Ultimately the issues of ecosystem stability and complexity are of central importance; however, the relationship between the two is enigmatic (302, 342). In particular, theory predicts that increasing complexity imparts stability whereas experimental data, mostly from the tropics, demonstrate the fragility of complex communities (302). It is clear that monocultures are at greater risk of deterioration when subjected to stress (323) than their multispecies counterparts. In these low-diversity communities, population responses govern, to a large extent, the fate of the ecosystem (342). This same hypothesis of the central importance of population response is extended to natural ecosystems in the event of stress sensitivity being exhibited by species having pivotal functional roles in the ecosystem (51, 211,350,436). In this situation sensitivity predisposes the system to respond, while the final outcome is determined by species interactions.

In summary, the response of terrestrial ecosystems to assorted stresses, particularly at low and chronic levels, is not totally predictable since the response is governed by the nature and magnitude of the stress and its effect on the performance of the plant-animal community (3). As regards a pollutant stress,

its fate, distribution and toxicity are important. Any stress that is selectively fractionated within the environment or the biota has the potential for unexpected ecological impact, since ambient atmospheric levels do not accurately reflect concentrations in the ecosystem. Furthermore, stress assimilation by the biota may involve detoxification; therefore, the ecosystem response is determined by the ratio of the rates of application versus assimilation and detoxification. This latter factor is critical to gauging the effects of SO_2 on agricultural and natural ecosystems. The influence of the biotic community in determining stress responses lies in the resistance level of sensitive species as well as the integration of the species into the structural and functional stability of the system.

In a conceptual approach to the response of natural ecosystems to air pollution stress alone, Smith (400) outlined three categories of response depending on the level of pollution stress (Table 7-20). Acute pollutant levels for prolonged time periods lead to extensive simplification of the ecosystem as all life forms are adversely affected. The most conspicuous examples are areas near smelter operations, although the magnitude of deterioration cannot be attributed to air pollution alone since a multitude of other stress-factors (e.g., fire, logging, heavy metals) may also be important. At more moderate levels of pollution, only sensitive species are differentially affected; however, the impact is propagated to other species as a consequence of trophic and nutrient cycling interactions. With time, the stress and the ecosystem will establish a new equilibrium, seen especially as shifts in species composition. More subtle modifications of trophic relationships and nutrient cycling underlie these overt changes. Finally, when pollutant levels are low, effects are more difficult to predict and detect. Many pollutants tend to exhibit patterns of

TABLE 7-20. CONCEPTUAL SCHEME FOR CATEGORIZING ECOSYSTEM-LEVEL RESPONSES TO SO_2 AS A FUNCTION OF STRESS LEVEL AND SUBSEQUENT PLANT COMMUNITY RESPONSE

Class of response	Level of SO_2 stress	Plant community response	Ecosystem response	Example
I	High	Growth and reproduction of most species affected leading to local extinction of many species	Simplification of Structure: Reduced diversity Altered climate and hydrology Increased soil loss Function: Net nutrient loss Reduced energy flow	152, 133, 198, 326
II	Intermediate	Growth and reproduction of only SO_2-sensitive species initially affected; subsequent changes as a consequence of species interactions	Modification of: Structure: Changes in species composition Function: Altered flux of energy and materials	253,260,275,276,477
III	Low	Effect on growth and reproduction cumulative over time	Structure: Changes unknown Function: Sulfur incorporated into exciting pathways and sinks leading to progressive accumulation of sulfur in vegetation and soils	253,260,275,276,477

Source: Smith (400).

accumulation within one or several fractions of the biotic or abiotic components of the ecosystem. As a consequence, overt modifications will be gradual and lag several years behind the initiation of the stress. Although Table 7-20 shows a difference between ecological effects of intermediate and low pollution levels, this distinction is artificial since stress levels fluctuate and ecosystems vary in their susceptibility. Examples of ecosystems exhibiting class II and III responses include Kaybob, Whitecourt, and the Montana grasslands (see section 7.11.3).

The preceding material provides a framework for evaluating the impact of SO_2 and particles on terrestrial ecosystems. The gradient of responses included in classes II and III are areas of concern from an ecological perspective. This conclusion is most relevant in regional terms, since high SO_2 levels for prolonged time periods (class I) are precluded by pollution controls and atmospheric injection of point-source emissions well above the vegetation canopy. With subsequent atmospheric turbulence and transport, SO_2 products are mixed with other pollutants and distributed throughout the region. As a consequence, deposition of SO_2, which may be simultaneous with other gaseous and particulate pollutants, occurs at sites distant from the emission source. The effect on biota will vary depending on the rate of deposition and sensitivity of the biota. Episodes in which SO_2 levels are sufficient to induce extensive necrotic lesions are likely to be less important than variable-dose situations in which chronic levels during air stagnations are intermixed with the more common periods of low-level deposition rates (229).

In an attempt to pinpoint regions that are likely to experience pollution episodes (short-term high levels), Miller and McBride (313) devised a map that overlays the boundaries of 10 forested ecosystems with projections of the

TABLE 7-21. FATE AND DISTRIBUTION OF SO_2 AND ITS DERIVATIVES IN NATURAL ECOSYSTEMS

Source	Fate	Mechanism	Ecological concern
Atmosphere	Transport out of region	Atmospheric transport and dispersion	Contribution to another region pollution burden
	Deposition to landscape A. Vegetation B. Soil C. Water	Wet and dry deposition	Accumulation of SO_2 derivatives in and on foliage Increasing levels of SO_2 Derivatives in soil and water (e.g., H+ and SO_4)
Vegetation	Retention on surface	Adsorption	Altered leaf surface chemistry (e.g., H+ increase, cationic leaching)
	Assimilation	Sulfur metabolism	Physiological effects including chronic and physiological injury
	Soil	Washoff and litterfall	
Soil	Soil organic fraction	Detrital adsorption and litterfall	Change in soil chemistry: A. Selective accumulation of SO_2 derivatives
	Soil inorganic fraction	Microbial decomposition	B. Acidification C. Cationic leaching
	Water	Leaching	
Water	Transport out of region	Stream flow	Lake and stream acidification

number of atmospheric forecast days. The highest potential for air pollution episodes was found along the Pacific coast, while a second focus of episode intensity was within the interior of the middle and southern Atlantic States, including parts of West Virginia, Virginia, Kentucky, Tennessee, Georgia, and Alabama. Concern for SO_2 impacts along the Pacific Coast is limited to single sites near smelters. Conversely, in the East, high emission rates are common from the northeast southward to the Gulf States. Therefore, concern for air pollution episodes during which SO_2 concentrations increase in the atmosphere centers primarily along a broad band of insular regions of the Atlantic States. This region is dominated by the eastern deciduous forest.

There are problems in relying solely on the overlay of projected frequency of SO_2 episodes with natural ecosystems (313). This technique only projects the frequency of atmospheric conditions conducive to SO_2 build-up, not ecosystem response. Many biotic and abiotic factors mitigate or potentiate the response, including topographic features, local emission sources, biotic sensitivity, and environmental conditions.

Given the scenario of projected SO_2 levels, what ecological effects are likely? Based on Table 7-20, gradual shifts in community composition in some communities are expected as are elevated levels of sulfur throughout the ecosystem. A more detailed accounting of the fate and distribution of SO_2 in the environment as well as its effects on biota is outlined also in Table 7-21. Within the environment SO_2 is highly reactive with a variety of elements, and many of these derivatives are ecologically important. Once absorbed by foliage, SO_2 is oxidized to sulfites and sulfates, while absorption to the leaf surface and subsequent solubilization produce sulfate and hydrogen ions. In soils, sulfur occurs as both inorganic and organically bound sulfur. Many of these derivatives are selectively accumulated in different parts of the ecosystem and for varying time periods that range from hours (leaf surface) to seasons (internal

leaf tissue) to years (soils). The accumulation of SO_2 derivatives to toxic levels impairs physiological processes. In plants, net photosynthesis is notably responsive, whereas in the soil the microbiota exhibits shifts in species composition with increasing levels of sulfate and acidity. The SO_2-induced changes in the composition of the primary producer community are considered major criteria for judging pollutant effects on ecosystems; however, this overt response reflects an extensive and subtle modification of the ecosystem.

A similar analysis of particles must realistically assess the ecological importance of the water-soluble consituents more than that of the particulate matter. Once deposited, particles, inorganic elements, and organic molecules are mobilized within the system and either directly affect biota or tend to accumulate. Given the diversity of chemicals associated with particulate matter, a full accounting of the fate, distribution, and ecological impact of each chemical is beyond the scope of this document.

7.12 SUMMARY

The widespread occurrence of particulate matter and sulfur dioxide in the atmosphere frequently results in terrestrial vegetation being exposed simultaneously to these two pollutants and other phytotoxic pollutants. More is known about the effects of sulfur dioxide than about the effects of particulate matter, as the former has been studied more. Studies of the effects of particulate matter have generally focused on the effects of heavy accumulations and the reduction in the photosynthesis resulting from these accumulations. The more subtle effects of particulate matter on vegetation have not been extensively investigated and are, therefore, not well understood. Even less information is available concerning plant response following exposure to sulfur oxides and particulate matter in combination.

Sulfur dioxide must enter a plant through leaf openings termed stomata to cause injury. Sulfur dioxide entering plant stomata (leaf openings) is converted

to sulfite and bisulfite, which may then be oxidized to sulfate. Sulfate is about 30 times less toxic than sulfite and bisulfite. As long as the absorption rate of SO_2 in plants does not exceed the rate of conversion to sulfate, the only effects of exposure may be changes in opening or closing of stomata or changes in biochemical or physiological systems. Such effects may abate if SO_2 concentrations are reduced. Both negative and positive influences on crop productivity have been noted following low-dose exposures.

Symptoms of SO_2-induced injury in higher plants may be classified as preclinical or clinical. The former term refers to alterations in plant metabolism or physiology that may or may not develop into visible (clinical) symptoms. Reduced growth and yield and/or increased susceptibility to other biotic or abiotic stress-inducing agents may occur if alterations in plant metabolism or physiology persist for a period of time. Significant reductions in the growth and yield of major forest tree species and agronomic crops have been reported without the presence of visible symptoms.

Chronic injury symptoms include plant responses that usually involve chlorophyll disruption followed by a condition of chlorosis or yellowing of tissues. Pigmentation changes resulting in stippling or general discoloration characterize this type of injury. Chronic injury results from either high-dose or low-dose exposure; high-dose exposure may lead rapidly to acute injury. Acute injury includes necrosis or death of cells, tissues, organs, or the entire plant.

Clinical or visible symptoms result from both chronic and acute injury, and refer to plant response rather than to the exposure conditions and the dose received. Dose-response functions concern the interactions of the exposed plant, its biological response systems, and the environment with the dose of the pollutant.

Many species of plants are sensitive to low levels of SO_2. Some of these plants, listed in Table 7-2, may serve as bioindicators in the vicinity of

major sources of SO_2. Even these sensitive species may be asymptomatic, however, depending on the environmental conditions before, during, and after SO_2 exposure. Of the plants listed in Table 7-2, various species of lichens may be among the most sensitive. However, no plant species is equal in sensitivity to sophisticated monitoring equipment designed to detect parts-per-billion concentrations of SO_2.

The dose-response information presented in this chapter relates the length of exposure and pollutant concentration to plant response. Dose is defined as the concentration of pollutant multiplied by the length of the exposure period. Unfortunately, variations in exposure regiment and response measurements make it difficult to conpare the results of different studies.

The concept of dose-response can be demonstrated by a synthesis of the data presented in Tables 7-5, 7-6, and 7-7. The following conclusions were formed by summarizing the dose-response data without considering confounding environmental variables: (1) Yield of economically important agricultural species can be significantly suppressed by SO_2 concentrations in the range of 0.05 to 0.06 ppm if the exposure period is sufficiently long (2 weeks). Both crop quality and quantity can be negatively affected. (2) Fluctuating, long-term (seasonal, annual) SO_2 exposures averaging 0.05 ppm or less can cause economically and ecologically undesirable effects to productivity and stability of range and forest ecosystems. (3) As SO_2 concentrations increase to 0.25 ppm, a variety of agricultural crops such as alfalfa, timothy, range grasses, soybean, barley, wheat, cabbage, lettuce, spinach, tobacco, cucumber, eggplant, pea, and kidney bean respond with necrotic foliar injury or suppressed yield. Approximately 70 percent of the cultivated agronomic crop species exposed to 0.25 ppm or less respond to the SO_2 treatment with changes in stomatal aperature (leaf openings), foliar injury, or yield effects. Foliar injury on vegetables and suppression of yield are directly related to economic values. (4) Forest trees species such as pine, spruce, fir, beech, alder and

poplar, representing coniferous and deciduous forest ecosystems respond to 0.25 ppm or less of SO_2. Approximately 90 percent of the species tested in this range of SO_2 concentrations responded with physiological modifications, suppressed photosynthesis, foliar injury, death of buds, or suppressed foliar or woody growth. (5) Non-woody components of native ecosystems such as lichens and grasses respond to SO_2 concentrations below 0.025 ppm. Responses include suppressed growth, death, and reduced diversity in lichen populations and suppressed photosynthesis and growth of leaves, tillers, and stubble of grasses. (6) At SO_2 concentrations between 0.25 and 0.50 ppm, less than 50 percent of the agronomic species tested responded negatively to the sulfur dioxide treatments. At SO_2 concentrations less than 0.25 ppm, 90 percent of the species responded negatively. A comparison of the species response to the treatments at the concentrations ranging between 0.25 to 0.50 ppm with the response to concentrations below 0.25 ppm might be interpreted as suggesting that plant response is not positively correlated with dose. This is not the case. Exposure durations used in the studies at the higher SO_2 concentrations generally ranged from 1 to 8 hours while multiple-day exposures were frequently used at the lower concentrations of SO_2. All agronomic species responded to a concentration of 0.50 ppm at exposure durations ranging from 1.5 to 5 hours. A variety of responses occurred, including physiological modifications, foliar injury, and suppressed growth. These trends suggest that as SO_2 concentrations are increased (a) a shorter exposure duration is sufficient to elicit a plant response equal to or greater than that which occurred at a lower concentration; (b) responses become more severe; and (c) plants tolerant at lower concentrations become sensitive.

The lack of short- or long-term monitoring data makes assessment of the results of dose-response studies in the field difficult. When data are not available to determine whether short-term spike concentrations occurred, then only long-term averages have been used to define the dose. Obvious differences

between forests in areas with high SO_2 concentrations have been observed, There is usually no exact dose information for short-term influences. Therefore, in most field studies, only long-term averages are used to define the dose.

As the dose of SO_2 increases, plants develop more predictable and more obvious visible symptoms. Foliar symptoms advance from chlorosis or other types of pigmentation changes to actual necrotic areas, and the extent of necrosis increases with exposure. Studies of the effects of SO_2 on growth and yield have demonstrated a reduction in the dry weight of foliage, shoots, roots, and seeds, as well as a reduction in the number of seeds. At still higher doses, reductions in growth and yield increase. Extensive mortality has been noted in forests continuously exposed to SO_2 for many years.

The amount of sulfur accumulated from the atmosphere by leaf tissues is influenced by the amount of sulfur in soil relative to the sulfur requirement of the plant. After low-dose exposure to SO_2, plants grown in sulfur-deficient soils have exhibited increased productivity.

Sulfur dioxide and particulate sulfate are the main forms of sulfur in the atmosphere, and a plant may be exposed to these pollutants in several different ways. Dry deposition of particulate malter and wet deposition of gases and particles bring sulfur compounds into contact with plant surfaces and soil substrates. The effects of such exposure are more difficult to assess than those associated with the entry of SO_2 through plant stomata. Plant response to dynamic physical factors such as light, leaf surface moisture, relative humidity, and soil moisture may influence stomatal opening and closing, and hence play a major role in determing sensitivities of species and cultivars or the time of sensitivity of each on a seasonal basis. Dose-response relationships are significantly conditioned by environmental conditions before, during, and following exposure to SO_2.

Measuring sulfur accumulation in plants has been suggested as a tool for

determining the levels of sulfur in the atmosphere of a given area over time. Such data, however, cannot accurately define the dose received by a plant.

Very few studies have been conducted to determine the sensitivity of microorganisms to SO_2 or to explore the interactions of SO_2 with plant pathogens such as fungi, nematodes, or bacteria. Both inhibition and enhancement of disease processes have been reported, but more data are needed to provide reliable information on trends.

In ambient atmospheres SO_2 and other pollutants usually exist as diverse mixtures in which a multiplicity of chemical combinations can take place. Therefore, with the possible exception of a point source in which vegetation is exposed to a high dose of SO_2, the direct and indirect influences of other air pollutants in combination with SO_2 must be considered. Major phytotoxic air pollutants that have been studied in combination with SO_2 include ozone, oxides of nitrogen, and hydrogen fluoride. The interactions of SO_2 and O_3 have been most extensively investigated because of the incursions of ozone and other oxidant precursors into many rural areas, as well as their presence in urban areas. Many studies have demonstrated more than additive effects in symptom expressions, but relatively few studies have attempted to evaluate the impacts on growth and yield. Additionally, pollutant combinations with SO_2 have caused less than additive and/or additive effects depending upon doses applied. The influence of various physical and biological factors of the environment increase in complexity as the pollutants are combined together during exposures.

A few studies have reported that combinations of particulate matter and SO_2 or particulate matter and other pollutants increase foliar uptake of SO_2, increase foliar injury of vegetation by heavy metals, and reduce growth and yield. Because of the complex nature of particulate pollutants, conventional methods for assessing pollutant injury to vegetation, such as dose-response relationships are poorly developed. Studies have generally reported vegetation

responses relative to a given source and the physical size or chemical composition of the particles. For the most part, studies have not focused on effects associated with specific ambient concentrations. Coarse particles such as dust directly deposited on the leaf surfaces results in reduced gas exchange, increased leaf surface temperature, reduced photosynthesis, chlorosis, reduced growth, and leaf necrosis. Heavy metals deposited either on leaf surfaces or on the soil and subsequently taken up by the plant can result in the accumulation of toxic concentrations of the metals within the tissue.

Particulate matter is heterogeneous in size and composition ranging in mean diameter from <0.005 μm (molecular clusters) to >100 μm (visible dust particles). Particles occur in both solid and liquid phases and vary in chemical composition from a single chemical species (e.g., H_2SO_4) to complex combinations of chemical species. They are produced directly from stationary and mobile sources and are also formed secondarily in the atmosphere through chemical reactions.

While coarse particles (>2.0 μm in mean diameter settle rapidly, fine particles (<2.0 μm in mean diameter) have prolonged atmospheric residence times and are not influences by gravity. Because of the complex nature of particulate matter, doseresponse studies are very difficult to conduct and data, therefore, are not available for making generalized statements. Reports of the effects of particulate matter on vegetation have usually dealt with response to a given source or the physical size and/or chemical composition of the particles rather than mentioning concentrations. Coarse particles (dusts, etc.) directly deposited on the leaf surfaces result in reduced gas exchange, increased leaf surface temperature, reduced photosynthesis, chlorosis, necrosis, and reduced growth. Heavy metals deposited on either leaf surfaces or the soil and subsequently taken up by the plant can accumulate to toxic concentrations.

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Natural ecosystems are integral to the maintenance of the biosphere. They are the support system for all life on earth. Disruption of ecosystem functions can have long range effects which cannot be predicted. Approximately 60 percent of the atmospheric sulfur in the northeastern United States is deposited on terrestrial and aquatic ecosystems; however, the subsequent distribution of sulfur through the ecosystems is not fully understood. The sulfur may reach the ecosystems through dry or wet deposition. (The wet depositon of sulfur compounds is discussed in Chapter 8 under acidic precipitation). The effects of the dry deposition of sulfur, principally as SO_2, on terrestrial ecosystems has been studied only in a few widely divergent areas of North

America. Though the effects of dry deposition have been emphasized in these studies, wet deposition has also occurred.

Vegetation within terrestrial ecosystems is sensitive to direct SO_2 toxicity, as evidenced by changes in physiology, growth, development, survival, fecundity, and community composition. Responses of individual organisms reflect both direct or indirect effects. Habitat modification by SO_2 results in indirect effects occurring. Nutrient cycling appears to be a sensitive indicator of subtle, yet important, environmental modification.

At the community level, chronic exposure to SO_2 may result in a shift in the species composition due to the elimination of individuals or populations sensitive to the pollutant. The tendency for SO_2 derivatives to accumulate in the soil may have consequences for the microbiota inhabiting the upper soil horizons. The gradual accumulation of pollutant derivatives may cause a change in soil chemistry and influence nutrient cycling and ecosystem productivity.

Particulate emissions have their greatest impact on terrestrial ecosystems near large emission sources. However, other ecosystems within the same geographic region may also be affected. Most of the material deposited by wet and dry deposition on foliar surfaces in vegetated areas is transferred to the soil. Ecological modifications may occur if the particles contain toxic elements, even though deposition rates are moderate. Particulate matter in itself constitutes a problem only in those areas where deposition rates are high. Solubility of particle constituents is critical, since water-insoluble elements are not mobile within the ecosystem. Foliage may serve as a transitional site of accumulation if previously deposited dry material becomes highly concentrated during precipitation. Soils are long-term sites for the retention of many constituents found in particulate matter. Accumulation in the soil-litter layer influences ecological processes such as decomposition, mineralization, nutrient cycling, and primary production.

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Note to Reader

Chapter 8: Acidic Precipitation

The story of acidic precipitation is an everchanging one. New information concerning its far-reaching effects is forthcoming nearly every day. The Environmental Protection Agency, therefore, is continually revising its data base as new information becomes available. The International Conference on the Ecological Impact of Acidic Precipitation, sponsored by the SNSF Projct of the Agricultural Research Council of Norway, was held March 11-14, 1980 at Sandjeford, Norway, to discuss the latest discoveries concerning the effects of acidic precipitation at about the time the chapter that follows was being completed. It was, therefore, not possible to incorporate the information presented at the conference into the chapter. Several areas in the present chapter which will receive expanded treatment in the next version due to new information are: (1) problems associated with the liming of lakes, streams, and forests; (2) the short-term beneficial effects of sulfur oxide deposition on nitrogen deficient forest soils and the long-term detrimental effects; (3) additional information on the role of aluminum in causing the death of fish; (4) the detrimental effects of aluminum in the soil on root hairs of plants; (5) the role of acidic precipitation in lowering the pH and increasing the aluminum content of ground water.

The economic import of acidic precipitation as present in the chapter is very preliminary. It is based on some early studies made by the State of

New York. The Environmental Protection Agency is currently involved in a study to determine as accurately as possible the cost of acidic precipitation effects. EPA believes the costs will run much higher than those cited in the present chapter. Swedish studies estimate the cost of liming their acidified lakes, streams, forests, and soils would run from 50 to 100 million dollars.

8. ACIDIC PRECIPITATION

8.1 INTRODUCTION

Acidic precipitation is a major environmental concern in many regions of the United States, Canada, northern Europe, and Japan. It has caused measurable damage to aquatic ecosystems in Scandanavia, eastern Canada, and the northeastern United States. Acidic precipitation has, by acidifying lakes, induced the extinction of fish, caused the breakdown of nutritional food webs, and reduced life in lakes to a few acid tolerant species. Acidic precipitation, in addition, has the potential for damaging national monuments and buildings made of stone, for degrading natural terrestrial ecosystems, for impoverishing sensitive soils, and for causing damage over the long-term (over several decades) to forest ecosystems.

Precipitation, more specifically rain, has long been considered beneficial to all life. Rain falling on forest, field, lake, and stream brings to earth not only the water of life but also elements essential for the existence of plants and animals. Has precipitation changed? How? Why is it acidic?

Precipitation acts as a scavenger, bringing to earth substances present in the atmosphere. The composition of rain, therefore, depends on the substances present in the atmosphere. Among the substances present in the atmosphere are emissions from both natural and anthropogenic sources. On a global scale natural emissions of sulfur oxides exceed man's contributions; however, man-made emissions are localized in specific geographic areas, where they may be concentrated in the atmosphere or transported meteorologically to other areas downwind (see Chapter 4).

In an atmosphere relatively free of natural or man-made emissions of oxides of sulfur and nitrogen, precipitation would be expected to have a pH of 5.6 due to carbon dioxide in the atmosphere dissolving in water vapor to form carbonic acid. The chemistry of precipitation has changed, however, due chiefly to the emission of large amounts of sulfur and nitrogen oxides being released from the combustion of fossil fuels (particularly coal and oil). In addition, precipitation is acidified by transformation products of other gases, aerosols, and particulate matter from natural and man-made sources, such as the smelting of ores and the use of nitrogen fertilizers of agricultural and forest land.

Sulfur and nitrogen oxides are transformed in the atmosphere to sulfates and nitrates. Sulfates and nitrates upon hydrolysis in the atmosphere contribute hydrogen ions (H^+). If hydrogen ions are present in significant quantities, precipitation becomes acidic. The acidity of precipitation is a reflection of the balance between the major cations and anions in precipitation. It is essential that in addition to all the major anions and cations, particularly H^+, NH_4^+, NO_3, and SO_4^2, that K^+, Na^+, Ca^+, Cl, CO_3^{2-}, and PO_4^{3-} ions should also be measured. Currently, the acidity of precipitation in the northeastern United States is between 4.0 and 5.0.

The ratio of sulfuric to nitric acids in precipitation varies from time to time and place to place. In much of the eastern United States, the average annual ratio of sulfuric to nitric acids is currently 2:1; however, nitric acid is becoming progressively more important as a contributor of hydrogen ions.

The tall stacks (some as high as 1200 ft.) from power plants have decreased local pollution problems but increased the widespread wet and dry deposition of sulfur and nitrogen oxides by permitting them to be carried long

distances by air streams. Analysis of air-mass movements and chemical transformations in the atmosphere indicates that acidic precipitation in one state or region of the United States or Canada results in large part from emissions which enter the atmosphere in other states or regions, often many hundreds of miles from the original source.

Acidic precipitation is only one special feature of the general phenomenon of atmospheric deposition. There is in addition to precipitation (wet deposition) also dry deposition. The major anions and cations that are transferred into ecosystems via acidic precipitation (wet deposition) are also present in the gases, aerosols, and particulate matter that are transferred into ecosystems by dry deposition when it is not raining or snowing. It is, therefore, impossible to distinguish chemically the biological effects of acidic precipitation from the biological effects of dry deposition.

In addition to the direct wet and dry deposition of acidic substances into ecosystems, some substances in ionic form (notably various complexes of ammonium and sulfate ions), although chemically neutral or nearly so, are acidifying in their effects when taken up by plants and animals. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation".

Included in wet and dry deposition, besides the acidic substances, are certain organic or inorganic substances which are potentially injurious to the ecosystems into which they are introduced. Among the inorganic substances are: <u>manganese</u>, <u>zinc</u>, <u>copper</u>, <u>iron</u>, <u>boron</u>, flourine, bromine, aluminum, lead, iodine, nickel, cadmium, vanadium, mercury, and arsenic. The underlined elements in the list above are essential micronutrients that are required by plants in small amounts. However, at concentrations above the amount required,

these same elements, can be toxic to plants and animals. The non-essential elements can also be toxic to plants or animals when present in large amounts or when their mobility and solubility is increased due to soil acidity. Also the deposition of these metallic substances in precipitation can affect the foliage and roots of plants and injure microorganisms or animals that may ingest the plants. In addition, these substances can harm animals (including man) which may drink water containing these elements as well as aquatic animals (especially fish) that live in the water.

The increased deposition of acidic substances into aquatic ecosystems has, as of 1979, caused hundreds of lakes in the Adirondack Mountain region of New York State, certain lakes in northern Minnesota, and many hundreds of lakes in various parts of southern Ontario and Quebec to show acid stress. Reduction or extinction of fish and other plant and animal populations has occurred. Lakes and streams in other regions of the United States and Canada are also potentially vulnerable to stress by acidic precipitation. Damage or injury to aquatic or terrestrial organisms is most likely to occur when a particularly sensitive life form or life stage (one with a narrow range of tolerance) developing in poorly buffered waters or soils coincides in time and/or space with major episodic injections of acidic precipitation or other injurious substance.

An example of a major episodic injection of acids and other soluble substances occurs when these substances present in polluted snow are released as polluted meltwater during warm periods in winter or early spring. The release of pollutants can cause major and rapid changes in acidity and chemical properties of stream and lake waters. Fish kills are a dramatic consequence of such episodic injections into aquatic ecosystems.

Equally dramatic long-term changes in aquatic ecosystems also occur from the wet and dry deposition of acidic substances because the chemical composition of precipitation and dry deposition determine in part the chemical composition of lake, stream, and ground waters. The terrestrial watershed also plays a significant role as the chemical composition of precipitation is modified by chemical and biological weathering and exchange processes which take place as precipitation washes over vegetation, percolates through the soil and interacts with the underlying bedrock of the drainage basin in which the precipitation occurs. The situation is analogous to a gigantic, regional scale titration with the lakes and streams acting as receiving vessels for acidic additions from the atmosphere. The titration end point of each lake is predetermined by its hydrology and the capacity of the soils in the drainage basin to assimilate the incoming acid. If the soils and drainage basin can no longer assimilate the incoming acids, the lake and stream waters are changed from conditions that are favorable for fish and other aquatic organisms to conditions that inhibit reproduction and/or recruitment of populations of fish and other aquatic organisms, some of which are food for fish.

Studies indicate that at pH's between 6.0 and 5.0, reproduction of many species of aquatic organisms is inhibited and at a pH below 5.0 populations of many fresh-water fish become extinct. Interference with normal reproductive processes in fish occurs not only because of acidity itself but also due to increased concentrations of certain metallic cations, notably aluminum, which become mobilized in acidified lakes and streams.

Terrestrial and aquatic ecosystems are so intimately linked that it is unrealistic to consider the effects of acidic precipitation in aquatic ecosystems without considering its effects on terrestrial vegetations, soils, and the geology of the drainage basin.

The dry deposition of toxic gases, aerosols, and particulate matter causes substantial damage to crops in certain regions of the United States. The possible effects of acid deposition must be considered together with the serious economic damage occurring to crops caused by sulfur dioxide, ozone, oxides of nitrogen, fluoride, and hydrogen chloride.

Direct and indirect injury to crops and forests have been reported based on laboratory, greenhouse, and field experiments in which simulated acidic rains were used. The following biological effects were observed:

- Formation of necrotic lesions and spots on foliage.
- Accelerated erosion of waxes on leaf surfaces.
- Loss of nutrients due to leaching from exposed plant surfaces.
- Inhibition of nodulation of legumes leading to decreased nitrogen fixation by symbiotic bacteria.
- Reduced yield of marketable crops.
- Reduced rates of leaf litter decomposition leading to decreased mineralization of organically-bound nutrients.

Soils differ by orders of magnitude in their susceptibility to acidification. Acidic additions are unlikely to damage calcareous (calcium carbonate) soils, but metal deposition may. Soils with very low cation exchange capacities are very susceptible to increased acidification. In addition, the consequences of acidic additions to soils vary greatly, depending upon the rates and recent history of acidic injections, the character of the vegetation, natural rates of acid formation in the soil, and the physical-chemical properties of the parent material of the soil.

Acidic precipitation may indirectly influence plant productivity by altering the supply and availability of soil nutrients. Increased additions

of hydrogen ions may result in a gradual acidification of the soil. Soil acidification increases leaching of plant nutrients such as calcium, magnesium, potassium, iron, and manganese and increases the rate of weathering of most minerals. It also makes phosphorous less available to plants. Acidification also decreases the rate of many soil microbiological processes such as nitrogen fixation and the breakdown of organic matter. Various processes important in nutrient cycling and critical in most ecosystems are known to be inhibited by increasing the soil acidity. Included among these processes are: nitrogen fixation by Rhizobium bacteria on legumes and by the free-living Azotobacter; mineralization of nitrogen from forest litter; nitrification of ammonium compounds; and overall decay rates of forest floor litter.

Acidic precipitation increases the solubility and mobility of many cations in the soil thus increasing the concentration of toxic metal cations such as aluminum, manganese, and zinc in soil solutions. Solubility and mobility of other heavy metals is also enhanced. These toxic or nutrients ions leached from the soil are transferred into surface and ground waters from which they may enter lakes or streams and drinking water. Plant nutrients leached in the same way are lost to vegetation.

Large quantities of hydrogen ions are added to soils as acidic precipitation and as a result of soil amendment and fertilization practices. Acidification by these processes can be readily controlled through normal soil management practices such as liming. Large areas of the United States, however, are not cultivated and have soils that are poorly buffered. These soils are susceptible to further acidification. Many of these sour soils occur in forest and wilderness areas. Some of these soils could be helped by the significant quantities of plant nutrients, including nitrogen and sulfur that are being

added to soil in precipitation and by dry deposition. In some ecosystems these additions may be important in the overall nutrient budgets; however, the additions are subject to the vagaries of wind and weather.

Though various specific biological effects of simulated acidic rain have been demonstrated in controlled field and laboratory experiments, reliable evidence of economic damage to agricultural crops, forests, and other natural vegetation and to biological processes in soil by naturally occurring acidic precipitation has been reported very rarely.

Acidic precipitation plays an important role in the deterioration of stone buildings, cultural monuments, and a variety of materials. Stone has traditionally been considered one of the most durable building materials used by man. What is forgotten is that the structures built with stone which were not durable have long since disappeared.

High acidity promotes corrosion because hydrogen ions act as a sink for the electrons liberated during the critical corrosion process. Acidic precipitation forms a layer of moisture on the surface of material and by adding hydrogen and sulfate ions increases corrosion. Atmospheric sulfur compounds react with the carbonates in limestone and dolomites, calcareous sandstone, and mortars to form calcium sulfate. Blistering, scaling, and loss of surface cohesion occurs, which in turn induces similar effects in neighboring materials not in themselves subject to direct attack. Acid rain may also leach ions from stonework just as acidic runoff and ground water leaches ions from soil bedrock.

The discussion which follows is EPA's most up-to-date review of acidic precipitation. Though the emphasis in this chapter is on the environmental effects resulting from air pollution causing acidic precipitation, it should

be noted that the substances which are transferred from the atmosphere onto the earth when it is raining or snowing also come to earth as dry deposition in the form of gases, aerosols, and particulate matter. Because ecosystems are subjected to both wet and dry deposition, it is impossible to attribute all of the observed biological effects to acidic precipitation alone. Likewise, since both sulfur and nitrogen oxides are involved in the formation of acidic precipitation, it is necessary to look at the whole picture rather than attempting to limit the effects to sulfur oxides, the principal subject of this document.

Chapter 7 emphasizes the effects of the dry deposition of sulfur oxides and particulate matter on vegetation and ecosystems. The sources and emissions of sulfur oxides are discussed in Chapter 4 and those of nitrogen oxides in Air Quality Criteria for Oxides of Nitrogen. Chapter 6 discusses the transformation, transport and removal of sulfur oxides. Ambient air concentrations are discussed in Chapter 5.

8.2 EFFECTS OF ACIDIC PRECIPITATION

8.2.1 Ecosystems

The effects of acidic precipitation on individual organisms, populations, communities and ecosystems can be better understood if the biological principles which govern the responses of organisms to their environment are elucidated. The discussion which follows outlines the principles which are mentioned in more detail when the effects on specific organisms or ecosystems are discussed.

Climatic, physicochemical, or biological changes in the environment, regardless of the source, affect the functioning of organisms and the ecosystem of which they are a part. Acidic precipitation, by changing the chemical environment of a variety of organisms, has already caused measurable damage to aquatic ecosystems and possesses the potential for causing injury to terrestrial ecosystems.

Organisms vary in their ability to withstand environmental changes. At any moment in time an organism is the product of the interaction of its total environmental history and its inherited genetic code. Organism-environment relationships are governed by certain ecological principles. Three of these which help to explain the effects of acidic precipitation are: (1) the principle of limiting factors, (2) the principle of the holocoenotic (holistic) environment, and (3) the principle of trigger factors.

The ability of an organism to withstand injury from polluted air, weather extremes, changes in the acidity of the environment, or other disturbances is dependent on its "range of tolerance", that is, the range between too much or too little, within which an organism can survive and function (also termed "law of tolerance" (Figure 8-1)). Organisms vary in their susceptibility to injury by polluted air, climate, or other disturbances due to their genetic make up. The range of tolerance of organisms also varies depending on their age, stage of growth, or growth form. Highly specialized organisms usually have a narrow range of tolerance (or adaptability) and are either reduced in numbers or eliminated by environmental changes. Limiting factors are, therefore, factors which, when scarce or overabundant, limit the growth, reproduction, and distribution of an organism.[1] Acidic precipitation is such a factor since it changes the acidity of the environment in which an organism exists.

If or when one limiting factor is removed, another immediately takes its place. No barriers exist between the various environmental factors or between an organism or biotic community and its environment. The environment is a complex of interacting factors. If one factor is changed almost all will change eventually. Organismal- or community-environmental relationships are

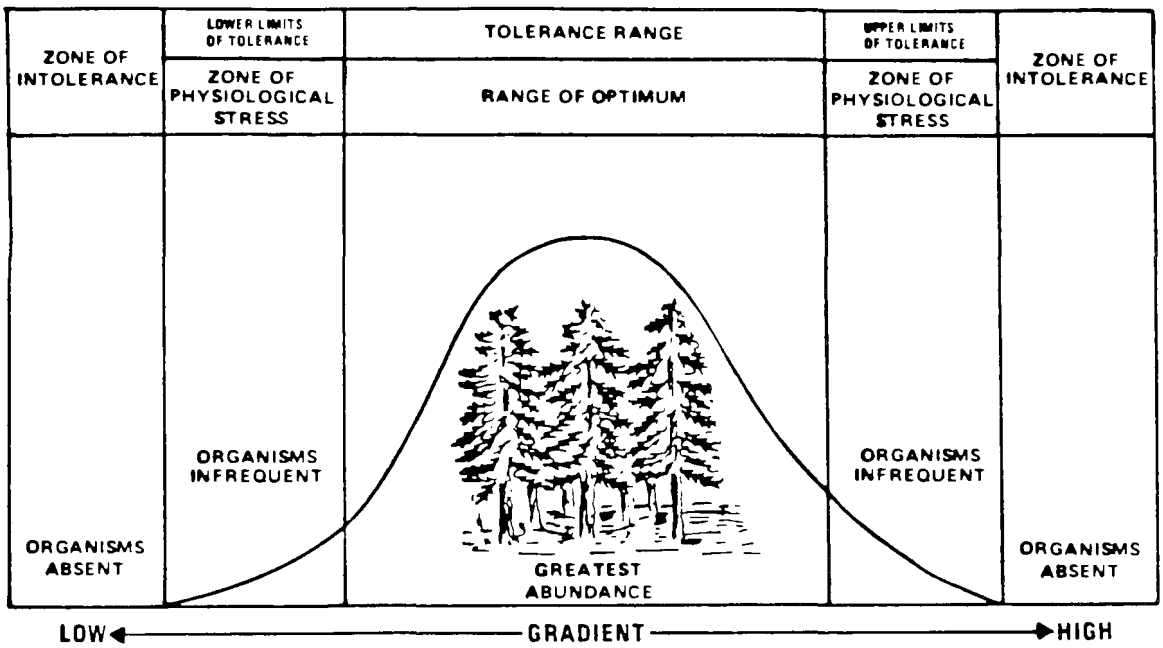


Figure 8-1. Law of tolerance.

holocoenotic, that is, "The ecosystem reacts as a whole. It is practically impossible to wall off a single factor or organism in nature and control it at will without affecting the rest of the ecosystem."[1] In other words, everything in our world, is related to everything else. "Any change no matter how small is reflected in some way throughout the ecosystem: no 'walls' have yet been discovered that prevent these interactions from taking place."[1] The chain reaction caused by acidic precipitation in aquatic ecosystems illustrates this principle.

Acidic precipitation may also be termed a "trigger factor". As indicated above, the removal of a limiting factor usually creates a far-reaching chain reaction in an ecosystem and occasionally may be the cause of one ecosystem replacing another. The addition of a new substance to the environment, such as acidic precipitation, may also be a trigger factor. Trigger factors may act quickly or slowly and almost imperceptibly and require centuries before changes are noted. The migration of the alewife (*Alosa pseudoharengus*) and the sea lamprey (*Pentromyzon marinus*) into the Great Lakes through the Erie and Welland Canals illustrates how slowly trigger factors may act. The Erie Canal was opened in 1819 and the Welland in 1829. The migration of the alewife into the lakes via the Erie Canal was not observed until 1873, while the presence of the sea lamprey was first observed in Lake Ontario only in the 1880s. It was first caught in 1921 in Lake Erie which it entered by the Welland Canal. The invasion of both of these species of fish has had catastrophic effects on the populations of native and economically important fish species.[3] Regardless of whether the trigger is a new factor which has been added or a limiting factor which has been removed, life in the affected ecosystem is never again the same.

Ecosystem diversity and structure are usually changed the most by a limiting or trigger factor, such as acidic precipitation, due to the sensitive species of flora and fauna being eliminated. In a forest ecosystem the selective removal of the larger overstory plants favors plants of small stature.[4,5] The result is a shift from the complex forest community toward the less complex hardy shrub and herb communities. The opening of the forest canopy changes the environmental stresses on the forest floor causing differential survival and, consequently, changed gene frequencies in subcanopy species.

Associated with the reduction in diversity and structure in an ecosystem is a shortening of food chains, a reduction in the total nutrient inventory, and a return to a simpler successional stage.[4,5] In addition, in forest ecosystems the pollutants often act as predisposing agents; thus, an increase in the activity of insect pests and certain diseases may occur.[4,6] Ecosystems are usually subjected to a number of stresses at the same time, not a single perturbation, so the effects of any particular stress will be exacerbated or mitigated by interaction with the other stresses acting upon the ecosystem.

Plants, animals, and microorganisms usually do not live alone but exist as populations living and interacting with each other and the environment. Populations live together and interact as communities. Communities, because of the interactions of their populations and of the individuals that comprise them, respond to pollutant stress or other perturbations differently from individuals. Man is an integral part of these communities and, as such, is directly involved in the complex ecological interactions that occur within the communities and within the ecosystem of which they are a part.

An ecosystem (e.g., the planet earth, a forest, a pond, lake or stream, old field, or a fallen log) is an ecological unit comprised of living (biotic)

and physical (abiotic) components through which the cycling of energy and nutrients occurs (Table 8-1). The relationship between the various components is a structured rather than a haphazard one. The biotic units are linked together by functional interdependence, while the abiotic units comprise the totality of physical factors and chemical substances that interact with the biotic units. The processes occurring within the biotic and abiotic units and the interactions between them are subject to environmental influences.[1,8]

Ecosystems tend to change with time, and it is usually possible to recognize sequential changes in the types of populations within a community. Adaptation, adjustment, and evolution are constantly taking place as the biotic component, the populations, and communities of living organisms interact with the abiotic components in the environment. The interaction and exchange of energy and nutrients over time result in sequential or, in some cases, cyclic or telescoped changes in populations and communities. The sequential replacement of one population by another in a continual series, going from pioneer (first and less diversified) populations to so-called climax (mature and more diversified) communities, is termed succession.[1,8] Climax communities are structurally complex and more or less stable, and are held in a steady state through the operation of a particular combination of biotic and abiotic factors. Man often is a factor as, for example, when his grazing cattle maintain a pasture.[1,8] It is obvious once the cattle are removed that the pasture will change. New plant and animal species will come in and there will be a transition toward a different climax community. The disturbance or destruction of a climax community or ecosystem results in its being returned to a simpler and less stable stage.[4,5] The simpler or successional stages are less stable, as the variety of species necessary to develop the interspecific relationships and environmental

TABLE 8-1. COMPONENTS OF THE ENVIRONMENT OF A TERRESTRIAL ORGANISM, VEGETATION, OR BIOLOGICAL COMMUNITY

Source Domain	Physical Components	Biological Components
Universal Space	Universal "space-time" gravity Meteorites and "space dust" Primary cosmic radiation particles Solar radiation electromagnetic particles	
Atmosphere	Secondary, tertiary, etc. cosmic radiation Sky, reflected, and thermal radiation Radioactivity including fallout Atmospheric gases Pressure Wind Water (vapor, cloud, and precipitation) Heat and temperature Fire Pollutants	Plants Animals Microorganisms Man DNA
Lithosphere	Rock and soil particles Minerals Water Radioactivity Heat and temperature Gases Topography (indirect)	Plants Animals Microorganisms Man DNA
Earth Mass	Gravity	

[1]For aquatic plants or community, interpose a liquid water course domain between atmosphere and lithosphere of substitute it for the lithosphere in deep water. This aquatic source domain will provide many of the same components included in the atmosphere and lithosphere - but not all. Table is adapted from Billings (1974).[8a]

interactions necessary for stability are not present. Therefore, simple communities, such as agricultural monocultures or natural communities which are in transition, are more subject to change due to disturbances of biotic or abiotic factors than are the structurally complex communities where intricate energy and nutrient exchange relationships make the breaking down of the system difficult. It is easier to keep the weeds out of a cornfield than out of the pasture.

Woodwell[7] has suggested that the possible effects of pollutants on ecosystems fall into two categories: short-term and long-term effects. In most terrestrial ecosystems, short-term effects are dominated by the consequences of differential species sensitivity to environmental change. The long-term effects are established by those same consequences, plus effects on reproductive capacity and genetic characteristics. Existing studies indicate that changes occurring within ecosystems, in response to pollution or other disturbances, follow definite patterns that are similar even in different ecosystems. It is, therefore, possible to predict broadly the basic biotic responses to the disturbance of an ecosystem.[3,4,7,9,10] These responses to disturbances are:

1. Reduction in standing crop, i.e., the number of plants and animals which make up the species structure of an ecosystem.
2. Inhibition of growth or reduction in productivity, i.e., reproduction.
3. Differential kill (removal of sensitive organisms at the species and subspecies level).
4. Food chain disruption.
5. Successional setback, i.e., return to an earlier more simple stage.
6. Changes in nutrient cycling rates.

Mature ecosystems, because of their greater diversity, are less susceptible to the disruption of their normal structure and function by any type of perturbation. For example, a forest ecosystem in which the communities are composed of many species would show less immediate damage by stress than successional stages having only a few species. Even greater damage would be anticipated in an agroecosystem, which may be considered the simplest of successional stages, since often a single producer species is present.

Ecosystems are dynamic systems. Energy flow and nutrient cycling are constantly occurring. The sources of energy are external to the ecosystem and energy flow is unidirectional through the system. Nutrients, however, are continuously cycled through the system. The concept of balance is associated with the flow of energy and nutrients. Theoretically, it is possible for the composition and cycling of energy and materials to remain essentially the same for long periods of time so that a steady state is achieved. Very few ecosystems actually ever reach this condition. Environmental changes, removal of limiting factors, or the presence of trigger factors usually prevent an ecosystem from achieving a steady state. It should be noted, however, that an ecosystem is in delicate balance. Any change, natural or manmade, may lead to a result that cannot be forseen or predicted.[1,2,8,11] The following sections discuss ecosystem changes resulting from acidification of the local environment.

8.2.2 Aquatic Ecosystems

The disappearance of natural fish populations from acidified freshwater lakes and streams in southern Norway was first noted during the 1920's. During the past 50 years, the problem has become more severe. The effect on inland fisheries became serious during the 1940's and 1950's with the disappearance of the brown trout (*Salmo trutta* L.) populations from an increasing number of lakes in Sørlandet (southern Norway).[12] The cause of the

acidification remained a mystery until the late 1950's as the increase in acidity of lakes and streams could not be related to industrial, municipal, or agricultural effluents, or to the draining of bogs and peatlands. Acidic precipitation was postulated by Dannevig in 1959[13] as the cause of acidification of freshwaters in southern Norway when data from the European Atmospheric Chemistry Network in the late 1950's revealed that the precipitation falling on southwestern Scandinavia was acidic with a pH <4.7. Acidic precipitation was, therefore, indirectly the cause of fish having been eliminated.[12]

Laboratory and field experiments have shown that acidification of lakes and streams is the reason for fish disappearing. Many studies have shown that the reproductive stages are most sensitive to changes in water chemistry.[12]

Increased acidity in freshwater ecosystems is the trigger factor which causes many changes to occur within the communities of organisms living there. Most of the changes cause decreases in biological activity and limit nutrient cycling. Decrease in biological activity is due to a decrease in numbers of individuals in a number of groups of organisms. Disturbances occur at all trophic (food) levels. Phytoplankton, zooplankton, bottom fauna, and a number of other groups of organisms decrease, greatly affecting the variety of food for fish and other animals. Shifts in plant communities occur. Higher plants disappear, and mosses take their place. Shifts in plant communities influence nutrient cycling and lead to a reduction in the activity of microorganisms involved in decomposition.[14-17] In addition to the direct results occurring from acidification, mobilization of heavy metals often occurs. Pertinent details of the effects are described in the following sections.

8.2.3 Effects on Fish

The decline of fish populations in acidified lakes and streams has been reported from Norway,[12,14,16,18] Sweden,[15,22,23] Canada,[19] and the United States.[20] Surveys in southern Norway indicate that fish populations, especially trout and salmon, have been affected by acidification in 20 percent of the waters lying south of latitude 63°N.[16] As mentioned previously, the disappearance of fish was initially noted 50 years ago. However, there has been a sharp increase in the rate of disappearance during the past 15 years, a period that coincides with increases in fossil fuel combustion. While the salmon catch for the entire country shows no decrease, records for 79 Norwegian rivers since the late 1800's show that nine rivers in Sørlandet declined rapidly between 1885 and 1925.[22] Similar changes have been observed in Sweden[15,23] where it is estimated that 10,000 lakes have been acidified to a pH value less than 6.0 and 5,000 below a pH of 5.0. The acidification of lakes and the loss of fish in the Sudbury, Ontario, region have been well documented by Beamish and his coworkers.[19,24] In the northeastern United States, a survey in the Adirondack Mountains of New York has revealed that 50 percent of the lakes above 610 m elevation have pH values below 5.0, and that 90 percent of those lakes are devoid of fish (Figure 8-2). A similar survey in the 1929 to 1937 period showed that only 4 percent of the same lakes had a pH <5 or were devoid of fish (Figure 8-3).[21] The State of New York has identified 170 lakes and ponds in the Adirondack Park which have been acidified to a point where they no longer support viable sport fish populations.[26] In Pennsylvania, 314 different bodies of water or locations within streams for which pH and alkalinity data were available at intervals of at least one year were examined to determine pH. Of these, 107 (34 percent) showed decreases in pH, alkalinity,

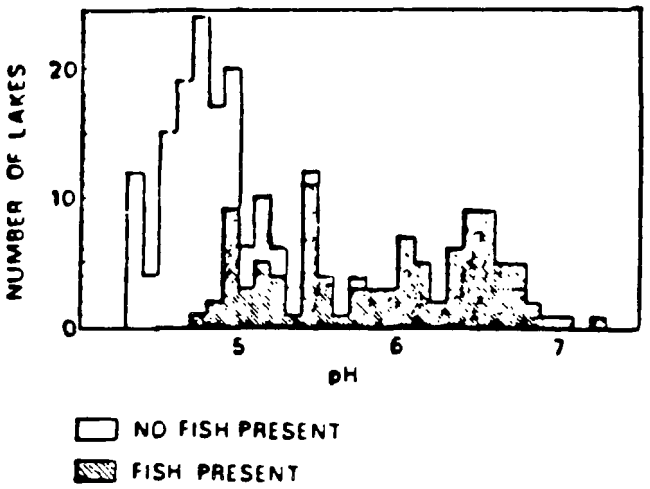


Figure 8-2. Frequency distribution of pH and fish population status in Adirondack Mountain lakes greater than 610 meters elevation. Fish population status determined by survey gill netting during the summer of 1975.[21]

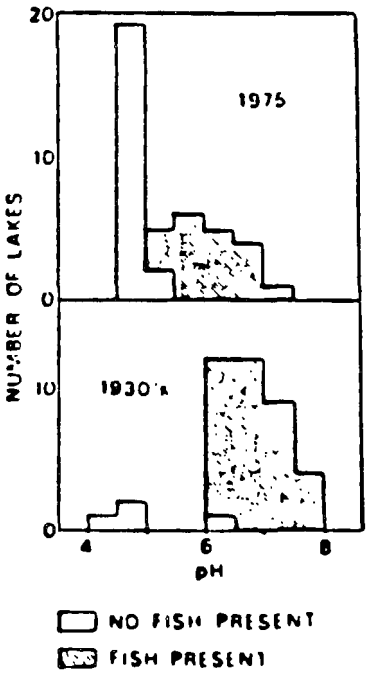


Figure 8-3. Frequency distribution of pH fish population status in 40 Adirondack lakes greater than 610 meters elevation, surveyed during the period 1929-1937 and again in 1975.[21]

or both. The average decrease in pH was 0.4 units and in alkalinity it was 15.1 mg/l as $CaCO_3$. The average span of time between earliest and most recent samples was 8.5 years. In seventy-one of the 107 sites showing pH decreases, fish collection data indicate that in 41 cases (58 percent) there had been a decrease in the number of fish species.[26a] The current trend needs to be documented with further data.

Because of their economic and recreational value, the death of fish in acidified freshwater lakes and streams has been more thoroughly studied than any other aspect of lake and stream acidification. Field surveys in Norway,[12,22] Sweden,[15] Canada,[34] and the United States[21] indicate that most fish species disappear from acidified lakes when the pH drops below 5. Disappearance of the fish is usually not due to massive fish kills, but due to reproductive inhibition at a pH between 5 and 6 (Table 8-2).[18,21,22,27-32] Laboratory experiments indicate that fish eggs and fry are first affected by acidic water.[18] Jensen and Snekvik[18] report that the lower limit for normal reproduction for salmon is pH 5.0 to 5.5; for sea trout, pH 4.5 to 5.0; and for brown trout, approximately pH 4.5.

Field surveys in New York State[32] and Norway [12] indicate that most fish species disappear from acidified lakes when the pH drops below 5. Both inhibition of gonad maturation[24,27] and mortality of eggs and larvae[12,29,30] can contribute to reproductive failure in populations inhabiting acidified water.[12,23] Reduction of egg deposition is due to disrupted spawning behavior or effects on the reproductive physiology of maturing adults. Females failed to release ova even though the ovaries were mature prior to the normal spawning period. The ova became flaccid and watery, and the material from the ovaries appeared

TABLE 8-2. SUMMARY OF EFFECTS OF pH CHANGES ON FISH

pH	Effects
11.5 - 11.0	Lethal to all fish.
11.5 - 10.5	Lethal to salmonids; lethal to carp, tench, goldfish, pike if prolonged.
10.5 - 10.0	Roach, salmonids survive short periods, but lethal if prolonged.
10.0 - 9.5	Slowly lethal to salmonids.
9.5 - 9.0	Harmful to salmonids, perch if persistent.
9.0 - 6.5	Harmless to most fish.
6.5 - 6.0	Not harmful unless >100 ppm CO_2.
	Significant reductions in egg hatchability and growth in brook trout under continued exposure.
6.0 - 5.0	Not harmful unless >20 ppm CO_2, or high concentrations of iron hydroxides present.
	Rainbow trout do not occur. Small populations of relatively few fish species found. Fathead minnow spawning reduced. Molluscs rare.
	Declines in a salmonid fishery can be expected.
	High aluminum concentrations may be present in certain waters causing fish toxicity.
5.0 -	Tolerable lower limit for most fish.
5.0 - 4.5	Harmful to salmonid eggs and fry; harmful to common carp; tolerable lower limit for most fish.
4.5 - 4.0	Harmful to salmonids, tench, bream, roach, goldfish, common carp; resistance increases with age. Pike can breed, but perch, bream, and roach cannot.
4.0 - 3.5	Lethal to salmonids. Roach, tench, perch; pike survive.
3.5 - 3.0	Toxic to most fish; some plants and invertebrates survive.

Modified and updated from ref. 34

to be resorbed by the fish.[24] This process was reported as the primary cause for failure of fish populations to reproduce in the Sudbury area lakes in Ontario, Canada, while studies conducted in Norway, Sweden, and the United States suggest that eggs and newly hatched larvae are the most vulnerable stages in the fish life history (see Table 8-2).[21,31,35]

The disappearance of fish from lakes and streams usually follows two general patterns. One pattern results from the long-term decrease in the pH of the water and the other when sudden short-term shifts in pH occur.[33] Based on field observations, prolonged acidity interferes with reproduction and spawning so that changes in the structure of the population occur over time. These changes include a decrease in population density and a shift in size and age of the population to one consisting primarily of older and larger fish.[19] This pattern has been observed in Norway,[18,33] Sweden,[15] Canada[19,24] and the United States.[20,21] The process is insidious, and effects on yield are often delayed and not recognizable until the population is close to extinction. This is true particularly for late maturing species with long lives. Large increases in the mortality rate are not necessary to bring about population extinction. Even small increases (5 to 50 percent) in mortality of fish eggs and fry can decrease yield and bring about population extinction.[21]

Acid shock, i.e., sudden short-term changes in pH, may cause fish mortality Sudden decreases in pH cause severe physiological stress that may cause fish kills at pH concentrations above those normally toxic to fish.[21,22,33] Sudden decreases in pH often occur in early spring when melting of the snowpack releases the acid pollutants accumulated during the winter. In Norway the pH in the Frafjord River ranged from 3.9 to 4.2[33] during a period of mild weather in the winter of 1948. In the spring of 1975 a similar episode occurred in

the Tovdal River.[33] For salmonid fishes the yolk-stage, which appears to be the most sensitive portion of the life cycle, occurs in the spring and is, therefore, the stage which is likely to be subjected to the most acidic conditions.[33] Species of fish vary in their ability to resist acidic shocks.

Physiologic stress resulting from osmoregulatory dysfunction (body salt regulating mechanism) at low pH and low calcium concentration has been identified as a primary source of mortality in dilute acidified waters.[12,21,23,37] The physiological mechanisms involved in mortality of fish in acidic waters may vary in response to different levels of acidity and the presence of such synergistic components as heavy metals and carbon dioxide. At the pH concentration of 4 to 5 usually encountered in the acidified lakes, disturbance of normal ion and acid-base balance is the most likely cause of mortality.[16,21] Laboratory experiments using several species of salmonid fish demonstrate that in water with a low pH and salinity, sodium uptake is inhibited. Increasing the salt concentration of water effectively lowers the lethal pH level.[16,21,37] Field observations corroborate these results, in that fish populations tend to disappear from the most dilute lakes first.[16,21] The laboratory experiments also explain why fish kills occur at pH concentrations higher than those normally considered toxic to fish.[21,37] In general, indications are that it is interference with osmo- and ionic regulation mechanisms in fish which causes mortality at the pH concentration range experienced when freshwater bodies become acidified.[35,37]

Studies indicate that in the Adirondacks the mobilization of toxic metals, particularly aluminum, is an additional factor which occurs at low pH values.[32,34] Soil leaching and mineral weathering by acidic precipitation results in high concentrations of dissolved aluminum in surface and ground waters. The increased aluminum in water at concentrations of approximately 0.2 mg/liter or higher

can lead to fish mortality. Increased transport of aluminum into aquatic systems may affect phosphorus availability.[36]

Biotic, physical, and chemical factors affect the tolerance of fish to acidic waters.[35] Biotic factors determining tolerance are: (a) species, (b) strain, and (c) age and size of fish. Species, as well as different strains of species, vary in their tolerance to low pH. A fairly well established order of tolerance exists among salmonid species. Rainbow trout are most sensitive, salmon are next, and brown and brook trout follow. Among other European species, minnow and roach are most sensitive, while eel and pike are most tolerant.[35] The data available are based on experiments in which fish have been maintained at a constant pH. Data are not available on species' response to transient changes of pH.

Strains of the same species have shown different survival times. The differences in some cases have been shown to be based on genetics; in others they are based on differences in acclimative ability. Different strains of the same species can spawn at different times of the year (± 1 or 2 months) and thus miss the acidic episodes.[35] Based on laboratory data, larger fish are more tolerant than those at younger stages. The sensitivity of eggs also varies with the species of fish.[35] Table 8-3 lists some of the different species of fish and the pH at which they are sensitive. Beamish[24] noted that fish populations in the acidic La Cloche Mountain lakes of Canada appeared to be affected in the pH range of 4.5 to 6.0. The most sensitive species of fish (smallmouth bass, walleye, and lake trout) were also the most desired sport fish. Reproduction appeared to be the most sensitive major physiological process critical to the survival of the species.

TABLE 8-3. APPROXIMATE pH AT WHICH FISH IN THE LA CLOCHE MOUNTAIN LAKES, CANADA, STOPPED REPRODUCTION

pH	Species	Family
6.0 + to 5.5	Smallmouth bass *Micropterus dolomieui*	Centrarchidae
	Walleye *Stizostedion vitreum*	Percidae
	Burbot *Lota lota*	Gadidae
5.5 to 5.2	Lake trout *Salvelinus namaycush*	Salmonidae
	Troutperch *Percopsis omiscomaycus*	Percopsidae
5.2 to 4.7	Brown bullhead *Ictalurus nebulosus*	Ictaluridae
	White sucker *Catostomus commersoni*	Catostomidae
	Rock bass *Ambloplites rupestris*	Centrarchidae
4.7 to 4.5	Lake herring *Coregonus artedii*	Salmonidae
	Yellow perch *Perca flavescens*	Percidae
	Lake chub *Couesius plumbeus*	Cyprinidae

From Ref. 24

Temperature, season, and hydrology are physical factors influencing the survival rate of fish. Laboratory bioassays indicate that the higher the temperature, the shorter the survival time. Thus, acid episodes occurring at different water temperatures may differ in toxicity.[35] Survival of a species has also been found to vary with the season. It has been suggested that survival may be related to changes in the nutritional and physiological condition (e.g., total salt content) of fish.[35] Water quality exhibits considerable temporal and spatial variations. Water quality in streams usually shows greater fluctuations than lakes fed by the same streams. The chemistry of surface waters over short time periods can be altered by meteorological conditions.[35]

Chemical factors influencing fish survival include the ionic composition of water, synergism or antagonism of toxic ions, and toxic organics. Calcium has been shown to be important in enhancing fish survival at low pH. Physiologically calcium reduces the permeability of the gill membrane to both sodium and hydrogen ions. Magnesium does not prolong survival when present as the only non-hydrogen cation; however, when it is added to water in which other ions are present, it can have an ameliorating effect thus indicating that ions behave differently when present alone or in combination with other ions.[35]

Aluminum has been observed to be toxic at pH values as low as 4.0. The solubility of aluminum increases below the pH of 4.0, but toxicity ceases due to a change in the chemical form of aluminum. Gill damage has been said to be a symptom of aluminum toxicity. However, it is not specific to aluminum, and it is not clear whether it is the mechanism causing mortality. Manganese also is released from minerals in acidic waters and is suspected of being toxic, but its effect at low pH is yet unknown.[35]

Data on the toxicity of organic acids are not available at present. It is thought that the presence of organic acids may be protective since they may chelate some of the harmful ions (aluminum and manganese) and reduce the effective concentrations. Calcium, however, could also be made less available. The availability of ions to the physiological mechanisms of fish is more important than their overall concentration.[35]

8.2.4 Effects on Aquatic Ecosystem Dynamics

The elimination of fish populations is the most obvious biological effect of the acidification of fresh water lakes and streams. Less obvious, but of equal if not greater importance, are the effects which occur to other aquatic organisms. Organisms at all trophic (feeding) levels are affected. Species are reduced in number, alteration of the biomass (total amount of living organic material) occurs, and primary production and decomposition are impaired.[15,16,21,24,23,40-42]

8.2.4.1 Effect On Primary Production and Food Web--Organisms in aquatic habitats obtain their food (energy) directly or indirectly from solar energy. Sunlight, carbon dioxide, and water are used by producers (phytoplankton, other algae, mosses, and macrophytes) in the process of photosynthesis to form sugars which are used by the plants or stored as starch. The stored energy may be used by the plants or pass through the food chain or web. Energy in any food chain or web passes through several trophic levels. (Transfer of energy, usually as food, from one organism to another is termed a trophic level.) Energy moves unidirectionally along two main pathways, the grazing food chain and the detrital food chain.[1,11] Green plants are the food base in the grazing food chain in which plants are eaten by animals and animals by other animals, etc.[1,11] In the detrital food chain, the base is dead organic matter. Decomposers (bacteria, fungi, and some protozoa) use dead plant and animal matter

as food and release minerals and other compounds back into the environment[1,11] (see Figure 8-4). Energy flow and nutrient cycling are two processes which occur in all ecosystems. Disruption of either of these processes illustrates the holocoenotic nature of the ecosystem relationships by creating a chain reaction which disrupts the whole ecosystem.

A change in pH causes changes to occur in the composition of the aquatic plant communities involved in primary production. Kwiatkowski and Roff[44] noted in the lakes they studied in Ontario that the increased hydrogen ion concentrations were progressively reflected in changes "in the species composition, standing crop and production of the phytoplankton community." In the highly acidic lakes, many of the phytoplankton species common in the more neutral lakes were either eliminated or appeared only occasionally. Of the lakes studied, the pH in Daoust Lake ranged from 6.32 to 7.15 while in Ruth and Roy Lake it ranged from 4.05 to 4.6. In these lakes the species of Chlorophyta (Green Algae) were reduced from 26 to 5, the Chrysophyta (Golden Brown) from 22 to 5 species, and the Cyanophyta (Blue-Green) from 22 species to 10.[44]

The relative dominance of the algal flora also changed. The Chlorophyta comprise between 40 and 50 percent of the total algae population and the Cyanophyta approximately 30 percent in more neutral lakes. In acidified lakes, the Chlorophyta population is reduced to 25 percent and the Cyanophyta increased to 60 percent. In addition, as the H^+ concentration increased, new species of Chlorophyta appeared. The studies of Brock[45] suggest that at pH 4.0 the Cyanophyta are reaching the lower limits of their growth range.

Primary productivity in lake water is generally thought to be limited by the nutrients, phosphorus and nitrogen. In the lakes studied by Kwiatkowski and Roff, the difference in nutrient levels were not sufficient to account for

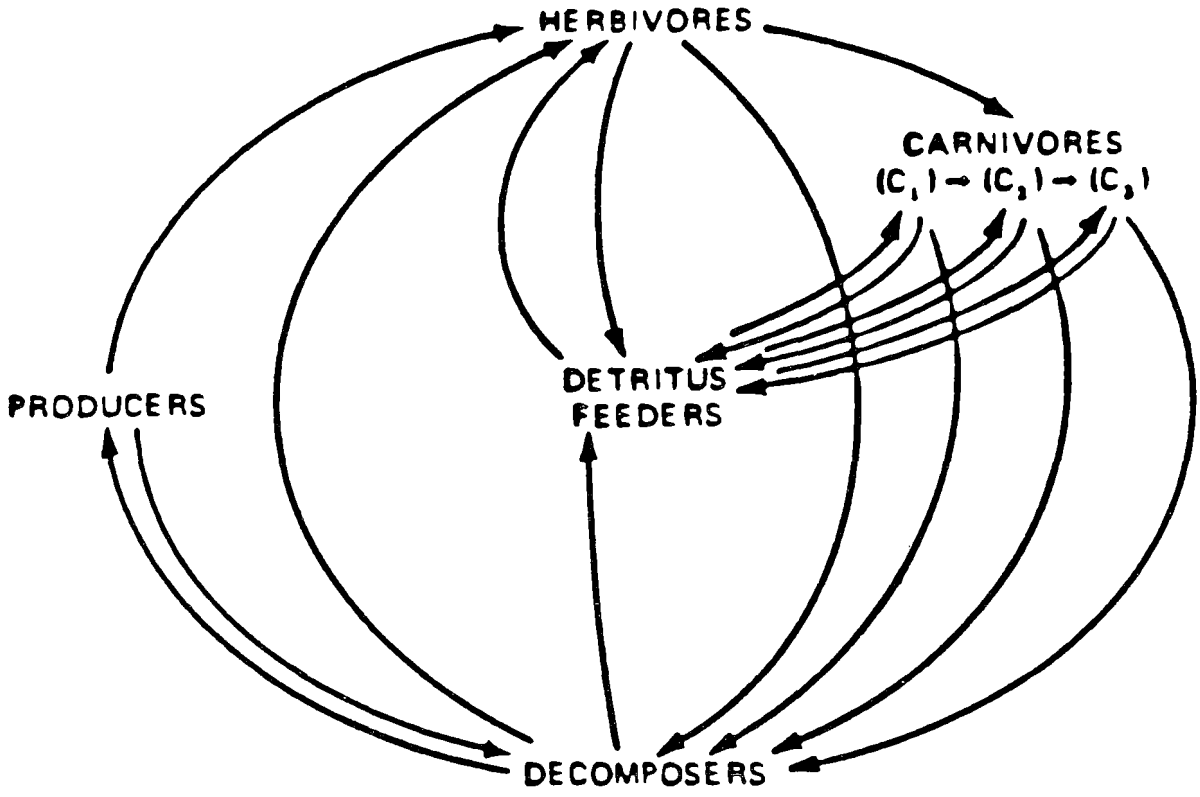


Figure 8-4. Pathways among the producers and consumers of an ecosystem. [43]

the differences in productivity rates. Acidity appeared to be the limiting factor. Primary productivity increased as the pH of the lakes approached neutrality.[44]

A study of the phytoplankton populations of 115 lakes in the west coast region of Sweden supports the findings in Ontario.[16] On the average, the biomass of all algal groups was equally distributed at pH 6 or above. The critical pH range appeared to lie between pH 5 and 6. Below 5.0 most of the diatoms and green algal species disappear, but as the pH increases toward 5.8 there is an increase in number.[16] The species composition of lakes with a pH lower than 5 lacked diversity, and the size of the population was limited.[15]

Similar phenomena were observed in a regional survey of 55 lakes in southern Norway[33] and in a study of four lakes in Ontario, Canada.[46] Phytoplankton biomass was low (<1 mg/liter) in these acidic lakes and was correlated with the concentration of phosphorus which generally decreased at a lower pH. In the Ontario lakes, phytoplankton biomass at pH values near 4.5 was only one-ninth to one-third as much as when the pH was near 6.5.[46] Yan and Stokes,[47] however, on the basis of experimental studies conducted by varying the pH _in situ_ of an already acidic lake feel that phytoplankton species number and community structure are more sensitive indicators of lake acidification than phytoplankton community biomass. Further, their studies suggest that continued addition of acid into the Canadian lakes with low buffering capacities will ultimately result in major shifts in the phytoplankton community structure of these lakes.

Diatoms (Chrysophyta) are important components of the phytoplankton. They form assemblages of species which are broadly characteristic of the aquatic environment in which they are growing; therefore, changes in water quality

parameters, such as pH, can be investigated by analyzing diatom communities.[16] Samples of periphytic diatoms collected at seven locations in Norway in 1949 were compared with samples collected from the same sites in 1975. Qualitatively the species were similar; however, changes had occurred in the proportions of the various species present. A shift toward the more acid tolerant species had occurred.[16]

In all of the lakes investigated, the species composition of the phytoplankton was less diverse and reduced in population size in acidic lakes when compared with neutral oligotrophic lakes and a reduction in primary production usually resulted.

Acidification of lakes also reduces the species diversity of the macrophyte community and reduces productivity. Studies of the succession of macrophyte communities in six lakes in Sweden indicate that in 5 of the 6 lakes Lobelia Isoetes communities were being replaced by Sphagnum.[40,42] In the most acidic lakes (pH 4.5), the Sphagnum covers approximately 70 to 80 percent of the lake bottom at the 0 to 2 m depth. In the least acidic lake (pH 5.5), coverage is approximately 50 percent.[42] The rate of Sphagnum invasion has been greatest in the shaded and sheltered areas of the lake and at a depth of 4 to 6 m. The abundance of Sphagnum mats in the different lakes is positively correlated with the lowering of the pH. The consequences of the Sphagnum occupying ever larger areas of the lake bottoms are that several base ions (e.g., Ca^{++}) necessary for biological production are bound to the mass tissue due to its strong ion exchange capacity and are, therefore, not available to other organisms. There is also a deterioration of the benthic habitat because moss is a very poor substrate for bottom fauna. Under these conditions two filamentous algae, Mougeotia (a Green alga) and Batrochospermum (a Red alga), in addition

to Sphagnum, become important components of the benthic communities. In Lake Oggevatn, a clear-water lake in southern Norway with a pH of 4.6, not only is Sphagnum beginning to choke out Lobelia dortmana and Isoetes lacustris, but these macrophytes have been observed to be festooned with filamentous algae.[41]

Experimental studies by Leivestad et al.[16] support the findings of Grahn et al.[41] and Grahn[42] as discussed above. Sediment cores containing Lobelia dortmanna L. were incubated at three different pH concentrations. The rate of growth was less at pH 4.0 when compared to the higher pH values and flowering time was delayed. Mougeotia spp. began to grow upon the Lobelia after 30 to 40 days at pH 4.0.[16]

Heavy growths of filamentous algae and mosses not only occur in acidified lakes, but also have been reported in Norwegian streams affected by acidification In experiments conducted in artificial stream channels in which water and naturally seeded algae from an acidified brook (pH 4.3 to 5.5) were used, increasing the acidity to a pH of 4 through the addition of sulfuric acid led to an increased accumulation of algae, when compared with that in an unmodified control.[40,48] The flora was dominated by Binuclearia tatrana, Mougeotia spp., Eunotia lunaris, Tabellaria flocculosa, and Dinobryon spp., each accounting for at least 20 percent of the flora at one time or another.[40]

Root systems of higher plants are important in supplying oxygen to lake sediments. A reduction in oxygen supply due to reduction in viability of macrophytes could affect the decomposer organisms in the sediments.[16]

Simplification of the vegetational communities in lakes and streams involved in primary production reduces the variety of food available to the next trophic level and therefore reduces energy flow within the ecosystem. Changes in plant communities also cause a reduction in nutrient supply. A reduction in both energy flow and nutrient supply limits the number of organisms which can exist within that system.

8.2.4.2 Effects On Decomposition--Acidification of lakes reduces microbial activity causing a reduction of the processes of decomposition and an accumulation of organic matter in aquatic ecosystems. An abnormal accumulation of coarse organic matter (detritus) was observed on the bottoms of six Swedish lakes where a decrease in pH by 1.4 to 1.7 units occurred during the last 30 to 40 years. Layers of leaves and the remains of *Sphagnum* and other macrophytes covered large areas of the lake bottoms.[41] In Gardsjön, 85 percent of the lake bottom in the zone 0-2 m deep was covered with a thick felt of fungus. Bacterial activity had apparently decreased and the mineralization of organic matter was being accomplished by fungi at a very slow rate. Liming raised the pH of the lake and caused the rapid decomposition of the organic litter and a great reduction in the fungal felt, thus indicating that bacterial activity had been inhibited at a low pH.[16, 49] A similar neutralization of acidified lakes in Canada resulted in a significant increase in aerobic heterotrophic bacteria in the water.[50] Results from field and laboratory experiments with litterbags in Norwegian lakes indicated reduced decomposition of leaves in acidic water.[40] In laboratory experiments conducted at pH 6 and pH 4, decomposition of the leaves was significantly higher at pH 6 after 1 year of exposure. Similar results were obtained when experiments were conducted in lakes and brooks.[16]

The organic matter in lakes is either produced there through the process of photosynthesis (autochthonous) or enters from outside the lake dissolved in rain, via wind or streams flowing into the lake (allochthonous). The relative importance of each of the sources varies greatly from lake to lake.[38,39]

Organic litter from land sources (allochthonous detritus) is an important source of energy for bottom-dwelling invertebrates. In fact, detritus plays a

central role in the energetics of lake ecosystems.[15,16,40-42,44,48-51] The metabolism of detrital organic matter is an integral part of the complex carbon cycles that dominate both the structure and function of aquatic ecosystems and provide, according to Wetzel,[51] a fundamental stability to the system. Detritus in aquatic ecosystems may be defined as nonliving particulate (>0.45 μm particle diameter) organic matter together with the associated microbiota (e.g., fungi, bacteria, protozoa, and other microinvertebrates).[52,53] Organic matter smaller than 0.45 μm is classified by Boling et al.[52] as dissolved organic matter.[52] The biochemical transformations of particulate and dissolved organic matter via microbial metabolism are fundamental to the dynamics of nutrient cycling and energy flux. The trophic relationships within lake systems are almost entirely dependent on detrital structure.[51] A generalized scheme of food relationships in a lake is shown in Figure 8-5.

From Figure 8-5, it may be noted that bacteria are central to the food relationships in a lake. Experiments have demonstrated that a shift in the populations of decomposer organisms from bacteria to fungi occurs with a lowering of the pH.[16,40] Accompanying the shift in populations was a decrease in the zooflagellate fauna.[40] In addition, laboratory studies have shown the inhibition of biochemical processes as well as a decrease in the total cell count and species number of ciliate protozoa.[16,40]

Interference with nutrient cycling through the disruption of the detrital trophic structure is a major consequence of changes occurring in microdecomposer populations brought about by acidification.[40] Accumulation of organic litter and the formation of extensive mats of fungal hyphae as observed in Swedish lakes [16,41] causes the sealing off of mineral sediments from interaction with the overlying water, and holds organically bound nutrients that would otherwise

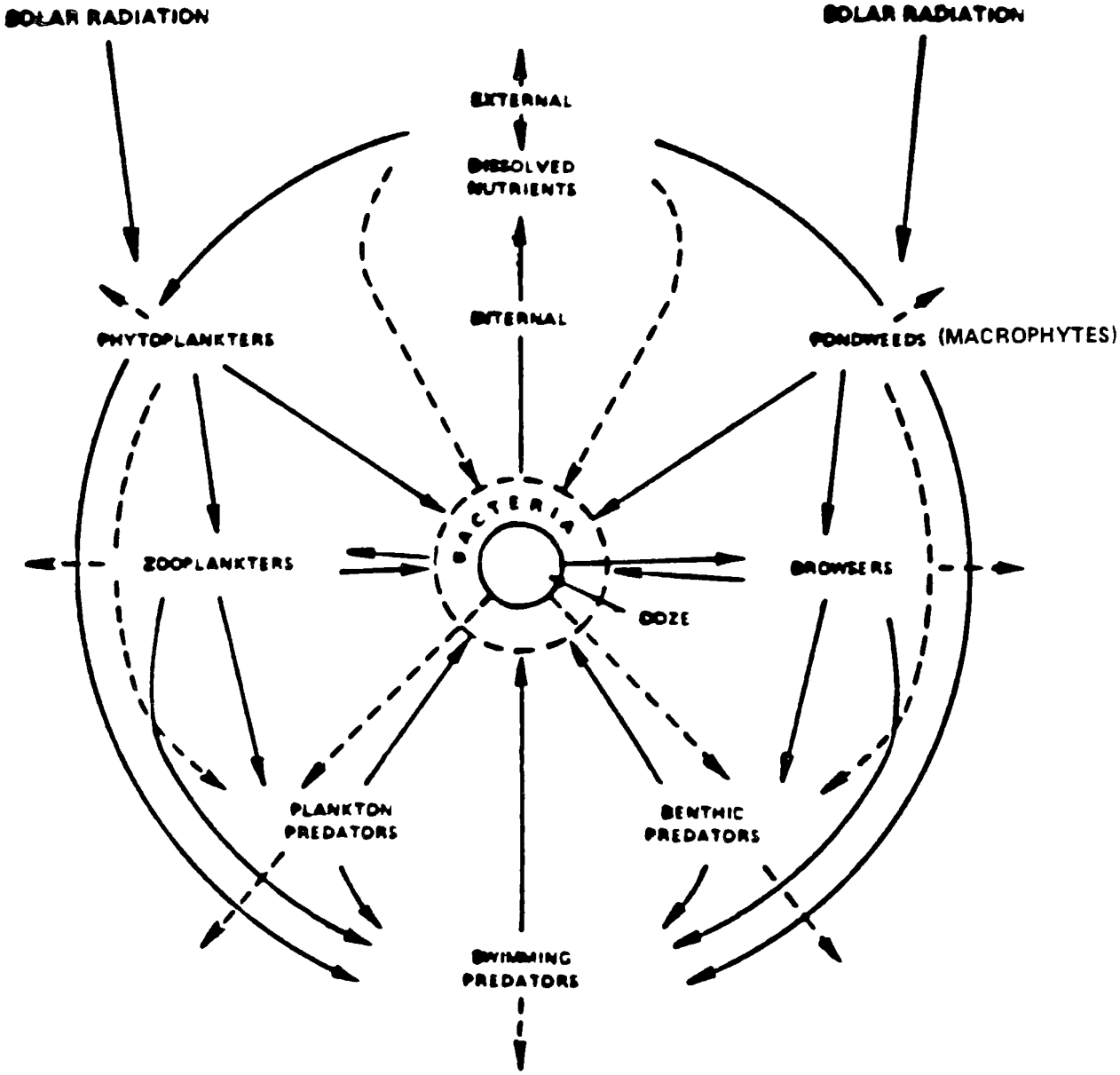


Figure 8-5. Generalized scheme of food relationships in a lake. Efficiency in utilization of food increases in the higher consumer levels.[43]

become available if normal decomposition occurred.[41] The reduction in nutrient availability can be expected to have a negative feedback effect on the microorganisms, further inhibiting their activities. The reduction of nutrient supplies to the water column from the sediments, because of the physical covering, and from reduced mineralization of organic materials in the water itself, will lead to reduced phytoplankton productivity.

Reduction of microdecomposer activities can have a direct effect on invertebrates. Although some benthic invertebrates appear to feed directly on the allochtonous detritus material, it seems that "conditioned" material (that colonized by microorganisms) is preferred and that the nutritive value of the detritus is highly increased by the conditioning process.[52]

Bacteria and detrital organic matter are a source of food for filter-feeding zooplankton. An inhibition of the microbiota or a reduction in microbial decomposition processes has a direct impact on the non-predatory detrital pathways and on animal communities in lakes.[51]

Invertebrate communities are affected by acidification of freshwater bodies.[16,40,41] Surveys at many sites in Norway, Sweden, and North America have shown that lakes and streams affected by acidic precipitation have fewer species of benthic invertebrates than waters with a higher pH.[33,46,49,54]

Zooplankton analyzed from net samples collected from 84 lakes in Sweden showed that acidification caused limitation of many species and led to simplification of zooplankton communities.[15] Crustacean zooplankton were sampled in 57 lakes during a Norwegian lake survey in 1974[33] and the number of species observed was found to be related to the pH (see Figure 8-6). The distributions and associations of crustacean zooplankton in 47 lakes of a region of Ontario affected by acid precipitation were strongly related to the pH and to the

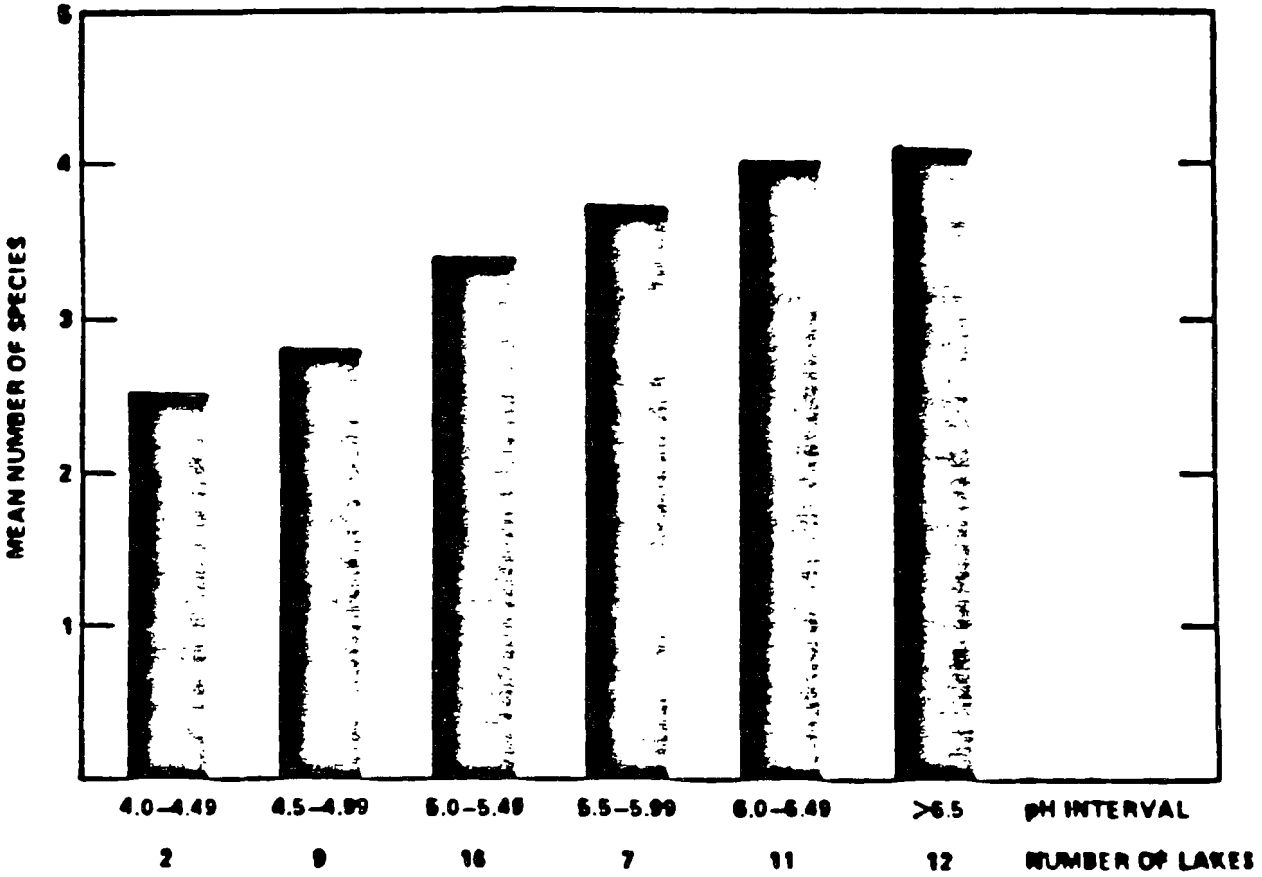


Figure 8-6. The number of species of crustacean zooplankton observed in 57 lakes during a synoptic survey of lakes in southern Norway.[40]

the number of fish species in the lakes. However, fish and zooplankton were each correlated with the same limnologic variables, especially pH.[55] As acidity increases, the complexity of zooplankton communities decreases. Sprules[55] found that many species of zooplankton did not occur below a pH of 5. At a pH of 5 an abrupt change from complex to simple zooplankton communities occurred. Lakes with a pH >5 had 9 to 16 zooplankton species, while lakes with a pH <5 had fewer than 7 species. In some lakes only a single species was found. Reduced diversity in zooplankton communities affects the food supply, feeding habits of consumer populations, and thus causes changes in the community structure of organisms dependent on the zooplankton as a food source.

Gastropods are also adversly affected by acidic waters. In 832 Norwegian lakes, no snails were found where the pH was below 5.2; snails were rare at a pH of 5.2 to 5.8, and they occurred less frequently at a pH of 5.8 to 6.6 than in more neutral or alkaline water.[16,56] The amphipod Gammarus lacustris, an important element in the diet of trout in Norwegian lakes where it occurs, is not found in lakes with a pH less than 6.0.[16,40,57] Experimental investigations have shown that the adults of this species cannot tolerate 2 days of exposure to a pH of 5.0[16,40] (see Figure 8-7). Eggs were reared in water at 6 different pH levels ranging from 4.0 to 6.8. Below a pH of 5.5 a majority of the animals died within 48 hours. The short-term acidification which often occurs during the spring melt of snow could eliminate these species from small lakes.

In the River Duddon in England, acid from precipitation is the overriding factor that prevents permanent colonization of the upper acidified reaches of the river by a number of species of benthic invertebrates, primarily herbivores.[59] In the more acidic tributaries (pH <5.7), the epiphytic algal

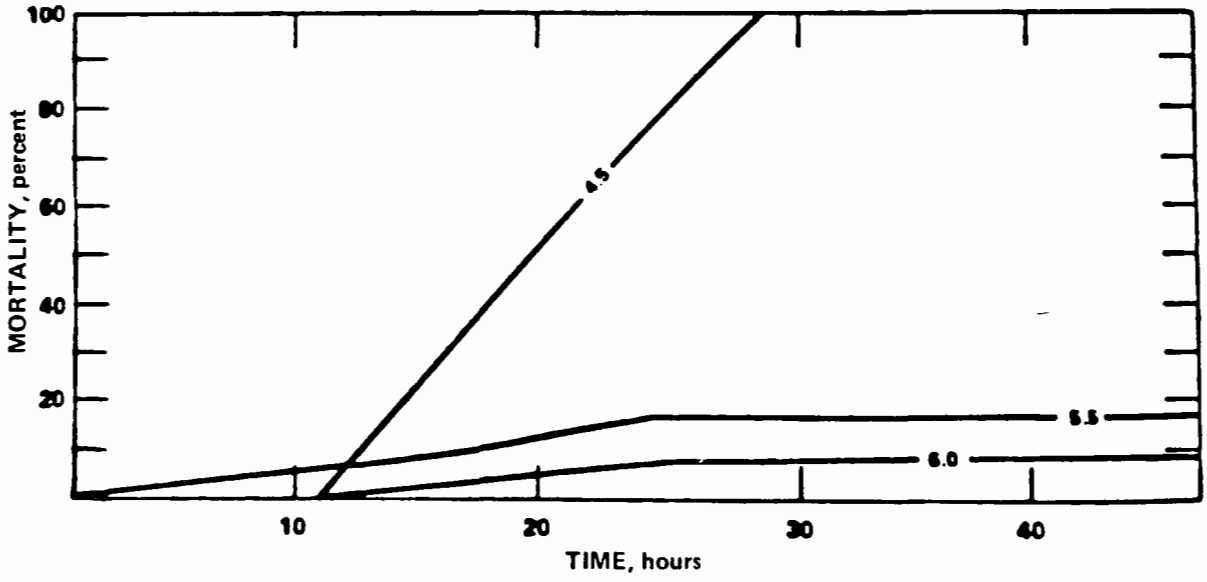


Figure 8-7. Cumulative mortality of Gammarus lacustris adults at several pH levels.[16]

flora was reduced (in contrast with increases noted in Norway), and leaf litter decomposition was retarded. The food supply of the herbivores was apparently decreased, and this may have played a role in the simplification of the benthic fauna.

As mentioned previously, macrophyte communities of Lobelia and Isoetes in some Swedish and Norwegian lakes[41,42] are heavily overgrown with filamentous algae and are being choked out by dense mats of Sphagnum. Under these conditions, benthic invertebrate populations will be depleted by starvation, evacuation, or extinction due to the loss of preferred habitat. Chironomids[60] and other benthic invertebrates will, in many situations, be affected by altered decomposition cycles and variations in available foods caused by increased acidification.

The tolerance of aquatic invertebrates to low pH varies during their life cycles. Adult insects seem to be particularly sensitive at emergence. Broadly speaking, the percentage of aquatic insects which emerge successfully decreases as the pH of the water decreases.[61] Bell,[61] in studies with Epimeroptera found emergence patterns to be affected at pH of 5.3 to 5.5 for extended periods of time (greater than 30 days). Trichoptera, however, are very tolerant of low pH. In general, aquatic insects differ markedly in pH tolerance, but based on available data, a value of pH 5.5 or higher is necessary for 50 percent successful emergence.[61]

Many species of aquatic insects emerge early in the spring through cracks in the ice and snow cover. Because the spring meltwater is often contaminated by atmospheric pollutants, these early emerging insects are in many cases exposed to the least desirable conditions.[62-64]

Damage to invertebrate communities influences other components of food chains. Benthic invertebrates assist with the essential function of removing dead organic material. In experiments in which litterbags were used, leaf decomposition by invertebrates was much greater at a higher pH than at a low pH.[40] The accumulation of attached algae in acidified lakes and streams may result from a reduction in the number of grazing benthic invertebrates.

In unstressed lake ecosystems, a continuous emergence of different insect species is available to predators from spring to autumn. In acid-stressed ecosystems the variety of prey is reduced, and periods may be expected to occur in which the amount of prey available to fish (and waterfowl) is diminished.

8.2.4.3 Effects On Vertebrates Other Than Fish--Amphibians may be the vertebrate animals most directly affected by acidic precipitation. Amphibians' reproductive habits make them susceptible to changes in pH of the ponds which they lay their eggs. Frogs, toads, and approximately half of the terrestrial salamanders in the United States lay eggs in ponds.[65] Not only do these vertebrates breed in water, but many species breed in ephemeral pools. These temporary pools are usually completely dry during some period of the year and are refilled by rain or snow shortly before the amphibians enter them to lay their eggs. These pools depend on rain, drainage water, or snow melt to fill them. Because these pools are small and collect drainage from a small area, and because no buffering occurs since they are filled before deciduous trees have sprouted leaves, the acidity of the water in the pools is strongly influenced by the pH of the precipitation that fills them.[65]

Frog embryos have observed to develop abnormally when the pH range is between 3.7-4.6. A pH of <4.0 is usually lethal.[66]

Spotted salamander reproduction is impaired by an increase in the acidity of the breeding pools. Pough and Wilson,[65] in a study of the effects of pH on salamanders, observed that spotted and Jefferson salamanders tolerated pH values of 5 to 10 and 4 to 6, respectively. Young hatched best when the pH range was 7 to 9 for the spotted salamander and 5 to 6 for the Jefferson's. A pH lower than 6.0 can inhibit the development and increase the egg mortality of spotted salamanders.[67] Based on the data available, it appears that in amphibians, as in fish, a lowering of the pH first affects reproduction.[68]

Frog populations in Tranevatten, a lake near Gothenberg, Sweden, acidified by acidic precipitation were investigated.[69] The lake has a pH ranging from 4.0 to 4.5. All fish have disappeared, and frogs belonging to the species Rana temporaria and Bufo bufo are being eliminated. At the time of the study (1977) only adult frogs 8 to 10 years old were found. Many egg masses of Rana temporaria were observed in 1974, but few were found in 1977, and the few larvae observed at that time died.[69]

Frogs and salamanders are important predators on invertebrates, such as mosquitos and other pest species, in pools, puddles and lakes.[38] They also are themselves important prey for high trophic levels in an ecosystem.[67]

The elimination of fish and vegetation from lakes by acidification will have an indirect effect on a variety of vertebrates. Species of birds, e.g., the bald eagle, loon and osprey, and fish-eating mammals such as mink and otter will be affected. It has been estimated that 70 percent of the Canadian population of the common loon and hooded merganser and 50 percent of the range of the bald eagle lies within the affected area. Dabbling ducks which feed on vegetation also will be affected. In fact, any animals which depend on aquatic organisms (plant or animal) for a portion of their food will be affected.

Increasing acidity in freshwater habitats results in shifts in species, populations, and communities. Virtually all trophic levels are affected.

A summary of the changes which are likely to occur in aquatic biotia with decreasing pH is listed in Table 8-4 while a summary of the effects of decreasing pH on aquatic organisms is listed in Table 8-5.

8.2.4.4 Water Chemistry--The discussion in the previous section suggests that the increasing acidity of freshwater lakes and streams appears to be the chief environmental factor stressing aquatic ecosystems in certain regions of the United States,[20,21,74] Canada,[19,24] Norway,[12,14,18] and Sweden.[15,23,33] The pH appears to be the limiting factor which has triggered the major ecological changes that have taken place.

Wide variations in relative acidity and alkalinity occur in natural waters not only in the amount of dissolved materials producing the acidity or alkalinity but also in actual pH values.[51] Dilute concentrations of alkalines and alkaline earth compounds of bicarbonates, carbonates, sulfates, and chlorides dominate the ionic composition of fresh waters. The concentrations of four major cations, Ca^{++}, Mg^{++}, Na^{+}, K^{+} and four major anions HCO_3^-, $CO_3^=$, $SO_4^=$ and Cl^-, usually constitute the total ionic salinity of water. Ionized components of nitrogen (N), phosphorus (P), iron (Fe), and numerous minor elements are of great biological importance, but from the standpoint of the chemical composition of water, their concentrations are not as important.[51] Salinity is the chemical term for the ionic composition expressed in mg/l or mg/l, which units are essentially equivalent as mass or volume in dilute solutions. The chemical composition of open lakes with an outlet is governed largely by the composition of influents from precipitation and the drainage basin.[51]

TABLE 8-4. CHANGES IN AQUATIC BIOTA LIKELY TO OCCUR WITH INCREASING ACIDITY

1. Bacterial decomposition is reduced and fungi dominate saprotrophic communities. Organic debris accumulates rapidly.

2. The ciliate fauna is greatly inhibited.

3. Nutrient salts are taken up by plants tolerant of low pH (mosses, filamentous algae) and by fungi. Thick mats of these materials may develop which inhibit sediment-to-water nutrient exchange and choke out other aquatic plants.

4. Phytoplankton species diversity, biomass, and production are reduced.

5. Zooplankton and benthic invertebrate species diversity and biomass are reduced. Remaining benthic fauna consists of tubificids and Chironomus (midge) larvae in the sediments. Some tolerant species of stone flies and mayflies persist as does the alderfly. Air-breathing bugs (water-boatman, backswimmer, water strider) may become abundant.

6. Fish populations are reduced or eliminated.

7. Changes in populations and communities occur at virtually all trophic levels.

From reference 38

TABLE 8-5. SUMMARY OF EFFECTS ON AQUATIC ORGANISMS WITH DECREASING pH

8.0-6.0	• Long-term changes of less than 0.5 pH units in the range 8.0 to 6.0 are likely to alter the biotic composition of freshwaters to some degree. The significance of these slight changes is, however, not great.
	• A decrease of 0.5 to 1.0 pH units in the range 8.0 to 6.0 may cause detectable alterations in community composition. Productivity of competing organisms will vary. Some species will be eliminated.
6.0-5.5	• Decreasing pH from 6.0 to 5.5 will cause a reduction in species numbers and, among remaining species, significant alterations in ability to withstand stress. Reproduction of some salamander species is impaired.
5.5-5.0	• Below pH 5.5, numbers and diversity of species will be reduced. Many species will be eliminated. Crustacian zooplankton, phytoplankton, molluscs, amphipods, most mayfly species, and many stone fly species will begin to drop out. In contrast, several pH-tolerant invertebrates will become abundant, especially the air-breathing forms (e.g., Gyrinidae, Notonectidae, Corixidae), those with tough cuticles which prevent ion losses (e.g., Sialis lutaria), and some forms which live within the sediments (Oligochaeta, Chiromomidae, and Tubificidae). Overall, invertebrate biomass will be greatly reduced.
5.0-4.5	• Below pH 5.0, decomposition of organic detritus will be severely impaired. Autochthonous and allochthonous debris will accumulate rapidly. Most fish species will be eliminated.
4.5 and below	• Below pH 4.5, all of the above changes will be greatly exacerbated, and all fish will be eliminated. Lower limit for many algal species.

Modified from reference.[38]

Soft waters contain low concentrations of salinity and are usually derived from drainage of acidic igneous rocks while hard waters contain large concentrations of alkaline earths derived from the drainage of calcareous deposits.[51]

The major ion chemistry of acid lakes has been studied in southern Norway,[71] the west coast[72] and west-central[4] regions of Sweden, the La Cloche Mountains of southeastern Ontario,[24] and Sudbury, Ontario, Canada.[73] The data obtained in these studies as well as data from unacidified lakes in west-central Norway[71] and the Experimental Lakes Area of northwestern Ontario, Canada,[74] are listed in Table 8-6. Data from these indicate that the unaffected soft-water lakes are calcium-magnesium bicarbonate waters while the water in acid lakes is dominated by hydrogen-calcium-magnesium sulfate. Sulfate in these lakes comes from man-made sources and seawater. The sulfate coming from seawater can be estimated, if it is assumed that all of the chloride comes from seawater and that the amount of sulfate attributable to sea salts is proportional to the sulfate/chloride ratio in seawater.[75] The contribution of saltwater to the concentration of other ions can also be estimated in a similar way. Because of their proximity to the ocean, coastal lakes receive more ions from sea spray than inland lakes.[75]

In acidified lakes sulfate replaces bicarbonate as the major anion.[24,75,76] Since the bicarbonate lost in acidified lakes has been replaced by an equivalent amount of sulfate, the concentration of excess sulfate serves as an index of the amount of acidification that has taken place.[76] The pH of natural water is governed to a large extent by the interaction of

TABLE 8-6 CHEMICAL COMPOSITION (MEAN ± STANDARD DEVIATION) OF ACID LAKES (pH <5) IN REGIONS RECEIVING HIGHLY ACIDIC PRECIPITATION (pH <4.5), AND OF SOFT-WATER LAKES IN AREAS NOT SUBJECT TO HIGHLY ACIDIC PRECIPITATION (ph >4.8) LESS s w = CONCENTRATIONS AFTER SUBTRACING THE SEAWATER CONTRIBUTION ACCORDING TO THE PROCEDURE EXPLAINED IN THE TEXT

Region		No. of lakes	µS/cm at 20°C	H (pH)	Na	K	Ca	Mg	µeq/l HCO_3	HCl	SO_4	NO_3	Σ cations	Σ anions	Reference
I. LAKES IN ACID AREAS															
Scandinavia															
Southernmost	Measured	26	27±10	18±11 (4.76)	70±40	5±3	56±35	41±16	11±26	71± 45	100±33	4±2	189	186	71
Norway	Less s w			18	9	4	50	25	11	0	92	4	106	107	
Westcoast	Measured	12	72*	43* (4.37*)	330	20	——— 280 ———		0	440	200	8	673	648	72
Sweden	Less s w			43	-50	13	-	-	0	0	155	8	-	-	
West-central	Measured	6	47±23	22±15 (4.66)	165±120	15±8	75±10	80±40	-	170±90	200±70	19±4	360	390	41
Sweden	Less s w			22	20	12	70	50	-	0	180	19	175	200	
North America															
La Cloche Mtns,	Measured	4	38±8	20±9 (4.7)	26±4	10±3	150±25	75±8	0	22±6	290±40	-	280	310	24
Ontario	Less s w			20	9	10	150	65	0	0	290	-	255	290	
Sudbury, Ontario	Measured	4	120±40	36±5 (4.5)	100±30	40±10	450±180	310±120	8±2	50±20**	800±290	-	940	850	74
	Less s w			36	50	40	450	300	8	0	800	-	880	800	
II. LAKES IN UNAFFECTED AREAS															
Scandinavia															
West-central	Measured	23	13±3	6±2 (5.2)	50±20	3±1	18±9	16±5	13±8	46±21	33±8	5±2	93	97	71
Norway	Less s w			6	9	3	16	7	13	0	30	5	41	48	
North America															
Experimental Lakes	Measured	40	19	0.2-2 (5.6-6.7)	40	10	80	75	60	40	60	<1.5	200	160	74
Area, Ontario	Less s w			0.2-2	4	10	80	65	60	0	55	<1.5	160	120	

*Data for 112 lakes
**Measured after chemical treatment of the lakes

From reference 75, Wright and Gjessing, 1976.

H^+ ions resulting from the dissociation of H_2CO_3 and from OH^- ions that result from the hydrolysis of bicarbonate. Beamish[24] noted that the high sulfate concentrations in the lakes were found in association with low pH and by balancing anions and cations, it can be demonstrated that part of the sulfate ion is balanced with the H ion, indicating the low pH results from the presence of H_2SO_4. Comparison of the major ions found in four of the acidified lakes in Ontario with unacidified lakes indicated that, except for H^+ and sulfate ions, the ionic compositon was similar.[24] Wright and Gjessing[75] also noted that in lakes with a low pH (<5) sulfate is the major anion, while in lakes with a pH >5 bicarbonate is the major ion.

8.2.4.5 Metal Concentrations in Acidified Waters--Significant changes in the concentrations of heavy metals in acidified lakes have been observed.[24,75,76] (Table 8-7.) Increased concentrations of aluminum, manganese, zinc, copper, cadmium, and nickel have been reported.[24,75,76] Mobility of all of these metals is greatly increased at low pH concentrations. Beamish[24] suggested that in Canada the increased concentrations of nickel and copper were probably the result of precipitation loading; however, copper concentrations in acidified lakes were not significantly greater than in non-acidified lakes. Zinc concentrations were much higher in the acidified lakes but when compared to the average concentration obtained from the analysis of more than 1500 samples from waters within the United States, they were normal.[24] Zinc concentrations were similar to those found in acidified lakes in Sweden. Manganese concentrations also were similar to those noted in Sweden. Increase in the concentrations of aluminum, manganese, and zinc are associated with increased leaching from soils and lake sediments. Schofield[79] noted high concentrations of aluminum in

TABLE 8-7. CHEMICAL COMPOSITION OF FOUR ACID LAKES AND NON-POLLUTED LAKES IN A REMOTE AREA OF N.W. ONTARIO. RANGE IN BRACKETS

	O.S.A.	Muriel	George	Lumsden	102 lakes E.L.A. N.W. Ontario
pH	4.5(4.4-4.9)	4.7(4.5-4.8)	5.0(4.8-5.3)	4.8(4.7-5.3)	6.5
Sulfate mgl^{-1}	15(14-17)	15(14-15)	14.3(12-16)	10.7(10.0-12.6)	3.8
Chloride mgl^{-1}	1(<1-1)	<1(<1-1)	1.0(0.6-1.6)	0.7(0.5-1.2)	0.8
Na mgl^{-1}	0.6(0.6-0.8)	0.6(0.6-0.7)	0.8(0.7-1.0)	0.4(0.4-0.8)	0.9
Ca mgl^{-1}	3.2(2.9-3.7)	3.4(3.1-3.4)	3.2(1.8-4.0)	2.2(1.4-2.9)	2.0
Mg mgl^{-1}	0.9(0.7-1.0)	0.9(0.7-0.9)	1.0(0.9-1.6)	0.7(0.5-1.0)	0.6
K mgl^{-1}	0.4(0.3-0.5)	0.3(0.3-0.4)	0.5(0.3-0.6)	0.3(0.2-0.4)	0.3
Hardness (as $CaCO_3$) mgl^{-1}	11(10-14)	11(11-12)	12.3(7.9-16.4)	8.4(5.6-11.3)	7.5
Total dissolved solids mgl^{-1}	23(7-59)	16(15-16)	28(10-49)	18(10-25)	---
Total suspended solids mgl^{-1}	1(0-2)	1(0-1)	<1(<1-4)	<1(<1-4)	2
Bicarbonate alkalinity (as $CaCO_3$) mgl^{-1}	0.5	<0.5	<0.5	<0.5	10
Conductivity µmho cm^{-2}	48(46-53)	32(8-47)	40(35-45)	32(27-35)	19
Fe µg l^{-1}	23(18-29)	40(34-46)	27(7-45)	35(13-77)	143
Ni µg l^{-1}	11(8-13)	12(10-15)	10(5-15)	8(6-9)	<3
Cu µg l^{-1}	4(2-6)	2(2-4)	2(1-8)	4(2-16)	2
Zn µg l^{-1}	36(30-48)	29(25-31)	24(8-45)	32(17-35)	<1
Cd µg l^{-1}	<1	<1	<0.5(<0.5)	0.4(0.2-0.5)	<0.1
Pb µg l^{-1}	4(2-6)	1(0-3)	<2(<2)	2(1-3)	<1
Mn µg l^{-1}	---	---	220(160-260)	258(210-310)	3

From reference 24

stream runoff at the time of snow melts. Leaching of aluminum from watersheds has also been reported.[83]

Aluminum concentrations in acidified waters in regions where acidic precipitation occurs are characteristically high.[79] Aluminum concentrations in acidified lakes in southern Norway,[75] Sweden,[83] and the northeastern United States[75,83] are five to ten times higher than aluminum concentrations in circumneutral waters from these same regions. Aluminum appears to be the primary element mobilized by strong acids from acidic precipitation in regions where the watershed is characterized by acidic, base deficient soils.[83] In the acidified soft surface waters of the Adirondack Mountains of New York State, aluminum is highly variable in concentration and form.[37a] Organically complexed aluminum is the dominant form. Labile inorganic aluminum appears to be the form toxic to fish.[37a] Temporal changes in concentration of hydrogen ions and organic carbon appear to have a significant effect on the chemistry of aluminum in these aqueous systems.[37a]

The increased concentrations of heavy metals in acidified lakes are not only the result of direct deposition of these metals in precipitation, particularly, in areas such as Sudbury, Ontario which are near metal smelters, but also the result of mobilization and enhanced solubility of these metals in watersheds and sediments as a result of the acidification of precipitation.[75]

8.2.4.6 Effects on Human Health--Indirect effects of acidification that are potentially of concern to human health is the possible contamination by toxic metals of edible fish and of water supplies. Studies in Sweden,[84,87] Canada,[82,85] and the United States[82] have revealed high mercury concentrations in fish from acidified regions. Methylation of mercury to monomethyl mercury occurs at low

pH while dimethyl mercury forms at higher pH.[86] Monomethyl mercury in the water passing through the gills of fish reacts with thiol groups in the hemoglobin of the blood and is then transferred to the muscle. Methyl mercury is eliminated very slowly from fish, therefore, it accumulates with age.

Tomlinson[82] reports that in the Bell River area of Canada precipitation is the source of mercury. Both methyl mercury and inorganic mercury were found in precipitation. The source of mercury in snow and rain was not known at the time of the study.

Zinc, manganese, and aluminum concentrations also increase as the acidity of lakes increases.[21] The ingestion of fish contaminated by the metals is a distinct possibility.

Another human-health aspect is the possibility that, as drinking-water reservoirs acidify, owing to acid precipitation, the increased concentrations of metals may exceed the public-health limits. The increased metal concentrations in drinking water are caused by increased watershed weathering and increased leaching of metals from household plumbing. Indeed, in New York State, water from the Hinckley Reservoir has acidified to such an extent that "lead concentrations in water in contact with household plumbing systems exceed the maximum levels for human use recommended by the New York State Department of Health."[87] The lead and copper concentrations in pipes which have stood over night (U) and those in which the water was used (F) are depicted in Table 8-8.

TABLE 8-8. LEAD AND COPPER CONCENTRATION AND pH OF WATER FROM PIPES CARRYING OUTFLOW FROM HINCKLEY BASIN AND HANNS AND STEELE CREEK BASIN

Collection site and date	Pipe condition[1]	Copper (μg/l)	Lead (μg/l)	pH
Hinckley Dam				
Nov. 21, 1974	U	600	66	---
Nov. 21, 1974	F	20	2	7.4
Nov. 7, 1974	U	460	40	6.3
Nov.7, 1974	F	37	6	6.3
Oct. 1, 1974	U	570	52	6.8
Oct. 1, 1974	F	30	5	7.1
Aug. 15, 1974	U	760	88	6.3
Aug. 15, 1974	F	40	2	6.3
Amsterdam				
Jan. 6, 1975	U	2900	240	4.5
Jan. 6, 1975	F	80	3	5.0

[1]U, unflushed; (water stands in pipes all night) F, flushed
From reference 88

8.2.5 Acidification of Lakes

Precipitation enters lakes directly or as runoff from the watersheds which surround the lakes. The relative magnitude of the influents from the two sources is dependent on the surface area and volume of the lake, the size of the watershed, and the type of soil.[78] The watershed plays a dominant role in determining the composition of water entering the lake when the watershed is large and the lake area and volume are small. Precipitation plays a dominant role when lake areas are large in comparison to the size of the watershed. However, watersheds with poor soil and vegetational cover usually have little influence on the composition of the influents.[78]

The acidity of freshwater lakes reflects both the acidity of precipitation and the capability of the watershed and the lake itself to neutralize the incoming acid.[75] Schofield[32,79] has pointed out that the situation is analogous to a gigantic, regional-scale titration with the lakes serving as the receiving vessels for the acidity coming from the atmosphere. The titration endpoint of each lake is predetermined by its hydrology and the capacity of the soils in the drainage basin to assimilate the incoming acid.[35] Hardness of water is closely correlated with alkalinity and, therefore, with the capacity of water to neutralize (buffer) the acidity of precipitation entering a lake. Chemical weathering and ion exchange are two processes in watersheds that act to neutralize incoming acidic precipitation.[75] In soils, the cation exchange capacity and the buffering capacity are closely related. The rate at which the two processes take place depends on the physical and chemical nature of the bedrock, the overburden, and the soils. In areas with no appreciable amounts of carbonate-bearing materials, for example large parts of southern Norway, chemical weathering and ion exchange processes proceed too slowly to neutralize all of the incoming acid.[75]

Bicarbonate provides most of the buffering capacity in soft water lakes. The concentration of bicarbonate in these waters is highly pH dependent. Therefore, as pH of runoff and lake waters decreases the bicarbonate concentration decreases. Sulfate, supplied by acidic precipitation replaces bicarbonate and becomes the major ion.[75] In areas where the watersheds and lakes do not have the capability of neutralizing the incoming acid, acidic precipitation causes the pH of lakes to drop below 5.0. Bicarbonate in these lakes is essentially eliminated and no effective buffer system remains. These waters are, therefore, subject to large fluctuations in acidity in response to episodic injections of acidic pollutants such as those occurring the snowpack melts.[75]

Melting of the ice and snowpack on lakes and streams can result in a large influx of acidic pollutants.[32,37,75,79,80] streams, rivers, and small ponds, which usually are only slightly acidic or may even be alkaline, are subject to sharp increases in acidity for brief periods during the late winter and early spring thaws.[32,79] These episodes of high acidity result from the release of acids stored in the winter snowpack. Galvin and Cline[81] measured anions in the snow cover of the Adirondack Mountains and noted nitrates and sulfates were the only ones present in appreciable quantities. The concentrate of nitrates was greater than sulfate. The absence of chloride indicated that the sources of nitrate and sulfate were inland. Hagen and Langeland[80] also noted the snow covering Norwegian lakes and brooks in winter and spring contained great quantities of $SO_4^{=}$, NO_3^{-}, Zn and Pb, and were associated with high acidity. While studying the effect of the pH of snow and ice on lakes in Norway, it was observed that no change in either acidity or conductivity occurred between January and March, but in April and early May the pH decreased from 5.4 to 4.2 and the conductivity increased from 15 to 40. After the ice had melted at the end of May, the pH distribution returned to a normal 6.0.

Water from the snowmelt in the early stages percolates down through the snowpack and leaches the stored acids. The first flush of melt water is typically a highly concentrated, acid solution having pH levels of 3.0 to 3.5.[79] As the thaw ends, most of the pollutants have been removed from the remaining snow and the dilute melt water approaches the composition of distilled water with pH in the range of 5 to 6.

Tomlinson[82] studied the effects of the spring thaw of snow on the Bell River, a tributary of the Nottaway River, which flows into the Hudson Bay in Northern Quebec Province. The Bell River is a soft water river, and it was noted that its pH changed with the seasons. Throughout most of the year the pH values range from 6.1 to 6.5, but in the spring the values decrease due to melting snow. On april 19, 1977, the pH of two small creeks that flow into the Wedding River was 4.0 and 3.8, respectively while the pH of the Wedding River which flows into the Bell River, was 5.7. The pH of the Bell River was 6.1. By the following week (April 25, 1977), the ph of the Bell River had dropped to 5.6 while that of the creeks had moderated and was now 4.9 and 4.8, respectively. The pH of the Wedding River was 5.8. It was noted that the pH of precipitation occurring in the thinly wooded area surrounding the Bell River ranged from 4.1 to 4.7. The seepage of the acid through the snow results in the first runoff in the spring usually being somewhat lower in pH.

Laboratory and lysimeter experiments comparing the melting of snow with the time of release of 14 chemical elements in the snowpack conducted in Norway showed that the first 30 percent of meltwater contained 44 to 97 percent of the total amount of chemicals measured. No significant loss of water of or H^+, SO_4, NO_3, NH_4, and Pb ions occurred during the winter.[89] Observations indicated that a snowpack with a bulk pH of 4.4 could give rise to an initial

meltwater "wave" of pH 4.1. In lakes, the meltwater changes not only the pH, but the chemical composition, also.[89]

Strong acids, such as sulfuric and nitric are not the only acids contributing to lake acidification. Concentrations of weak and strong acids in the surface waters of the Tovdal River were measured during snowmelt. Though the strong acid anions, sulfate, and nitrate come largely from precipitation, the weak acids, humic and fulvic, are produced by biodegradation of vegetable material.[90] Inorganic weak acids based on hydrated alumininum, iron, and species of silica are also present. The presence of the weak acids is significant because they contribute to the hydrogen ion concentration and because they give an indication of the ground interaction effects.[90]

Sudden episodic drops in pH due to snowmelt and the injection of large concentrations of H^+ ions are the cause of massive fish kills which often occur at that time; fish are unable to adapt to the sudden pH change.[16,20,32,33,75,76,80] The sudden influx of H^+ ions also causes changes in pH and chemical composition of lakes for a short period of time even though they may normally have a circumneutral pH.

In general, acidification of surface waters by acidic precipitation in geologically sensitive regions is a continuous process involving water quality changes. The process which is analogous to the acidimetric-titration of a bicarbonate solution can be divided into three broad states that define the nature extent of water quality change and the associated biological inpacts.[94] In the initial stage, a decrease in alkalinity occurs, but the pH remains above 6.0 and bicarbonate buffering is maintained. The second stage is characterized by a loss of bicarbonate buffering and severe temporal pH fluctuations occur. Reproductive inhibition and episodic fish kills may initiate the

failure of recruitment and the eventual extinction of fish populations may begin at this stage. The third and final stage is characterized by a chronically depressed pH and an increase in concentrations of toxic metals. Fish have usually disappeared from waters when this stage of acidification is reached.[94]

8.3 SENSITIVE AREAS

8.3.1 Aquatic Ecosystems

Why do some lakes become acidified by acidic precipitation and others not? What determines susceptibility? Are terrestrial ecosystems likely to be susceptible; if so, which ones?

The sensitivity of lakes to acidification is determined by: (1) the acidity of both wet (precipitation) and dry deposition, (2) the hydrology of the lake, (3) the soil system and canopy effects, and (4) the surface water. Given acidic precipitation, the soil system and associated canopy effects are most important. The hydrology of lakes includes the sources, amounts and pathways of water entering and leaving a lake, while the capability of a lake and its drainage basin to neutralize acidic contributions as well as the mineral content of its surface water is largely governed by the composition of the bedrock of the watershed[51,75,92] as the chemical weathering of the watershed strongly influences the salinity (ionic composition) and the alkalinity (hardness and softness) of the surface water of a lake.[51,75,92] The cation exchange capacity of the watershed and the alkalinity of the surface water determine the ability of a lake to neutralize the acidity of precipitation.

Lakes vulnerable to acidic precipitation have been shown to have watersheds whose geological composition is highly resistant to chemical weathering.[75,78,92] In addition, the watersheds of the vulnerable lakes usually have thin, poor soils and are poorly vegetated. The cation exchange capacity of such soils is poor and, therefore, its buffering capacity is poor.[32,92]

Wright and Henriksen[92] point out that the chemistry of Norwegian lakes could be accounted for primarily on the basis of bedrock geology. They examined 155 lakes and observed that 59 of them lay in granite or felsic gneiss basins. Water in the lakes was low in most major ions and had low electrical conductivity. (The fewer the minerals in water the poorer its conductivity.[51]) The waters in the lakes surveyed were "among the softest waters in the world."[92] Sedimentary rocks generally weather readily, whereas igneous rocks are highly resistant. The Adirondacks, as pointed out by Schofield,[31,32] have granite bedrock with much of the area covered with a mantle of mixed gneisses. Shallow soils predominate in the area.

Limestone terrains are capable of buffering intense concentrations of acids and glacially derived sediment has been found to be more important than bedrock in assimilating acidic precipitation in the Canadian Shield area.[93] Generally, however, bedrock geology is the best predictor of the sensitivity of aquatic ecosystems to acidic precipitation.[94]

Areas with aquatic ecosystems that have the potential for being sensitive to acidic precipitation are shown in Figure 8-8. In Figure 8-8, the shaded areas on the map indicate that the bedrock is composed of igneous or metamorphic rock while in the unshaded areas it is of calcareous or sedimentary rock. Metamorphic and igneous bedrock weathers slowly, therefore, lakes in areas with this type of bedrock would be expected to be dilute and of low alkalinity (<0.5 meq HCO_3^-/liter).[78] Galloway and Cowling verified this hypothesis by compiling alkalinity data. The lakes having low alkalinity were concurrent with the regions having igneous and metamorphic rock.[78]

Henriksen[96] has developed a lake acidification "indicator model" using pH-calcium and calcium-alkalinity relationships as an indicator for determining

Figure 8-8. Regions in North America with lakes that are sensitive to acidification by acid precipitation.[78]

sensitive lake districts. The indicator is based on the observation that in pristine lake environments (e.g., NW Norway or the Experimental Lakes Area in NW Ontaria, Canada) calcium is accompanied by a proportional amount of bicarbonate, because carbonic acid is the primary chemical weathering agent. The pH - calcium relationship found for such regions is thus defined as the reference level for unacidified lakes. Acidified lakes (e.g., SE Norway and the Adirondack region) will exhibit lower pH than the reference lakes, at comparable calcium levels, due to the replacement of bicarbonate by strong acid anions.

Schofield[76] has illustrated the use of Henriksen's model by using data from Norway, the Adirondacks and the Experimental Lakes Area of Ontario, Canada. In the acidified lakes sulfate replaces bicarbonate as the major anion present (Figures 8-9 and 8-10) and is derived primarily from precipitation (Figure 8-11). Since the bicarbonate lost in acidified lakes has been replaced by an equivalent amount of sulfate, the concentration of excess sulfate serves as an index of the amount of acidification that has taken place. Henriksen[96] compared estimated acidification in Norwegian lakes to the pH and sulfate concentrations in the prevailing precipitation and concluded that significant lake acidification had occurred in areas receiving precipitation with an annual average (volume weighted) pH below 4.6 to 4.7 and sulfate concentrations above 1 mg/liter. This approximate threshold of precipitation acidity may be applicable to sensitive lake districts in other regions as well. For reference, the estimated annual, bulk deposition sulfate loading levels for the acidified lake districts in the Adirondacks and southern Norway are approximately 30 to 60 kg SO_4/ha., as compared with only 5 - kg SO_4/ha. in the reference areas of northern Norway and the Experimental Lakes Area in Ontario. A comparison of lake pH with regional sulfate loading levels in Sweden suggests that critical loading levels for sensitive lakes are in the range of 15 to 20 kg SO_4/ha./yr.

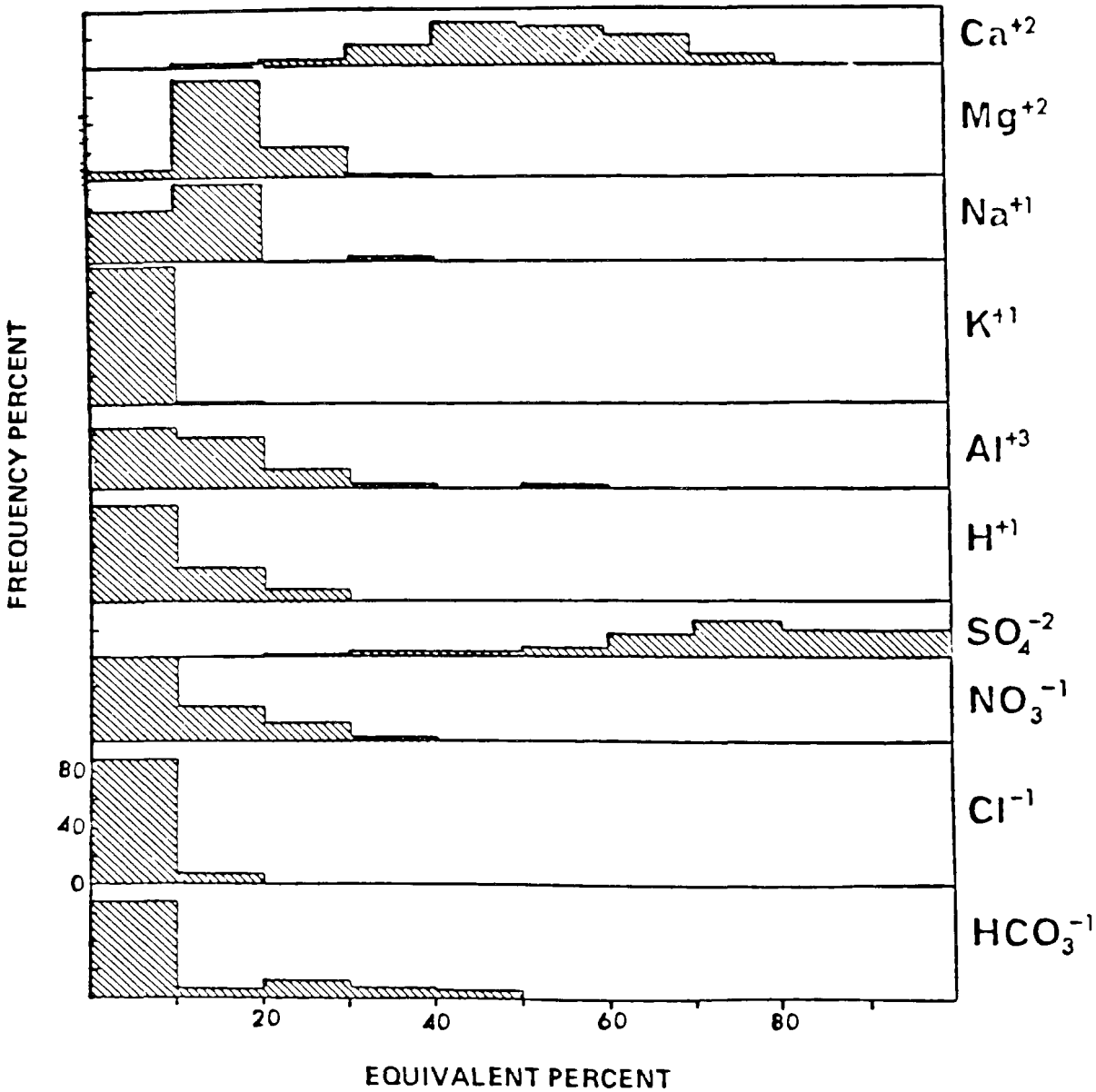


Figure 8-9. Equivalent percent composition of major ions in Adirondack lake surface waters (215 lakes) sampled in June 1975.[76]

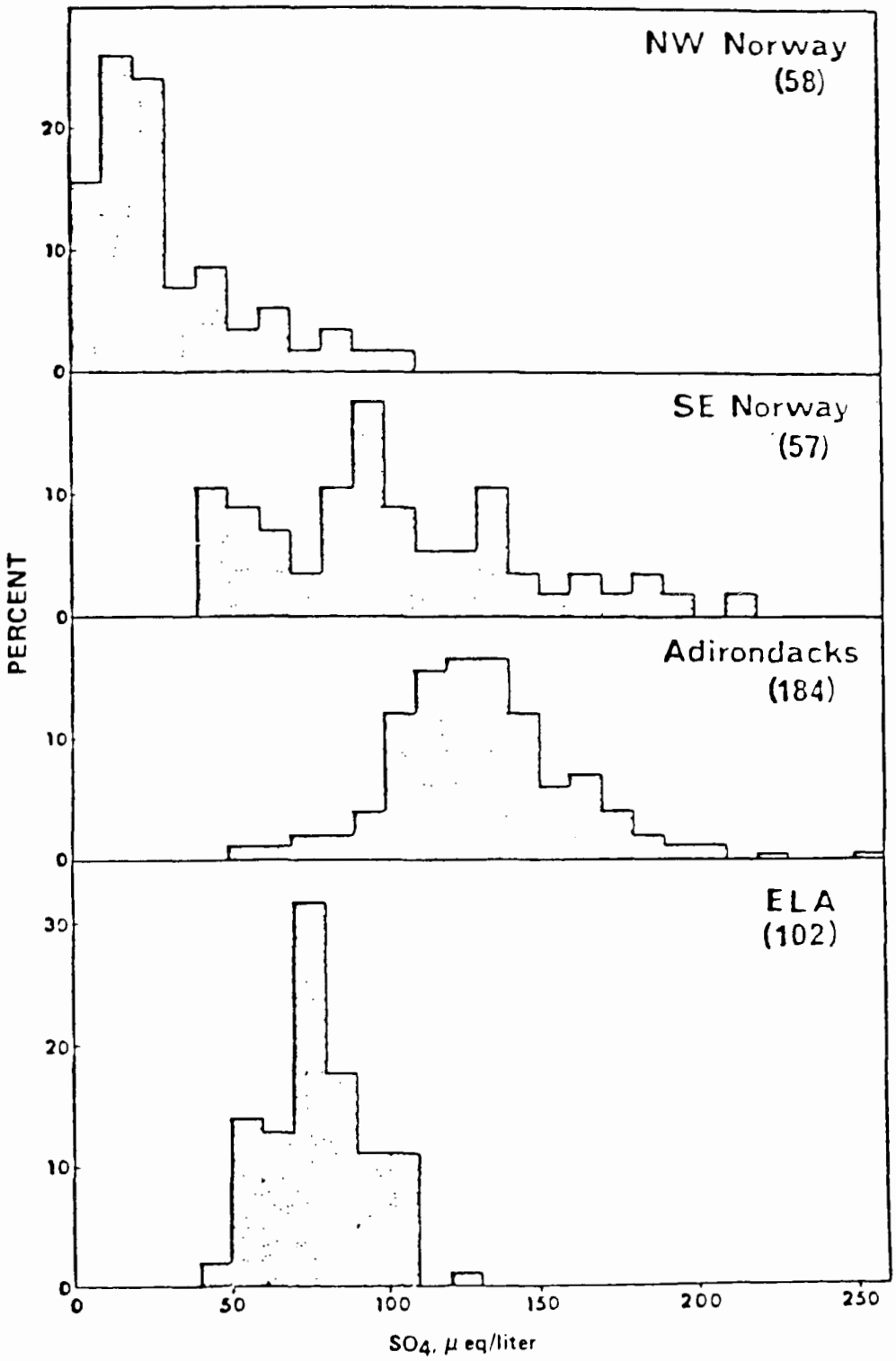


Figure 8-10. Percent frequency distribution of sulfate concentrations in surface water from lakes in sensitive regions.[76]

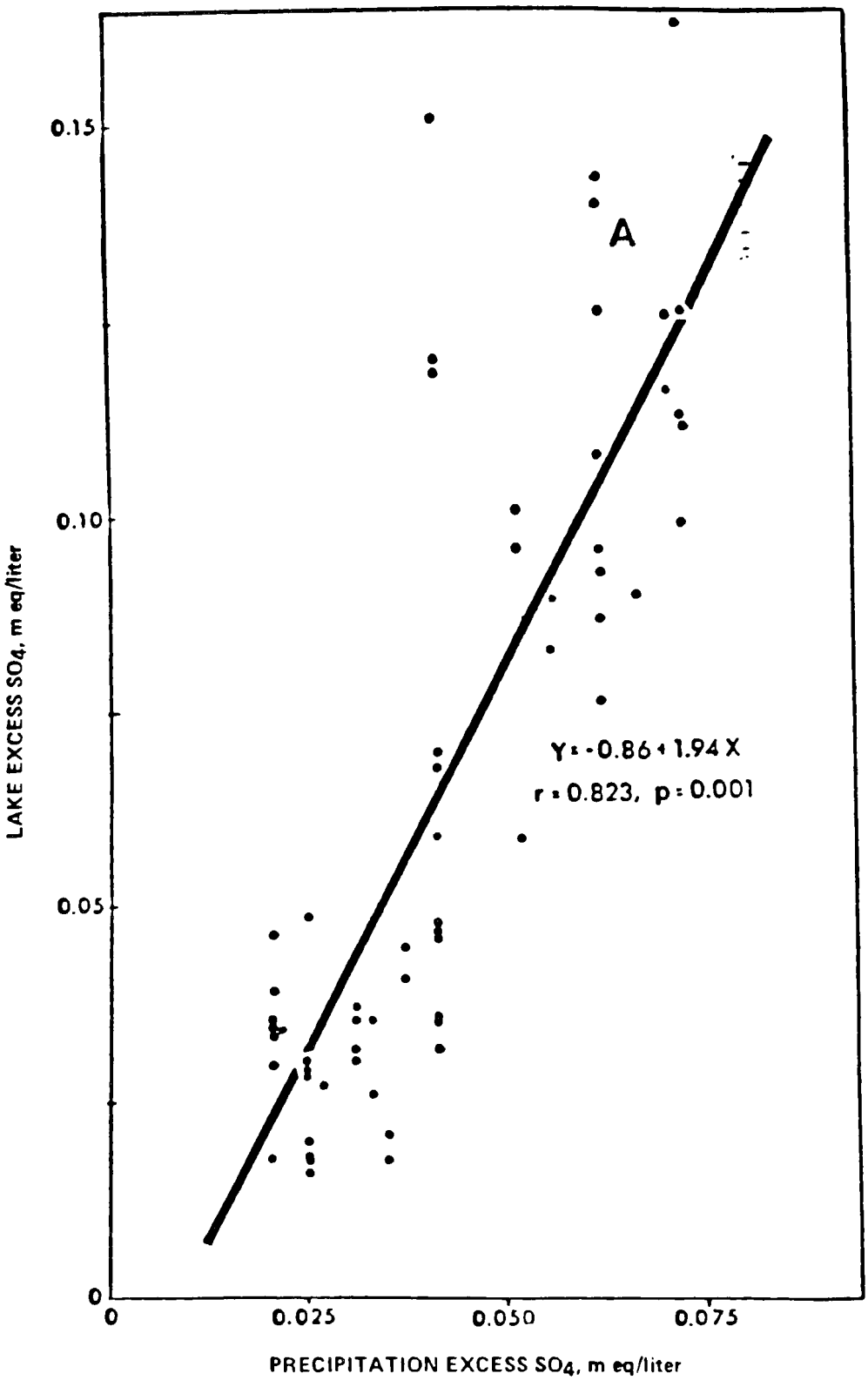


Figure 8-11. Relationship between precipitation excess sulfate and lake excess sulfate for lakes in Norway and the Adirondacks. (A = mean lake and precipitation sulfate for the Adirondack region.)[76]

Though bedrock geology generally is a good predictor of the susceptibility of an area to acidification due to acidic precipitation, other factors also have an influence. Florida, for example, is underlaid by highly calcareous and phosphate rock suggesting that acidification of lakes and streams is highly unlikely. Many of the soils, however, (particularly in northern Florida) are very mature, have been highly leached of calcium carbonate, and, as a result, some lakes in which groundwater inflow is minimal have become acidified.[94] Conversely, there are areas in Maine with granitic bedrock where lakes have not become acidified despite receiving precipitation with an average pH of approximately 4.3 because the drainage basins contain lime-bearing till and marine clay.[95] Small amounts of limestone in a drainage basin exert a strong influence on water quality in terrain which would otherwise be vulnerable to acidification. Soils in Maine in the areas where the pH of lakes has decreased due to acidic precipitation are immature, coarse, and shallow and are derived largely from granitic material and commonly have a low capacity for assimilating hydrogen ions from leachate and surface runoff in lake watersheds.[95a] Consequently, when predicting vulnerability of a particular region to acidification, a careful classification of rock mixtures should be made. Rock formations should be classified according to their potential buffering capacity and the type of soil overlying the formations should be noted.

8.3.2 Terrestrial Ecosystems

Predicting the sensitivity of terrestrial ecosystems to acidic precipitation is much more difficult than for aquatic ecosystems. With aquatic ecosystems it is possible to compare affected ecosystems with unaffected and note where the changes have occurred. With terrestrial ecosystems, comparisons are difficult to make because the effects of acidic precipitation have been difficult to detect. Therefore, predictions regarding the sensitivity of

terrestrial ecosystems must, as much as possible, use the data which links the two ecosystems, bedrock geology. Since, in most regions of the world, bedrock is not exposed but is covered with soil, it is the sensitivity of different types of soil which must be assessed. Therefore, the first step is to define "sensitivity" as it is used here in relation to soils and acid precipitation. Sensitivity of soils to acidification, alone, though it may be the most important long-term effect, is too narrow a concept. Soils influence the quality of waters in associated streams and lakes and may be changed in ways other than simple pH-base saturation relationships, e.g., microbiological populations of the surface layers, accelerated loss of aluminum by leaching. Therefore, criteria need to be used that would relate soil "sensitivity" to any important change brought about in the local ecosystem by acid precipitation.[97]

Soils are the most stable component of a terrestrial ecosystem. Any changes which occur to this component would probably have far-reaching effects. McFee[97] has listed four parameters which are of importance in estimating the sensitivity of soils to acidic precipitation. They are:

1. The total buffering or cation exchange capacity which is provided primarily by clay and soil organic matter.

2. The base saturation of that exchange capacity which can be estimated from the pH of the soil.

3. The management system imposed on the soil, is it cultivated and amended with fertilizers, lime, renewed by flooding or by other additions?

4. The presence or absence of carbonates in the soil profile.

In order that the factors listed above could be used in broad scale mapping of soils, McFee evaluated them for wide applicability and ready availability. In natural soils the most serious effects would be caused by changes in pH or due to leaching of soil minerals. Susceptibility of soils to

changes in either of these categories is most closely associated with the cation exchange capacity (CEC). Soil with a low CEC and a circumneutral pH is likely to have the pH rapidly reduced by an influx of acid. Soils with a high CEC, however, are strongly buffered against pH changes or changes in the composition of the leachate. Acid soils with a pH near that of acidic precipitation will not rapidly change pH due to acidic precipitation, but will probably release AL^{+3} ions into the leachate.[97] Soils having low CEC's are usually low in plant nutrients, therefore, significant changes in their productivity could occur with only a slight loss of nutrients.[97]

Even though CEC or buffering capacity does not completely define soil sensitivity to possible influents of acid, for the reasons given above it was the primary criterion used by McFee for the regional mapping of soil sensitivity to acidic precipitation in the eastern United States. Further, though it is frequently stated in much of the literature that soils with low CEC or sandy soils having low organic matter are likely to be most susceptible to effects of acidic precipitation, the "low CEC" values are not quantified. To develop a working set of classes, it was necessary to make certain assumptions and "worst case" calculations. Since soils in general are rather resistant to change due to additions of acid, a fairly high addition of acid was assumed and the question asked, "What is the maximum effect that it can have on soil, and how high would the CEc have to be to resist that effect?"[97]

To determine sensitivity of a soil, McFee arbitrarily chose a span of 25 years. It was hypothesized that a significant effect could occur if the maximum influx of acid (100 cm of precipitation at pH 3.7 per annum) during that period equaled 10 to 25 percent of the cation exchange capacity in the top 25 cm of soil. Soils are considered slightly sensitive if the top 25 cm of soil has an average CEC of 6.2 to 15.4 me/100 g (also assumes a bulk density

of 1.3 g/cc). If the same influx of acid exceeds 25 percent of the CEC in the top 25 cm, i.e., when the CEC is less than 6.2 me/100 g, the soils are considered sensitive.

Based on the above concepts, the soils of the eastern United States including farm effects were mapped (Figure 8-12) by McFee. The areas containing most of the soils potentially sensitive to acidic precipitation are in the upper coastal plains and Piedmont regions of the southeast, along the Appalachian Highlands, through the east central and northeastern areas, and in the Adirondack Mountains of New York.[97] The present limited state of knowledge regarding the effects of acidic precipitation on soils makes a more definitive judgment of the location of areas with the most sensitive soils difficult at the present time.

8.3.3 Aquatic and Terrestrial

The Boundary Waters Canoe Area Wilderness (BWCAW) and the Voyageurs National Park of Minnesota lies along 176 km (110 miles) of the Minnesota-Ontario border. It varies from 16 to 48 km (10 to 30 miles) in width and includes 439,093 ha (1,085,000 acres) of typical northwoods terrain with more than one third of the area composed of island-studded lakes. Glass and Loucks[98] assessed the BWCW-Voyageurs National Park area in order to predict the sensitivity of the region to emission from a major coal-fired power plant. Though Glass and Loucks[98] were concerned with the effects of all emissions from the power plant, one portion of their report estimates the sensitivity of the area to acidic deposition. To estimate the probable impact of acidic precipitation, Glass and Loucks used the basic concepts regarding sensitivity of aquatic ecosystems as discussed previously in this section on sensitivity. Taking the findings associated with the acidification of aquatic ecosystems in north-

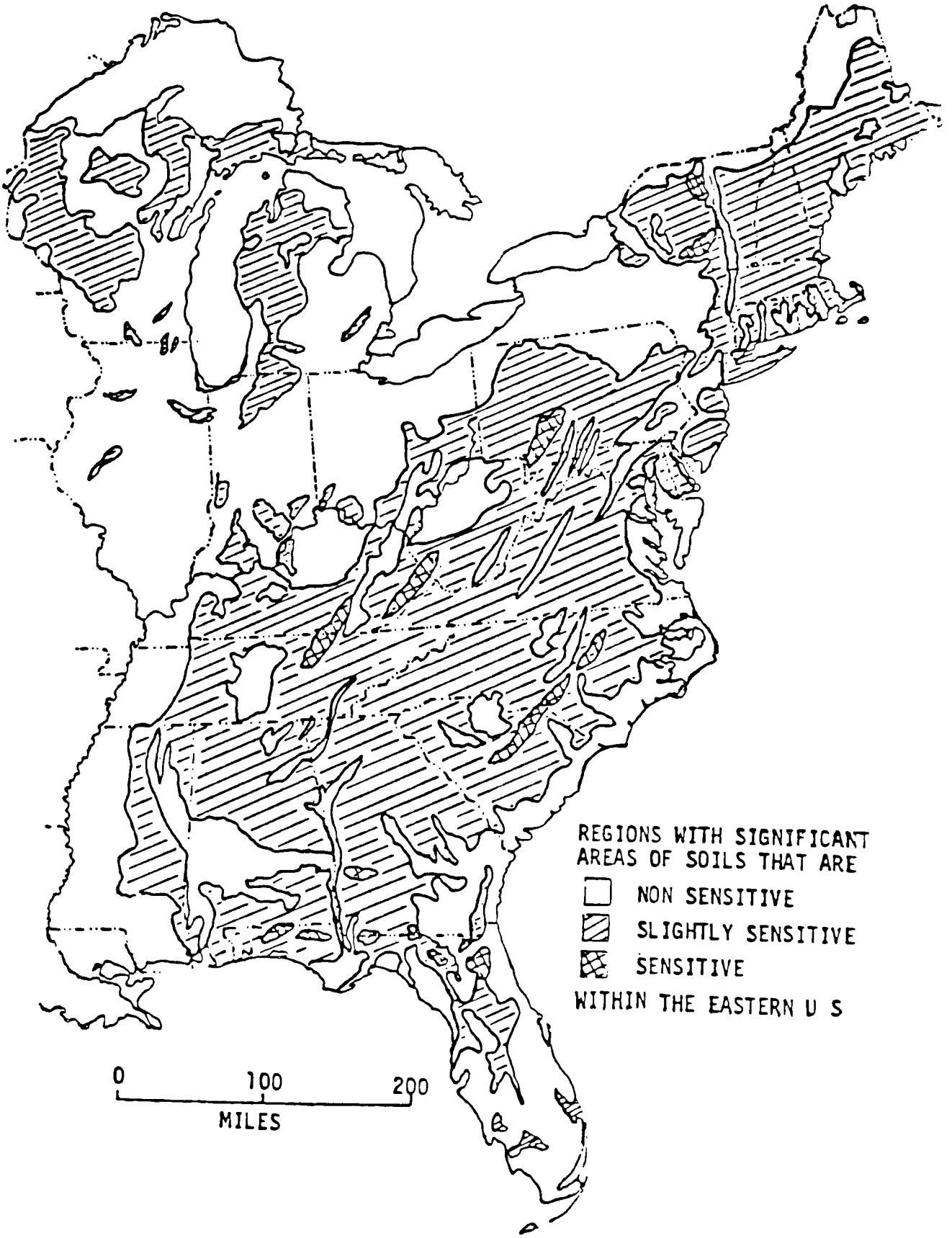


Figure 8-12. Soils of the Eastern United States sensitive to acid rainfall.[97]

eastern North America and Europe and applying these to the ecological receptors in the BWCA-Voyageurs National Park region they arrived at certain conclusions regarding the aquatic and terrestrial ecosystems in the area. They felt that 1) the vulnerable lakes in the region (poorly buffered headwater lakes with small watersheds and shallow soils of low buffering capacity) are already being affected by acidity from atmospheric sources. 2) Given the probable changes in the acidity of water, the responses of the biota in the aquatic ecosystem will result in changes similar to those seen in the acidified lakes of the eastern United States and Canada. These changes will occur over different time spans: for some lakes, several years; for others, several decades. 3) Probable increases in the acidity of the water will increase the severity of seasonal events such as acid flushing in the spring due to snow melt. 4) Increased acidity is likely to result in detrimental levels of aluminum and of other trace elements in the lake water by increasing leaching and creating more toxic forms of these elements.

The possible impact on the terrestrial ecosystems are more nebulous than for the aquatic areas. The structure of the soils in the region (mostly shallow (0 to 46 cm), of glacial origin, coarse textured, derived from granites and other acid bedrock types, low in cations and available nitrogen, and low in percentage base saturation suggests that acidic precipitation could result in the mobilization of elements toxic to terrestrial vegetation. Runoff wastes could also carry the same elements into small lakes. Small additions of acidity to the thin, rocky soils common in the BWCA, coupled with the geochemical weathering changes that are probable can be expected to have relatively rapid and irreversible effects on outputs from the nutrient cycles of these ecosystems. These changes will affect groundwater quality and produce

soil-mediated changes in cycling rates within the ecosystems. Although the net changes in cation leaching due to lowered soil pH are difficult to predict, H^+ additions to some soils will facilitate leaching of essential plant nutrients.

Lichens are an important part of the BWCA-VNP biota and make up the principal plant cover on 5 percent of the land area. Lichen species also have been shown to be an important source of nitrogen (through N fixation) in a number of nitrogen-limited coniferous forest areas. Acidic precipitation, as well as, sulfur oxides, could result in injury to these plants.

The conclusions reached by Glass and Loucks[98] can only be verified by long-term studies of the area.

8.4 EFFECTS ON TERRESTRIAL ECOSYSTEMS

Determining the effects of acidic precipitation on terrestrial ecosystems is not an easy task. In aquatic ecosystems it has been possible to measure change in pH that occur in acidified waters and then observe the response of aquatic ecosystems to the shifts in pH. In the case of terrestrial ecosystems the situation is more complex since no component of terrestrial ecosystems appears to be as sensitive to acidic precipitation as poorly buffered aquatic ecosystems.

Acidic precipitation may produce a direct effect on plants and the ecosystem in general or the effects may be indirect. Direct effects frequently will also result in many indirect effects. At the present time it has not been possible to observe or measure changes in naturally occurring terrestrial ecosystems which can be attributed directly to acidic precipitation. This does not mean that effects do not exist, rather that the capability of observing and measuring them is limited.

8.4.1 Effects of Acidic Precipitation on Vegetation

The atmosphere, as well as the soil, is a source of nutrients for plants. Chemical elements reach the plant surface via wet and dry deposition. Sulfates

and nitrates are not the only components of precipitation falling onto the plant surface. Other chemical elements at least partially soluble in water are deposited on the surface of vegetation and may be assimilated by it, usually through the leaves. An average rain drop deposited on trees in a typical forest washes over three tiers of foilage before it reaches the soil. The effects of acidic precipitation may be beneficial or deleterious depending on its chemical composition, the species of plant on which it is deposited and the physiological condition and maturity of the plant.[78]

It has generally been assumed that the free hydrogen ion concentration in acidic precipitation is the component that is most likely to cause direct, harmful effects on vegetation.[99] Experimental studies support this assumption; however, to date, there are no confirmed reports of exposure to ambient acidic precipitation causing foliar symptoms on field grown vegetation in the continental U.S.[99]

8.4.1.1 Direct Damage to Tissues--The formation of lesions or zones of dead tissues on the upper epidermis at the bases of trichomes, in guard cells and in epidermal cells above veins is the most frequently reported response to experimental exposure with simulated acidic rain.[99,107] A large percentage of the leaf area may exhibit lesions after repeated exposures to simulated acid rain at pH concentrations of 3.0, 2.7, 2.5 and 2.3.[102,108] Pinto bean leaves which have reached full expansion exhibited the greatest amount and most pronounced visible leaf injury.[100-102] Most injury to foliage by simulated acidic rain occurs on expanding or recently expanded leaves. Birch seedlings 14 days old are more sensitive than six-weeks-old seedlings.[104] Evans et al.[101] using six clones of Populus spp. hybrids have shown that leaves that had just reached full expansion were more sensitive to simulated acidic rain

than were unexpanded or those which were fully expanded. On two of the clones, gall formation due to abnormal cell proliferation and enlargement occurred. Hindawi and Ratsch[109] demonstrated that needle elongation will be inhibited if simulated acid rain solutions are applied to immature pine fasicicles.

In leaves injured by simulated acidic rain, collapse and distortion of epidermal cells on the upper surface is frequently followed by injury to the palisade cells and ultimately both leaf surfaces are affected.[110] Reductions in growth and yield have not been unequivocally associated with leaf injury. Premature abscission of leaves of bean plants has been associated with simulated acid rain.

Foliar response to acidic precipitation is dependent on the temporal and physical characteristics of the events. Duration and frequency of exposure, length of time between rain events and intensity of rainfall all influence the development of foliar symptoms.[99a] The acid content and size of rain drops may be of importance in producing effects. Environmental conditions during and after a precipitation event effect the response of plants by altering physiological processes, the degree of contact with rainfall, the amount of liquid remaining on leaf surface, or the rate of evaporation after rainfall has terminated.[99a] Table 8-9 summarizes the foliar effects of simulated acidic precipitation.

8.4.1.2 Leaching of Nutrients Leaching of chemical elements from exposed plant surfaces is one of the more important effects rain, fog, mist and dew have on vegetation. Substances leached include a great diversity of materials. All of the essential minerals, amino acids, carbohydrate growth regulators, free sugars, pectic substances, organic acids, vitamins, alkaloids and alleopathic substances are among the materials which have been detected in plant leachates.[113]

TABLE 8-9. MAXIMUM pH CONCENTRATION PRODUCING INJURY TO VEGETATION AFTER DIRECT CONTACT WITH SIMULATED ACIDIC PRECIPITATION

Effect	Receptor	pH value	Reference
Foliar lesions	Eastern white pine	2.3	108
Foliar aberrations decrease in growth	Bean	2.5	103
Foliar lesions, plasmolysis of cells, reduction in dry weight	Bean	2.5	108
Foliar necrotic spots	Scots pine birch (*Betula pubescens* Ehrb)	2.5	112
Necrotic lesions and chlorotic areas in leaves	Soybean	3.0	106
Foliar lesions, decrease in growth	Yellow birch (*Betula alleghaniensis* Britt)	3.1	104
Foliar lesions	Bean, sunflower	3.1	102
Bifacial necrosis	Oak (*Quercus phellos*)	3.2	109a
Foliar lesions	Hybrid poplar	3.4	101
Foliar lesions	Sunflower	3.4	99
Reduction in dry weight	Bean	4.0	111

Many factors influence the quantity and quality of the substances leached from foliage. They include factors associated directly with the plant as well as those associated with the environment. Not only are there differences among species with respect to leaching, but individual differences also exist among individual leaves of the same crop and even the same plant, depending on the physiological age of the leaf. Young, actively growing tissues are relatively immune to leaching of mineral nutrients and carbohydrates, while mature tissue which is approaching senescence is very susceptible. The stage of plant development, temperature, and rain water falling on foilage and running down plant stems or tree bark influences leaching. Rainwater, which naturally has a pH of about 5.6, washing over vegetation may become enriched with substances leached from the tissues.[114]

Leaching of organic and inorganic materials from vegetation to the soil is part of the normal functioning of terrestrial ecosystems. The nutrient flow from one component of the ecosystem to another is an important phase of nutrient cycling.[115,116] Plant leachates have an effect upon soil texture, aeration, permeability, and exchange capacity. Leachates, by influencing the number and behavior of soil microorganisms, affect soil-forming processes, soil fertility, susceptibility or immunity of plants to soil pests and plant chemical interactions.[113]

It has been demonstrated that precipitation of increased acidity can increase the leaching of various cations and organic carbon from the tree canopy.[112,117] Foliar losses of potassium, magnesium, and calcium from bean plants and maple seedlings were found to increase as the acidity of an artificial mist was increased. Below a pH of 3.0 tissue damage occurred, however, significant increases in leaching were measured at a pH 3.3 and 4.0 with no observable

tissue damage.[117] Hindawi et al.[108] also noted that as the acidity of acid mist increased so did the foliar leaching of nitrogen, calcium, phosphorous, and magnesium. Potassium concentrations were not affected while the concentration of sulfur increased. Abrahamsen and Dollard[118] in experiments using Norway spruce (Picea abies (L.) Karst.) observed that despite increased leaching at the most acid treatment, there was no evidence of change in the foliar cation content. Wood and Bormann[107] using Eastern white pine (Pinus strobus L.) also noted no significant changes in calcium magnesium and potassium content of needles. Tukey[113] states that increased leaching of nutrients from foilage can accelerate nutrient uptake by plants. No injury will occur to the plants as long as roots can absorb nutrients to replace those being leached. To date, the effects of the increased leaching of substances from vegetation by acidic precipitation remains unclear.

8.4.1.3 Indirect Effects on Plants--Acidic precipitation can have beneficial effects on plants. Wood and Bormann[107] reported an increase in needle length and the weight of seedlings of Eastern white pine with increasing acidity of simulated precipitation where sulfuric and nitric acid were used to acidify the mist. Increased growth was attributed to increased NO_3^- application. Irving and Miller[119] observed that the acidic simulant had a positive effect on productivity of field-grown soybeans as reflected by seed growth. Increased growth was attributed to a fertilizing effect extending the pod-filling period. Irving and Miller,[119] in the same study, also exposed soybeans to SO_2 and acidic precipitation. No visible injury was apparent in any of the plots, however, a histological study revealed significant increases in the number of dead mesophyll cells in all plots when compared to the control. The proportion of dead mesophyll cells of plants exposed to acid rain and SO_2 combined was more than the additive when compared to the effects of each taken singly.

Shriner[120] studied the effect of acidic precipitation on host-parasite interactions. Simulated acid rain with a pH of 3.2 inhibited the development of bean rust and production of telia (a stage in the rust life cycle) by the oak-leaf-rust fungus Cronartrium fusiforme Hedge and Hung. It also inhibited reproduction of root-knot nematodes and inhibited or stimulated development of halo blight of bean seedlings depending on the time in the disease cycle during which the simulated acidic rain was applied. Shriner[120] also observed that root nodulation by Rhizobium on common beans and soybeans was inhibited by the simulated acidic rain.

Plants such as mosses and lichens are particularly sensitive to changes in precipitation chemistry because many of their nutrient requirements are obtained directly through precipitation. These plant forms are typically absent from regions with high chronic SO_2 air pollution and acidic precipitation. Gorham[121] and Giddings and Galloway[122] have written reviews concerning this problem. Most investigations on the effects of air pollution on epiphytes have dealt with gaseous pollutants. Very few studies have considered acidic precipitation. Denison et al.[122a] however, did observe that the nitrogen-fixing ability of the epiphytic lichen Lobaria oregana was reduced when treated with simulated rainfall with a pH of 4.0 and below. Investigations concerning the effects of acidic precipitation on epiphytic microbial populations are very few.[118]

Limited fertilization could occur in the bracken fern Pteridium aquilinum under conditions of acidic precipitation (pH and sulfate concentrations) that prevail in the northeastern United States. Evans and Bozzone,[123] using buffered solutions to simulate acidic precipitation, observed that flagellar movement of sperm was reduced at pH levels below 5.8. Longevity of motility was reduced so

that no movement was observed 8 to 10 and 5 to 7 minutes after exposure to pH 5.6 and 5.2, respectively. Gametophyte survival and development was not affected by solutions of pH 5.8 to 2.2, however, fertilization was reduced after exposure to pH's below 4.2. Sporophyte production was also reduced by 50 percent at pH levels below 4.2 when compared to 5.8. Addition of sulfate (86 μM) decreased fertilization at least 50 percent at all pH concentrations observed.

In another study, Evans and Bozzone[124] observed that additions of one or more anions produced additive effects at all pH concentrations. Both sperm motility and fertilization in gametophyte of Pteridium aquilinum were reduced when anions of sulfate, nitrate, and chloride were added to buffered solutions. sulfate alone at 43.3 μM (equivalent to the sulfate concentration in rain in the northeastern United States) decreased sperm motility approximately 40 percent when compared with plants exposed to solutions without sulfate.

The effects of acidic precipitation on forest tree growth has been investigated in experiments using simulated acidic rain, and by comparing development of tree rings in the past with present ring formation in areas with different amounts of hydrogen ion deposition or in areas assumed to have different sensitivities to acidic precipitation.[118] Using the tree ring method, Jonsson and Sundberg[105] analyzed forest growth in southern Sweden from 1896 to 1965 and observed a 2 to 7 percent decrease in growth between 1950 and 1965. They attributed the reduction in growth to acidification. Similar studies in North America and Norway have not produced similar results.[112,125,126]

Acidifying already acid forest soils by acidic precipitation or air pollutants is a slow process. Growth effects probably could not be detected for a long time. To identify the possible effects of acidification on poor

pine forests, Tam et al.[127] conducted experiments using 50 kg and 100 kg of sulfur per hectare as dilute sulfuric acid (0.4 percent) applied annually with and without NPK (nitrogen, phosphorous, potassium) fertilizer. Nitrogen was found to be the limiting factor at both experimental sites. Acidification produced no observable influence on tree growth. Lysimeter and soil incubation experiments conducted at the same time as the experiments described above suggest that even moderate additions of sulfuric acid or sulfur added to soil affect soil biological processes, particularly nitrogen turnover. The soil incubation studies indicated that additions of sulfuric acid increased the amount of mineral nitrogen but lowered the amount of nitrate.

Simulated acidic precipitation was observed to increase the growth of Scots pine saplings in experiments conducted in Norway.[118] Saplings in plots watered with acid rain of pH 3.0, 2.5, and 2.0 grew more than the control plots. The application of acid rain increased the nitrogen and sulfur content of the needles. As the acidity of the artificial rain was adjusted using sulfuric acid only, the increased growth was probably due to increased nitrogen uptake.

Increasing acidic precipitation may cause a decrease in the fertility of forest soils. Laboratory investigations by Overrein[128] have demonstrated that leaching of potassium, magnesium and calcium, all important plant nutrients, is accelerated by increased acidity of rain. Field studies in Sweden correlate decreases in soil pH with increased additions of acid.[129] On the other hand, soil fertility may increase as a result of acidic precipitation as nitrate and sulfate ions, common components of chemical fertilizers, are deposited; however, the advantages of such additions are likely to be short-lived as depletion of nutrient cations through accelerated leaching should eventually retard growth.[130]

Another major uncertainty in estimating effects of acidic rain on forest productivity is the capacity of forest soils to buffer against leaching by hydrogen ions. Where the evidence is strongest for a direct effect of acidic precipitation on forest growth (e.g., Sweden), the soils are already highly leached, and the buffering capacity has been reduced. For much of the eastern United States, however, the soils still retain the major portion of their natural buffering capacity. This may explain why effects are not yet apparent in this region. In addition, forest canopies have been found to filter 90 percent of the hydrogen ions from rain (pH 4.0) falling on the landscape during the growing season.[131] As a result, solutions reaching the forest floor are less acidic (ph 5.0). Mayer and Ulrich,[132] however, point out that for most elements the addition by precipitation (wetfall plus dryfall) to the soil beneath the tree canopy is considerably larger than that by precipitation to the canopy surface as measured by rain gauges on a non-forested area. The leaching of metabolites, mainly from leaf surfaces, and the washing out from leaves, branches, and stems of airborne particles and atmospheric aerosols intercepted by trees from the atmosphere are suggested as the reason for the mineral increase. Using element balance data, Mayer and Ulrich came to the following conclusions regarding the effect of acidic precipitation on a forest ecosystem:

> "The buffering of protons, and to a minor extent accumulation of Fe in the mineral soil, is balanced by the loss of Al, Mn and, to a smaller extent, Na, K, Ca and Mg. This is possible by the weathering of silicates, or, as in the case of K, Ca and Mg, by desorption from the exchangeable fraction.
>
> These processes definitely change the soil chemical conditions in the uppermost 1 to 2 cm of the soil. While tree growth is probably not affected by the acidification of this layer, a disturbance of all plants rooting very close to the

In addition, the acidification of soil and the associated loss of magnesium may become a problem in the supply of this nutrient element in the near future. Many needle and leaf analyses indicated this possibility. The same is true for manganese.

A forest ecosystem is a complicated biological organization. Acidic precipitation will produce some responses within the ecosystem even though it is not possible at present to evaluate the changes which occur. The determination as to whether the changes are harmful or beneficial can only be determined with certainty over a long period of time.

8.4.2 Effects of Acidic Precipitation on Soils

The active factor in the acidification of soils is the hydrogen ion (H^+). In the soil hydrogen ions are derived from the following sources:[133]

1. nutrient uptake by plants. The root acidoids adsorb cation nutrients and desorb H^+;
2. CO_2 produced by plant roots and micro-organisms;
3. oxidation of NH_4^+ and S, FeS_2, and H_2S to HNO_3 and H_2SO_4;
4. very acid litter in coniferous forests, the main acidifying source for the A and horizons;
5. atmospheric deposition of H_2SO_4 and some HNO_3, NO_x, HCl and NH_4^+ (after nitrification to HNO_3).

A gradual acidification of the soil may result from an increased influx of H^+ ions. Soils become acidic when large numbers of the exchangeable cations are hydrogen (H^+) and various forms of aluminum. Most acid soils develop due to leaching. As water containing hydrogen cations (usually from weak acids) moves through the soil, some of the hydrogen cations replace adsorbed exchangeable cations, such as Ca^{++}, Mg^{++}, K^+ and Na^+. (See Figure 8-13). The removed cations are then carried deep into the soil profile or into the ground water. In addition to the acidifying factors listed above the use of ammonium fertilizers also adds hydrogen cations to the water solution. Ammonium fertilizers are oxidized by bacteria to form nitrate (NO_3^-) and hydrogen ions

(H^+).[134] (Many areas of the United States now use anhydrous ammonia as fertilizer to prevent soils from becoming acid.) Increased leaching causes soils to become lower in the basic Ca^{++}, Mg^{++}, Na^+ and K^+ cations.[134] Sensitivity to leaching is according to the following sequence: $Na^+ >> K^+ > Mg^{2+} > Ca^{2+}$.[133]

All soils are not equally susceptible to acidification. Sensitivity to leaching and to loss of buffering capacity varies according to the type of parent material from which a soil is derived. Buffering capacity is greatest in soils derived from sedimentary rocks, especially those containing carbonates, and least in soils derived from hard crystalline rocks such as granites and quartzites.[135] Soil buffering capacity varies widely in different regions of the country (Figure 8-8.) Unfortunately, many of the areas now receiving the most acidic precipitation also are those with relatively low natural buffering capacities.

The buffering capacity of soil depends on mineralogy, texture, structure, organic matter, pH, base saturation, salt content and soil permeability. Above a pH of 5.5 virtually all of the H^+ ions, irrespective of source are retained by ion exchange and chemical weathering. Below pH 5.5, the retention of the H^+ ion decreases with the soil pH in a manner determined by the composition of the soil.[134] With a successive drop in the soil pH below 5.0, an increasing proportion of hydrogen ions (H^+) and deposited sulfuric acid will pass through the soil and acidify run off water.[134] The sensitivity of different soils based on pH, texture and calcite content is summarized in Table 8-10.

Norton[136] has reviewed the potential effects of acidic rain on soils (Table 8-11). Most of the available information is from northern latitudes; much less in known about soils of temperate regions, where the largest

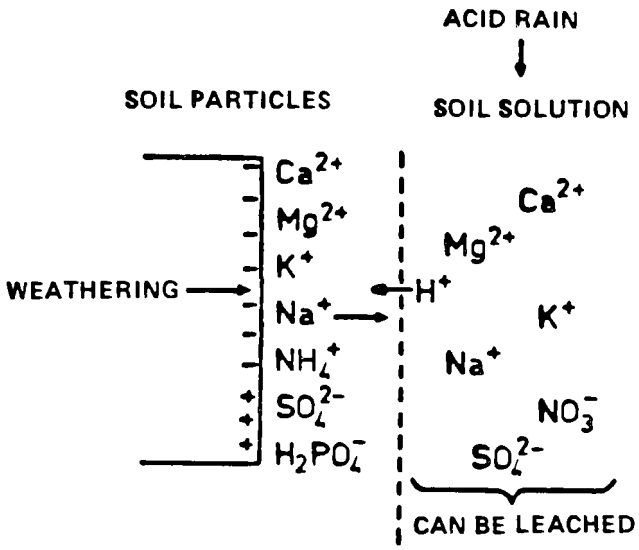


Figure 8-13. Showing the exchangeable ions of a soil with pH~7, the soil solution composition, and the replacement of Na^+ by H^+ from acid rain.[133]

increases in rainfall acidity are presently occurring. The types of effects that have been observed are destabilization and solution of clay minerals, loss of cation exchange capacity, increased rates of mineral losses and, consequently, increased rates pf podzolization. Overrein[128] has conducted extensive studies of effects of acidic precipitation on soils. Both accelerated leaching of calcium and loss of the capacity of the soil to buffer pH have been observed in lysimeter studies. Malmer[137] is in agreement with Overrein's findings. In field studies in Southern Sweden he noticed that increased leaching of calcium from the soil resulted when the acidity of the rain falling through the canopy decreased. He also mentioned that the buffering capacity of a soil may be better correlated with the base saturation than with cations exchange capacity and clay content.

Wiklander[133] notes that in humid areas leaching leads to a gradual decrease of plant nutrients in available and mobilizable forms. The rate of nutrient decrease is determined by the buffering capacity of the soil and the amount and composition of precipitation (pH and salt content). Leaching sooner or later leads to soil acidificaiton unless the buffering capacity of the soil is strong and/or the salt concentration of precipitation is high. Soil acidification influences the amount of exchangeable nutrients and is also likely to affect various biological processes in the soil.

Acid precipitation increases the amounts of SO_4^{2-} and NO_3^- entering the soils. Nitrate is easily leached from soil, however, because it is usually deficient for both plants and soil microorganisms, it is retained within the soil-plant system.[71, 112, 118] Retention of sulfate in soils appears to depend on the amount of hydrous oxides of iron and aluminum present. The amounts of these compounds present varies with the soil type. In significant

TABLE 8-10. THE SENSITIVITY TO ACID PRECIPITATION BASED ON: BUFFER CAPACITY AGAINST pH-CHANGE, RETENTION OF H^+, AND ADVERSE EFFECTS ON SOILS

	Calcareous soils	Noncalcareous clays pH > 6	Noncalcareous sandy soils pH > 6	Cultivated soils pH > 5	Acid soils pH < 5
Buffering	Very high	High	Low	High	Moderate
H^+ retention	Maximal	Great	Great	Great	Slight
Adverse effects	None	Moderate	Considerable	None - slight	Slight

Ref. 133

TABLE 8-11. POTENTIAL EFFECTS OF ACID PRECIPITATION ON SOILS

Effect	Comment
Increased mobility of most elements	Mobility changes are essentially in the order: monovalent, divalent, trivalent cations.
Increased loss of existing clay minerals	Under certain circumstances may be compensated for by production of clay minerals which do not have essential (stoichiometric) alkalies or alkali earths.
A change in cation exchange capacity	Depending on conditions, this may be an increase or a decrease.
A general proportionate increase in the removal of all cations from the soil	In initially impoverished or unbuffered soil, the removal may be significant on a time scale of 10 to 100 years.
An increased flux in nutrients through the ecosystem below the root zone	

SOURCE: Ref. 136.

amounts of the hydrous oxides of iron and aluminum are found in organic soils and therefore, sulfate retention is low.[118] Mineral soils vary in their sulfate retaining ability. Those with iron and aluminum hydroxides in their B horizons appear to retain the largest amounts of sulfate.

Leaching of soil nutrients is efficiently inhibited by vegetation growing on it. Plant roots take up the nutrients frequently in larger amounts than required by the plants. Large amounts of these nutrients will later be deposited on the soil surface as litter or as leachate from the vegetation canopy.[118]

In lysimeter experiments in Norway plots with vegetation cover were used. One plot had a dense layer of the grass, Deschampsia flexuosa V(L) Trin. and the other a less dense cover. The soil retained 50 percent of the SO_4^{2-} added to it. The greatest amount was retained by in the lysimeters covered with grass and the relative retention increased with increasing additions of sulfate.[118] Leaching of cations from the soil was reduced by the retention of the SO_4^{2-}, however, leaching of Ca^{2+} and Mg^{2+} increased significantly as the acidity of the simulated rain increased. In the most acid treatment leaching of Al was highly significant. The behavior of K^+, NO_3^- and NH_4^+ was different in the two lysimeter series. These ions were retained in the grass-covered lysimeters whereas these was a net leaching of K^+ and NO_3^- in the other series. Statistically significant effects were obtained only when the pH of the simulated rain was 3.0 or lower.[118]

The Scandinavian lysimeter experiments appear to demonstrate that the relative rate of adsorption of sulphate increases as the amounts applied are

increased. In control lysimeters the output/input ratio was approximately one. These results are in agreement with results of watershed studies which frequently appear to demonstrate that on an annual basis, sulfate outflow is equal to or greater than the amounts being added.[71, 118] Increased outflow may be attributed to dry deposition and the weathering of sulfur bearing rocks. The increased deposition of sulfate via acidic precipitation appears to have increased the leaching of sulphate from the soil. Together with the retention of hydrogen ions in the soil this results in an increased leaching of the nutrient cations K^+, Ca^{2+}, Mg^{2+}, Mn.[118]

The effects of acidic precipitation on soils are potentially long-lasting. Oden[138] has estimated that rainfall at pH 4.0 would be the cation equivalent of 30 kg Ca^{+2}/ha, which represents a considerable potential loss of cations essential for plant growth. McFee et al.[139] calculated that 1000 cm of rainfall at pH 4.0 could reduce the base saturation of the upper 6 cm of a midwestern United States forest soil by 15 percent and lower the pH of the A1 (A-One) horizon (the surface layer in most agricultural soils) by 0.5 units if no countering forces are operating in the soil. They note, however, that many counteracting forces could reduce the final effect of acidic precipitation, including the release of new cations to exchange sites by weathering through nutrient recycling by vegetation.

Lowered soil pH also influences the availability and toxicity of metals to plants. In general, potentially toxic metals become more available as pH decreases. Ulrich[140] reported that aluminum released by acidified soils could be phytotoxic if acidic rain continued for a long period. The degree of ion

leaching increased with decreases in pH, but the amount of cations leached was far less than the amount of acid added.[137] Baker et al.[141] found that sulfur dioxide in precipitation increased the extractable acidity and aluminum and decreased the exchangeable bases, especially calcium and magnesium. Although dilute sulfuric acid in sandy podsolic soils caused a significantly decreased pH of the leached material, the amount of acid applied (not more than twice the yearly airborne supply over southern Scandinavia) did not acidify soil as much as did nitrate fertilizer.[127] Highly acidic rainfall, frequently with a pH less than 3.0, in combination with heavy metal particulate fall-out has caused soils to become toxic to seedling survival and establishments according to observations by Hutchinson and Whitby.[142] Very low soil pH's are associated with mobility of toxic aluminum compounds in the soils. High acidity, high sulfur and heavy metals in the rainfall have caused fundamental changes in the structure of soil organic matter. The sulfate and heavy metals were borne by air from the smelters in the Sudbury area of Ontario and brought to earth by dry and wet deposition. Among the metals deposited in rainfall and dustfall were: nickel, copper, cobalt, iron, zinc, and lead. Most of these metals are retained in the upper layers of soil except in very acid or sandy soils.

The accumulation of metals is mainly an exchange phenomenon. Organic components of litter, humus and soil may bind heavy metals as stable complexes.[143] The heavy metals when bound may interfere with litter decay, nutrient cycling and in this manner interfere with ecosystem functioning.[143] Acidic precipitation by altering the equilibria of the metal complexes through mobilization may have a negative effect upon the residence time of the heavy metals with soil and litter.[143, 144]

Biological processes in the soil necessary for plant growth can be affected by soil acidification. Nitrogen fixation, decomposition of organic material, mineralization, especially of nitrogen, phosphorus and sulfur might be affected.[118, 127, 137, 145] Nearly all of the nitrogen, most of the phosphorus and sulfur as well as other nutrient elements in the soil are bound in organic combination. In this form, the elements are largely or entirely unavailable for utilization by higher plants.[145] It is only through the activity of heterotrophic microorganisms that nitrogen and phosphorus and sulfur are made available to higher plants. Thus, the microbial processes that lead to the conversion of the organic forms of these elements to the inorganic state are crucial for maintaining plant life in natural or agricultural ecosystems. The key role of these degradative processes is the fact that nitrogen is limiting for food production in much of the world and governs primary productivity in many terrestrial habitats.[145]

Many, and probably most, microbial transformations in soil may be brought about by several populations. Therefore the elimination of one population is not necessarily detrimental inasmuch as a second population not affected by the stress may fill the partially or totally unfilled niche. For example, the conversion of organic nitrogen compounds to inorganic forms is characteristically catayzed by a number of species, often quite dissimilar, and a physical or chemical perturbation affecting one of the species may not seriously alter the rate of the conversion. On the other hand, a few processes are in fact carried out, so far as it is now known, by only a single population, and elimination of that species could have serious consequences. Examples of this are the nitrification process, in which ammonium is converted to nitrate, and the nodulation of leguminous plants, for which the bacteria are reasonably specific according to the leguminous host.[145]

The nitrification processes is one of the best indicators of pH stress because the responsible organisms, presumably largely autotrophic bacteria, are sensitive both in culture and in nature to increasing acidify.[146] Although nitrification will sometimes occur at pH values below 5.0, characteristically the rate decreases with increasing acidity and often is undetectable much below pH 4.5. Limited data suggest that the process of sulfate reduction to sulfide in soil is markedly inhibited below a pH of 6.0[147] and studies of the presumably responsible organisms in culture attest to the inhibition linked with the acid conditions.[145]

Blue-green algae have been found to be absent from acid soils even though they have both adequate moisture and exposure to sunlight. Studies by Wodzinki et al.[148] attests to the sensitivity of these organisms to acidity. Inhibition of the rates of both CO_2 afixation and nitrogen fixation were noted.

Studies concerned with the acidification of soil by nitrogen fertilizers or sulfur amendments as well as comparisons of the microbial populations in soils with dissimilar pH values attest to the sensitivity of bacteria to increasing hydrogen ion concentrations. Characteristically, the numbers of these organisms decline and not only is the total bacterial community reduced in numbers but individual physiological groups are also reduced.[145] The actinomycetes (taxonomically considered to be bacteria) also are generally less abundant as the pH decreases, while the relative abundance of fungi increases, possibly due to a lack of competition from other heterotrophs.[146] The pH of soil not only influences the microbial community at large but also those specialized populations that colonize the root surfaces.[145]

It is difficult to make generalizations concerning the effects of soil acidification on microorganisms. Many microbial processes that are important for plant growth are clearly suppressed as the pH declines, however, the

inhibition noted in one soil at a given pH may not be noted at the same pH in another soil.[145] The capacity of some microorganisms to become acclimated to changes in pH suggests the need to study this phenomenon using environments that have been maintained at different pH values for some time. Typically the studies have been done with soils maintained only for short periods at the greater acidity.[145] The consequences of increased acidity in the subterranean ecosystem are totally unclear.

8.4.2 Precipitation as a Source of Nutrients

Precipitation is a major source of nutrients in terrestrial and aquatic ecosystems.[78,149]

The majority of the nutrients for lakes where the watershed is undisturbed and the ratio of lake surface area to drainage area is large[149] come from precipitation. Precipitation may be the source of 40 to 55% of the phosphorus and 45 to 75% of the inorganic nitrogen in some oligotrophic (low nutrient) lakes. The direct contribution of nutrients by precipitation to lakes is particularly important in areas with granite geological substrates. This is particularly true if the ratio of lake surface area to the watershed area is large.[150] In ecosystems where the watersheds are disturbed by man, the contributions from runoff is increased and the direct contribution of precipitation becomes less important (Table 8-12). Precipitation is having an even greater impact on aquatic ecosystems in undisturbed areas (those having no local anthropogenic source of sewage or industrial wastes). Fossil fuel combustion and long range atmospheric transport of its volatile combustion products has resulted in the ionic composition of precipitation in remote areas increasing.[78] For example, the concentration of NO_3^- in precipitation in the Ithaca, N.Y., has increased by a factor of approximately 4-5 from 1915-1976. (Figure 8-14) The increased nitrogen in precipitation increases

Table 8-12. SOURCES OF NITROGEN AND PHOSPHORUS FOR VARIOUS LAKES AS PERCENTAGES OF THE TOTAL ANNUAL INPUT

	Disturbed Watersheds					Undisturbed Watersheds			
Sources	Lake Mendota	Lake Rotorua	Lake Malaren	Lake Canandaigua	Cayuga Lake	Clear Lake	Rawson Lake	Mirror Lake	Dogfish Lake
Phosphorus									
Precipitation	6	2	4	2	2	61	50	17	82
Urban runoff and waste water	35	14	39	46	98[a]				
Rural runoff and ground water	59	83	57	52		39	50	83	18
Nitrogen									
Precipitation	17	6	4	3	7	75	50	78	
Urban runoff and waste water	11	11	25	6	93[a]				
Rural runoff and ground water	66	83	71	91		25	50	22	
Fixation	7	?	?	?	?	?	?	?	

[a]This value is a total for both "urban runoff and waste water" and "rural runoff and ground water."

Ref. 149

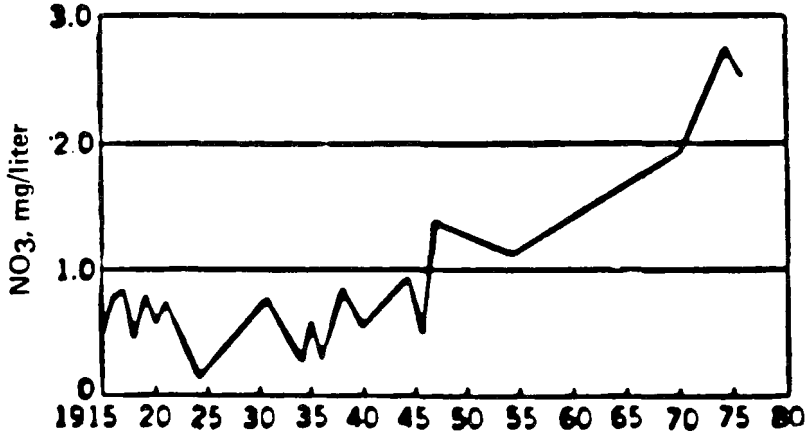


Figure 8-14. The weighted annual average of NO_3 concentration in bulk precipitation at Ithaca, N. Y. as a function of time.[151]

the fertilization effect of precipitation into undisturbed aquatic ecosystems, however, because the increased NO_3 concentration is associated with an increase in the H^+ concentration an acidification of sensitive lakes also results.[78] This effect is significant because aquatic ecosystems which previously because of their remoteness had remained pristine are now being influenced by man as a result of the increasing contamination of precipitation on a regional basis.[78]

Adding nitrate and other forms of nitrogen from the atmosphere to ecosystems is an integral function of the terrestrial nitrogen cycle. Higher plants and microorganisms can assimilate the inorganic forms rapidly. The contribution of inorganic nitrogen in wet precipitation (rain plus snow) is usually equivalent to only a few percent of the total nitrogen assimilated annually by plants in terrestrial ecosystems; however total nitrogen contributions, including organic nitrogen, in bulk precipitation (rainfall plus dry fallout) can be significant, especially in unfertilized natural systems.

Atmospheric contributions of nitrate can range from less than 0.1 kg N/ha-yr in the Northwest[152] to 4.9 kg N/ha-yr in the eastern United States.[153, 154] Inorganic nitrogen (ammonia-N plus nitrate-N) additions in wet precipitation ranged from less than 0.5 kg/ha-yr to more than 3.5 kg/ha-yr in Junge's[155] study of rainfall over the United States. On the other hand, total nitrogen loads in bulk precipitation range from less than 5 kg/ha-yr in desert regions of the West to more than 30 kg/ha-yr near barnyards in the Midwest. Total contributions of nitrogen from the atmosphere commonly range from about 10 to 20 kg N/ha-yr for most of the United States.[156]

In comparison, rates of annual uptake by plants range from 11 to 125 kg N/ha-yr in ecosystems selected from several bioclimatic zones.[156] Since the lowest additions are generally associated with desert areas, where rates of uptake by plants are low, and the highest additions usually occur in moist

areas where high plant uptake is high, the contributions of ammonia and nitrate from rainfall to terrestrial ecosystems are equivalent to about 1 to 10 percent of annual plant uptake. The typical additions of total nitrogen in bulk precipitation, on the other hand, represent from about 8 to 25 percent of the annual plant requirements in eastern deciduous and western coniferous forest ecosystems. Although these comparisions suggest that plant growth in terrestrial ecosystems depends to a significant extent on atmospheric deposition, it is not yet possible to estimate the importance of these contributions by comparing them with the biological fixation and mineralization of nitrogen in the soil. In nutrient-impoverished ecosystems, such as badly eroded abandoned croplands or soils subjected to prolonged leaching by acid precipitation, nitrogen additions from atmospheric depositions are certainly important to biological productivity. Such sites, however, are relatively limited in extent. In largely unperturbed forests, recycled nitrogen from the soil organic pool is the chief source of nitrogen for plants, but nitrogen to support increased production must come either from biological fixation or from atmospheric contributions. It seems possible, therefore, that man generated contributions could play a significant ecological role in a relatively large portion of the forested areas near industrialized regions.[156]

Sulfur, like nitrogen, is essential for optimal plant growth. Plants usually obtain sulfur from the soil in the form of sulfate. The amount of mineral sulfur in soils is usually low and its release from organic matter during microbial decomposition is a major source for plants.[134] Another major source is the wet and dry deposition of atmospheric sulfur.[134, 157, 158]

In agricultural soils crop residues, manure, irrigation water and fertilizers and soil amendments are important sources. The amounts of sulfur entering the soil system from atmospheric sources is dependent on proximity to

industrial areas, the sea coast and marshlands. The prevailing winds and the amount of precipitation in a given region are also important.[160] Near fossil fueled power plants, and industrial installations the amount of sulfur in precipitation may be as much as 150 pounds per acre or more.[158] By contrast, in rural areas the amount of sulfur in precipitation is generally well below the average 15 pounds per acre. Approximately 5 to 7 pounds per acre per year were reported for Oregon in 1966.[158] Shinn and Lynn[159] have estimated that in the northeastern United States, the area where precipitation is most acidic, approximately 5 x 10^6 tons of sulfate per year is removed by rain.[157] Hoeft et al.[161] estimated the overall average sulfur as sulfate deposition as 26 pounds of sulfur/acre per year (30 kg S/ha per year). Estimates for rural areas were 14 pounds of sulfur per acre per year (16 kg/ha). Approximately 40 to 50 percent of the sulfur additions occurred from November to February. Tabatabai and Laflin[162] found that SO_4-S deposition in Iowa was greatest in fall and winter when precipitation was low. They also estimated that the additions of sulfur by precipitation were the same in for Ames in 1976 as were reported for 1923, approximately 15 lbs/acre. The average annual additions of sulfur by precipitation is similar to that reported for rural Wisconsin by Hoeft et al.[161]

Experimental data have shown that even though plants are supplied with adequate soil sulfate they can absorb 25-35 percent of their sulfur from the atmosphere.[157] Particularly if the soil sulfur is low and the atmosphere sulfur high, most of the sulfur required from the plant can come from the atmosphere.[157] Atmospheric sulfur would be of benefit chiefly to plants growing on marginal lands with a low sulfur content, assuming of course that the sulfur was not leached before it could be absorbed by the plants or the deposition did not occur during the winter when in northern climes the uptake

activity of evergreens is low and crops are not grown. In addition, the fact that rainfall is highly variable within geographical areas, as well as the previously mentioned fact that rainfall does not fall uniformly throughout the year, may prevent nutrients being added to an ecosystem when their need is greatest.[163]

When discussing the effects of acidic precipitation, or the effects of sulfates or nitrates on soils, a distinction should be made between managed and unmanaged soils. There appears to be general agreement that managed, agricultural soils are less susceptible to the influences of acidic precipitation than are unmanaged forest or rangeland soils because fertilizers increase soil acidity much more than precipitation does. Ammonium fertilizers usually as ammonium sulfate $(NH_4)_2\ SO_4$ or ammonium nitrate, $NH_4\ NO_3$ (All ammonium fertilizers are acid forming. Only anlydrous ammonia is not.) are oxidized by bacteria to form sulfate (SO_4^{2-}) or nitrate (NO_3^-) and hydrogen ions (H^+).[134,157] The release of hydrogen ions into the soils causes the soil to become acidified. This is the same process that occurs when acidic precipitation by contributing hydrogen ions to the soil becomes "acidifying precipitation." Strongly acid soils are not productive for most crops for one of the following reasons:[134]

1 Aluminum toxicity.

2 Manganese toxicity.

3 Iron toxicity in a few soils.

4 Calcium deficiency.

5 Magnesium deficiency.

6 Molybdenum deficiency.

7 Very slow organic matter decomposition.

These are the same reasons, as has already been mentioned, that apply for uncultivated soils. The acidifying effects of fertilization or acidic precipitation is countered in managed soils through the use of lime. Liming tends to raise the pH and thereby eliminate most major problems associated with acids soils.[130,134,149] Costs of liming all natural soils would be prohibitive as well as extremely difficult to carry out.

Precipitation may add many chemicals not necessarily beneficial to terrestrial, aquatic ecosystems and agricultural ecosystems. In addition to sulfur and nitrogen, the biologically most important because they often limit biological productivity, are phosphorus and potassium.[149] Other chemicals of varying biological importance found in precipitation over North America are the following: chlorine, sodium, calcium, magnesium, iron, nickel, copper, zinc, cadmium, lead, manganese,[24,142,163] mercury,[163] and cobalt.[142] Rain over Britain and the Netherlands, according to Graham[121] contained the following elements not found in North American precipitation: aluminum, arsenic, beryllium, cerium, chromium, cesium, antimonry, scandium, selinium, thorium and vanadium. Again it is obvious that many of these elements will be found in precipitation in highly industrialized areas and will not be of biological importance until they enter an ecosystem where they may come into contact with some form of life as in the case of heavy metals in the waters and soils near Sudbury, Ontario. The chemical elements in the above list which are essential in small amounts for the growth of plants are underlined; however, at high concentrations these elements, as well as the other heavy metals, can be toxic to plants and animals. Furthermore, the acidity of precipitation can affect the solubility, mobility and toxicity of these elements to the foliage or roots of plants and to animals or micro-organisms

which may ingest or decompose these plants. Water in which these elements are soluble could be toxic to the animals living in it or to animals (including man) which may drink it.

Acidity is a critical factor in the behavior of natural or agricultural soils. Soil acidity influences the availability of plant nutrients and various microbiological processes which are necessary for the functioning of terrestrial ecosystems, therefore, there is concern that acidic precipitation over time could have an acidifying effect on soils through the addition of hydrogen ions. A number of observations can be made regarding the effects of acidic precipitation on soils.

Wiklander[133] has pointed out that based on the ion exchange theory, ion exchange experiments, and the leaching of soil samples, the following conclusions can be drawn about the acidifying effect on soils through the atmospheric deposition of mineral acids.

1. At a soil pH > 6.0 acids are fully neutralized by decomposition of $CaCO_3$ and other unstable minerals and by cation exchange.
2. At soil pH < 5.5 the efficiency of the proton to decompose minerals and to replace exchangeable Ca^{2+}, Mg^{2+}, K and Na^+ decreases with the soil pH. Consequently, the acidifying effect of mineral acids on soils decreases, but the effect on the runoff water increases in the very acid soils.
3. Salts of Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ in the precipitation counteract the absorption of protons and, in that way, the decrease of the base saturation. A proportion of the acids percolate through the soil and acidify the runoff.

The sensitivity of various soils to acid precipitation depends on the soil buffer capacity and on the soil pH. Noncalcareous sandy soils with pH > 5 are the most sensitive, irrespective of soil type.

Very acid soils are less sensitive to acidic precipitation because they are already adjusted by soil formation to acidity and are therefore more stable. In these soils easily weatherable minerals have disappeared, base saturation is low and the pH of the soil may be less than that of precipitation. The low nutrient level is a crucial factor in these soils. Even a slight decrease by leaching may have a detrimental effect on plant yield. Fertilization appears to be the only preventive measure.

In properly managed cultivated soils, acidic precipitation should cause only a slight increase in the lime requirement with the cost compensated for by the supply of sulfur, nitrogen, magnesium, potassium, and calcium made available to plants.

All of the major anions and cations transferred into ecosystems when it is raining or snowing (wet deposition) also are contained in the gases, aerosols, and particulate matter that are transferred from the atmosphere into ecosystems when it is not raining or snowing (dry deposition). Thus, in a chemical mass balance sense, it is both impossible and unrealistic to distinguish the biological effects of "acid precipitation" (wet deposition) from the biological effects of dry deposition.

In addition to the direct deposition of acidic substances into ecosystems as wet and dry deposition, some ionic materials (notably various complexes of ammonium and sulfate ions) although chemically neutral (or nearly so) are acidifying in their effects when they are taken up by plants and animals. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation".

The injurious substances in dry and wet deposition include not only acidic substances but also certain volatile organic substances as well as various other inorganic substances and heavy metals such as Mn, Zn, Cu, Fe, Mo, B, F, Br, Al, Pb, I, Ni, Cd, and V.

The elements underlined in the list above are essential elements required in small amounts by plants. At high concentrations, however, these same elements can be toxic to plants and animals. In addition, the acidity of precipitation can affect the solubility, mobility and toxicity of these elements when they contact the foliage or roots of plants, and are ingested by microorganisms during decomposition of plant parts or by animals eating the plants. When in water they can be toxic to animals, including man, which may drink the water containing these elements or to the animals (fish and other aquatic organisms) that inhibit the waters in which these elements are dissolved.

8.5 THE VALUE OF A NATURAL ECOSYSTEM

Ecosystems are evaluated by modern man solely on the basis of their economic value to him as expressed in dollars and cents. The basis of this evaluation depends on the extent to which man can manipulate the ecosystem for his own purpose. This single-purpose point of view makes it difficult to explain the many benefits of a natural ecosystem to man's welfare in terms of conventional cost-benefit analysis. Natural forests are among the most efficient in the use of solar energy. By comparison, agriculture is inefficient in fixing (using) solar energy; however, agriculture is emphasized because its benefits as food production for man is much more readily quantified.[170]

Attempts have been made to quantify the cost of lake acidification and the loss of fisheries resources of the Adirondacks to the state of New York. The Adirondacks service the outdoor recreational needs of local residents as well as those of vacationers from other states, New York City and the urban centers of the Hudson and Mohawk Valleys. These resources also contribute significantly to the economy of local communities. According to a 1973 survey, during 2 million fishing trips, anglers spent an estimated 26 million

dollars for bait, tackle, lodging and transportation. Acidic precipitation, therefore, has a potential for significantly affecting the economic base of the region.[171]

There are two obvious approaches to the management of acidified waters: 1) change the water to suit the fish, or 2) change the fish to suit the water.[171] The first approach involves increasing the pH of the lakes to the point where existing or newly-stocked fish populations can survive. The second, the development of strains of fish tolerant to acid waters. Both approaches have their limitations. The first approach is to lime the lakes. Since the mid-1950's, the New York State Bureau of Fisheries has added lime to 51 ponds at an average cost of $15 to $30 per acre of water per year depending on the accessibility of the lake or pond. The emphasis was on maintaining genetically unique fish populations or stocks having especially high recreational importance. In some instances, a single lime treatment has permitted reestablishment and maintenance of populations for three to four years. Under appropriate watershed conditions, liming not only increases the survival rate of fish in otherwise acid waters but can promote growth of invertebrate forage populations. Liming, however, is no easy chore. More than a ton of lime may have to be applied to each acre of water to obtain acceptable results. The application of lime to inaccessible Adirondack ponds is a difficult logistical exercise requiring the cooordination of truck, helicopter and ground crews. In practical terms, liming whole bodies of water is a feasible treatment only for smaller ponds which have low flushing rates. Refuge liming, or applying lime to less than the whole lake surface, is a possible option for larger waters. This involves liming littoral areas or tributary areas to provide a "safety zone" for fish during periods of high

acid input. These episodes are often associated with spring snowmelt. Further study is required on the feasibility and methodology of this approach. A treatment program covering all Adirondack waters presently known to be out of production would require an estimated 150,000 dollars per year in material and labor costs alone. Not quantified are the cost of inventorying and monitoring of the lakes to determine their potential for acidification and assessing the fish populations. It was estimated in 1978 that the cost of surveying 100 waters per year over the next five years would cost approximately $70,000 a year.[171]

The cost of the second approach, developing species of fish tolerant to acidic water conditions has not been as well quantified. The possibility exists of maintaining fish populations in some brook trout waters by stocking strains of trout that can survive conditions which are intolerable to native populations or the strains of brook trout presently being stocked. This approach has potential only for those marginal waters which have maintained a forage base capable of sustaining reasonable growth of stocked trout, and may be used to extend the effective life of lime applications.[171]

Liming of acidified lake ecosystems was first used in Scandanavia and was found to produce beneficial effects in some lakes. Wright[172] reviewed an early attempt in which addition of chalk to Swedish lakes increased pH and led to increased phytoplankton growth and improved fish survival. Addition of $CaCO_3$ and $Ca(OH_2)$ to two acidic lakes in Sudbury, Ontario, increased pH, decreased heavy metal concentrations, and caused a temporary decline in chlorophyll.[173] Reviews of liming experiments in Norway, cited by Wright[172] concluded that this practice would be feasible only for small ponds and

streams. One disadvantage of liming is that when the pH reaches the 5.0 to 6.0 range aluminum in waters with high concentrations becomes toxic.

The Boundary Waters Conoe Area occupies over a million acres of lakes and streams and complementing it is Ontario's Quetico Provincial Park of 1,120,000 acres. The cost of liming the lakes and streams over such a large area can only be imagined.

In Sweden, the cost of lost productivity of fish-stocks has been estimated at 16.5 million dollars per year solely in terms of the expected market value of commercially utilized species. Loss of income associated with tourism and recreational fishing is estimated to be in the range of 50 to 100 million dollars annually.

The previous discussion has dealt only with the estimatable costs for reclaiming a few lakes and streams. Many functions and benefits of natural ecosystems to man are unknown to the decision makers. In an attempt to quantify the values of natural ecosystems Gosselink, Odum and Pope have used a tidal marsh as an example. They have placed a value on a tidal marsh by assigning monetary values to the multiple contributions to man's welfare such as fish nurseries, food suppliers, and waste-treatment functions of the marsh. They estimate the total social values to range from $50,000 to $80,000 per acre.

Using four different categories, Gosselink, Odum and Pope,[174] developed a step-wise means of assessing the true value of natural tidal marshes to society as a whole. The value was based on commercial usage, social usage and the monetary value of natural ("undeveloped") estuarine environments.

The categories or levels of marshlands to which monetary values were assigned are: (1) commercial and recreational use, e.g., shell fish production and sport fishing; (2) potential for development, e.g., aquaculture, draining for industrial use; (3) waste assimailation or treatment, e.g. tertiary sewage treatment; and (4) total life support values, e.g., global cycling of nitrogen and sulfur, as protective "breakwaters." The round-figure values calculated in terms of (a) annual return and (b) an income-capitalized value were: (1) a. $100; b. $2,000; (2) a. $1,000; b. $20,000; (3) a. $2,500; b. $50,000; and (4) a. $4,100; b. $82,000.

The foregoing estimates for category (1) were based on identifiable 1974 commercial and recreational uses for which monetary values could be determined rather well. For category (2) the income-capitalization approach was used to estimate the values for development potential and for aquaculture. The estimates for tertiary sewage treatment (3) and life support (4) represent estimates of what man would have to pay for this useful work that is now performed by an acre of estuary were it not available to do this work.

Shortcomings exist in evaluating the environment solely in terms of direct uses or products. "Such cost-accounting ignores the extremely valuable life-support work that natural areas carry on without any development or direct use by man. It is this 'free work of nature' that is grossly undervalued, simply because it has always been taken for granted or assumed to be unlimited in capacity."[174] Development by man of a salt marsh may adversely affect its functioning in tertiary sewage treatment or as a life support system, therefore, it is important to evaluate it before deciding what kind of development, if any, is in the long-term best interest of both the environment and the economy.[174]

Westman[175] also evaluated the benefits of natural ecosystems by estimating the monetary costs associated with the loss of the free services (absorption of air pollution, production of oxygen, regulation of global climate and radiation balance, and soil binding) provided by the ecosystems. Westman estimated that the oxidant damage to the San Bernardino National Forest could result in a cost of $27 million per year (1973 dollars) for sediment removal alone due to erosion as long as the forest remained in the early stages of succession.

Estimates of the cost in currency of the values of items and qualities such as clean air and water, untamed wildlife, and wilderness, once regarded as priceless, are an attempt to rationalize the activities of civilization.[69] When estimating the monetary cost in currency of the values lost through the damaging of ecosystems, the assumption is usually made that the decision makers will choose the alternative which is most socially beneficial as indicated by costs compared to benefits. As Westman[175] points out, the assumption "that decisions that maximize benefit cost ratios simultaneously optimize social equity and utility" are based on certain inherent corollaries These are:

> "(1) The human species has the exclusive right to use and manipulate nature for its own purposes. (2) Monetary units are socially acceptable as means to equate the value of natural resources destroyed and those developed. (3) The value of services lost during the interval before the replacement or substitution of the usurped resource has occurred is included in the cost of the damaged resource. (4) The amount of compensation in monetary units accurately reflects the full value of the loss to each loser in the transaction. (5) The value of the item to future generations has been judged and included in an accurate way in the total value. (6) The benefits of development accrue to the same sectors of society, and in the same proportions, as the sectors on whom the costs are levied, or acceptable compensation has been transferred. Each of these assumptions, and others not listed, can and have been challenged."[175]

In the case of (4) above, for example, the losses incurred when the development of natural ecosystems are involved, include species other than man. These losses are seldom, if ever, compensated. The public at large also is usually not consulted to determine whether the dollar compensation is adequate and acceptable. Frequently, there is no direct compensation. Corollary (5) can never be fulfilled because it is impossible to determine accurately the value to future generations.

It should be remembered that ecosystems are life support systems and therefore their worth, in the final analysis, cannot be valued in dollars and cents.

8.6 EFFECTS OF ACIDIC PRECIPITATION ON MATERIALS

Acidic precipitation can damage the abiotic as well as the biotic components of an ecosystem. Of particular concern in this section are the deteriorative effects of acidic precipitation on materials and cultural artifacts of man-made ecosystems. The dominant factor in the formation of acidic precipitation is sulfur, usually as sulfur dioxide.[151,165] Because of this fact, it is difficult to isolate the effect of acidic precipitation from changes induced by sulfur pollution in general. (The effects of sulfur compounds on materials is discussed in Chapter 10.) High acidity promotes corrosion because the hydrogen ions act as a sink for the electrons liberated during the critical corrosion process.[164] Precipitation as rain affects corrosion by forming a layer of moisture on the surface of the material and by adding hydrogen (H^+) and sulfate (SO_2^{2-}) ions as corrosion stimulators. Rain also washes out the sulfates deposited during dry deposition and thus serves a useful function by removing the sulfate and stopping corrosion.[166] Rain plays a critical role in the corrosive process because in

areas where dry deposition predominates the washing effect is greatest, while in areas where the dry and wet deposition processes are roughly equal, the corrosive effect is greater.[166] The corrosion effect in areas where the pH of precipitation is very low, particularly of certain metals, may be greatly inhanced by precipitation.[166] In a Swedish study the sulfur concentration of precipitation, expressed as meg/m^2 per year, was found to correlate closely with the corrosion rate of steel. The metals most likely to be corroded by precipitation with a low pH are those whose corrosion resistance may be ascribed to a protective layer of basic carbonates, sulfates or oxides, as used on zinc or copper. The decrease in pH of rainwater to 4.0 or lower may accelerate the dissolution of the protective coatings.[166]

Materials reported to be affected by acid precipitation in addition to steel are: copper materials, linseed oil, alkyd paints on wood, antirust paints on steel and accelerated deterioration of limestone, sandstone, concrete and both cement-lime and lime plaster.[165]

Stone is one of the oldest building materials used by man and has traditionally been considered one of the most durable because structures, such as the pryamids, which have survived since antiguity are made of stone. What is usually forgotten is that the structure built with stone which was not durable has long since disappeared.[167]

Atmospheric sulphur compounds (mainly sulphur dioxide, with subsidiary amounts of sulphur trioxide and ammonium sulphate) react with the carbonates in limestone and dolomites, calcareous sandstone and mortars to form calcium sulphate (gypsum). The results of these reactions is blistering, scaling, and loss of surface cohesion which in turn induces similar effects in neighboring materials not in themselves susceptible to direct attack.[167]

Sulphates have been implicated by Winkler[168] as very important in the disintegration of stone. The surface flaking on the Egyptian granite obelisk (Cleopatra's Needle) in Central Park, NY is cited as an example. The deterioration accurred within two years of its erection.

A classic example of the effects of the changing chemical climate on the stability of stone is the deterioration of the Madonna at Herten Castle, near Recklinghousen, Westphalia in Germany. The sculpture of porous Baumberg sandstone was erected in 1702. Pictures taken of the Madonna in 1908 shows slight to moderate damage during the first 206 years. The features of the Mōdonna, eyes, nose, mouth and hair are readily discernable. In pictures taken in 1969 after 267 years, no features are visible.[165]

It is not certain in what form sulfur is absorbed into stone, as a gas (SO_2) forming sulphurous or sulphuric acid or whether it is deposited in rain. Rain and hoarfrost both contain sulfur compounds. Schaffer[169] compared the sulphate ion in both rain and hoarfrost (Table 8-13) and showed that the content of hoarfrost was approximately 7 times greater than rain at Heachingley, Leeds, England in 1932. Wet stone surfaces unquestionably increase the condensation or absorption of sulphates. Stonework kept dry and shielded from rain, condensing dew or hoarfrost will be damaged less by SO_2 pollution than stone surfaces which are exposed.[167]

Acid rain may leach ions from stonework just as acidic runoff and ground water leaches ions from soils or bedrock, however, at the present time it is not possible to attribute the deleterious effects of atmospheric sulphur pollution to specific compounds.

TABLE 8-13. COMPOSITION OF RAIN AND HOARFROST AT HEADINGLEY, LEEDS

	Average rain parts per million	Hoarfrost parts per million
Suspended matter	115	4620
Tar	15	158
Ash	28	67
Acidity	1.9	102.9
Sulphur as SO_3	22	148
Sulphur as SO_2	5.7	41.0
Total sulphur	27.7	189.0
Chlorine	7.3	94.6
Nitrogen as NH_3	1.98	8.57
Nitrogen as N_2O_5	0.196	0.0
Nitrogen as albuminoid	0.434	1.618

Ref.[169]

8.7 ACIDIC PRECIPITATION

8.7.1 Causes of Acidic Precipitation

Several lines of evidence suggest that the widespread acidification of rain began no earlier than 1950-1955. Athough this shift has been linked with changes in the amounts of SO_2 and NO_x emissions, the precise causes are still unclear. Likens and Bormann[206] suggested that acidification was partially a consequence of the decrease in emissions of alkaline fly ash from coal-burning power plants, coupled with increasing emissions of SO_2 and NO_x (from power plants, smelters, and industrial processes), and Likens[151] noted that the trend toward higher smokestacks to disperse pollutants may be responsible in part for the widening geographic extent of the acid deposition problem. The taller smokestacks are associated with a shift in the usage of coal from residential heating and railroads to use by the electric utilities to fire power generators.[224] Despite the shift, the actual amount of coal used does not show a great increase when figures for 1918-1928 are compared to those for 1979. Approximately 550 MM tons[224] were used during 1918-1928 compared to 672 MM[225] tons during 1979. There was, however, a seasonal shift in the pattern of coal consumption. Summer coal consumption has increased since 1960 while winter consumption has decreased due to increased summer usage by the electric utilities.

Cogbill and Likens[182] associated acidic rainfall in New York with high altitude air masses transported into the region from the Midwest, implying that the SO_2 and NO_x that cause acidic rain may be transported distances of 300 to 1500 km. A report by Miller et al.[202] dealing with the origin of air masses producing acidic precipitation at Ithaca, New York, points to the trajectories from the southwest sector as being the source of acidic precipitation. The trajectories from the southwest were high in sulfuric, nitric and

hydrochloric acids. The report by Miller et al.[202] supports the study made by Cogbill and Likens[182] which also concluded that precipitation was more acidic when upper level trajectories originated from the southwest (Figure 8-15). Emissions of sulfur and nitrogen oxides for the United States are depicted in Figures 8-15a, 8-15b.

Gatz[226] suggested that if trajectories of low altitude air masses are used to trace the source of acids in rainfall the major source of rainfall acidity in the Northeast is the Ohio River Valley of Ohio, Pennsylvania, West Virginia, plus Maryland, a region of large SO_2 emissions (Figure 8-15). Galvin et al.[195] also point to the Ohio River Valley as the source of trajectories passing Schoharie and Holland, New York. These air streams contained large amounts of sulfate.

Evidence from northern Europe also supports the idea that acidic rainfall is a large-scale regional problem involving long distances between emission sources and deposition of acidic rain. The acidic rains that have received intensive study in southern Scandinavia have been shown to result primarily from emissions of sulfur and nitrogen oxides in Great Britain and the industrial regions of continental Western Europe (e.g., Holland, Belgium, West Germany).[178]

Nisbet[198] compared estimated total SO_2 emissions with total deposition of sulfate in precipitation in eastern North America for the years 1955-1956, 1965-1966, and 1972-1973. Only 30 to 38 percent of the emitted sulfur could be accounted for by rainfall deposition. The fate of the remainder is uncertain; presumably some was deposited as dry fallout within the region studied and the rest was transported eastward over the Atlantic Ocean.

Transformation and transport of SO_2 and sulfate aerosol is discussed in Chapter 6 of this document, however, the following conclusions regarding the

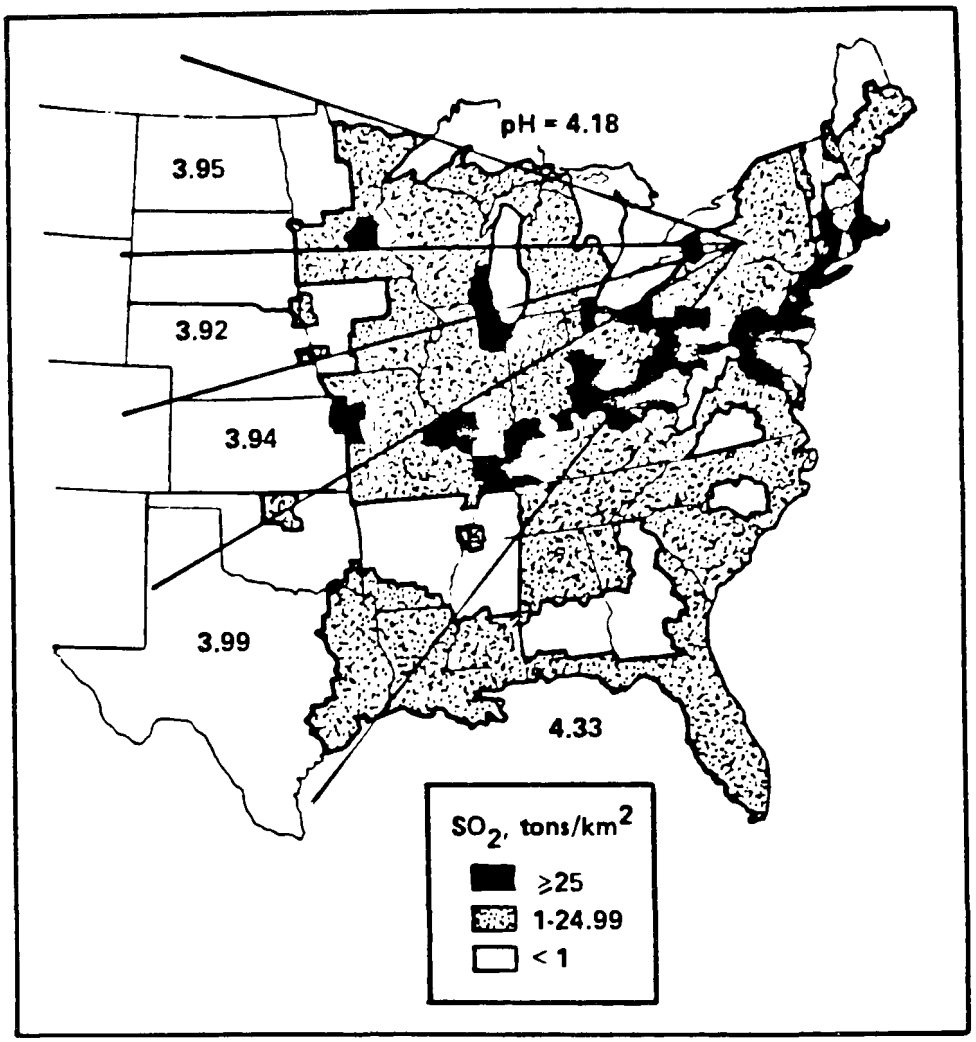


Figure 8-15. Trajectory map indicating source strengths for SO_2 emissions affecting the eastern United States.[206] Emission rates of SO_2 are shown by shading of the map. 500 mbar trajectory corridors from Cogbill and Likens[182] are superimposed on the map to indicate directions of movement of air masses at ca. 5500 m altitude for several days preceding specific rain events at Ithaca, New York. The numbers between the lines are mean pH values for rain events associated with each trajectory corridor.

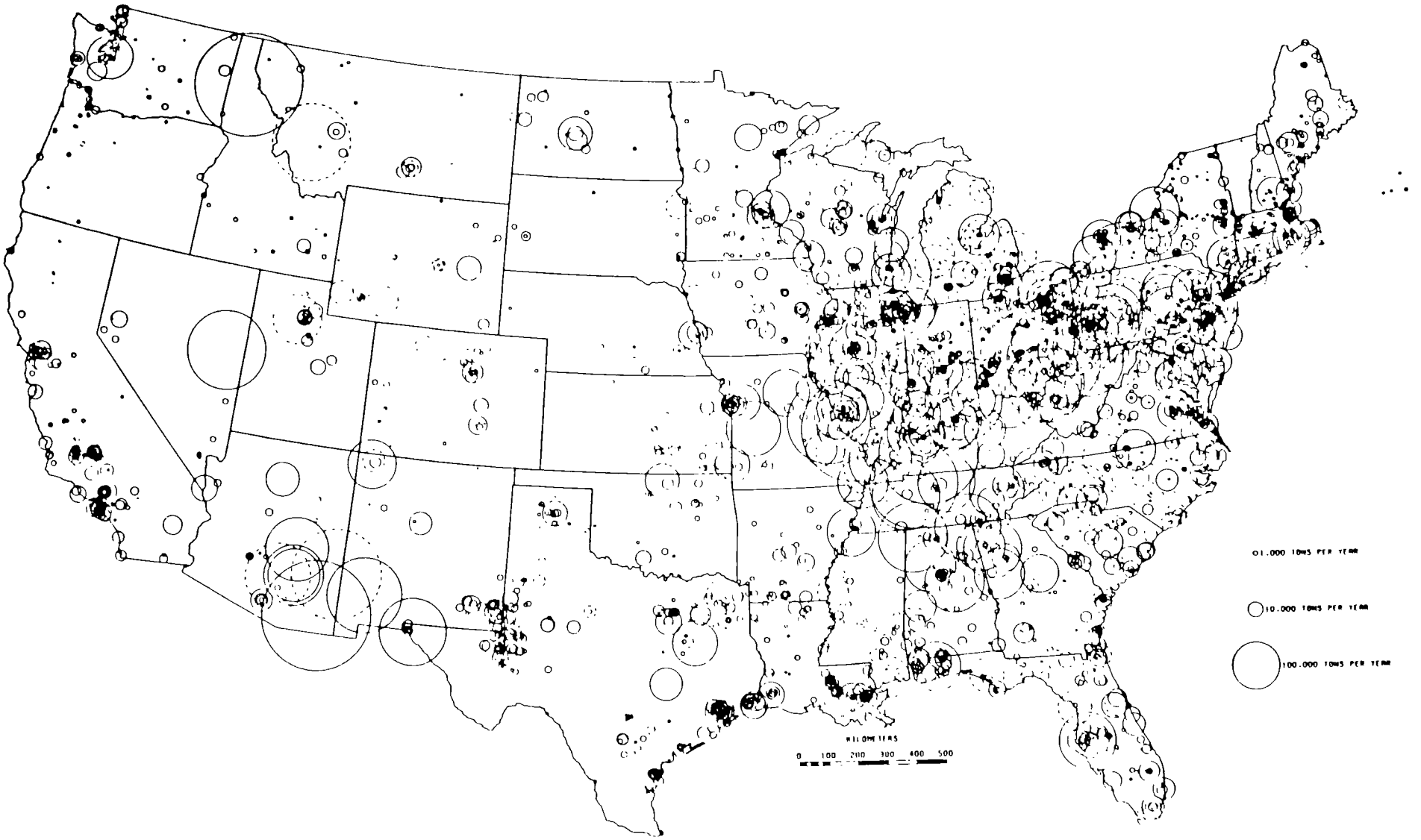


Figure 8-15a. SO_x emissions over 100 tons per year from NEDS.

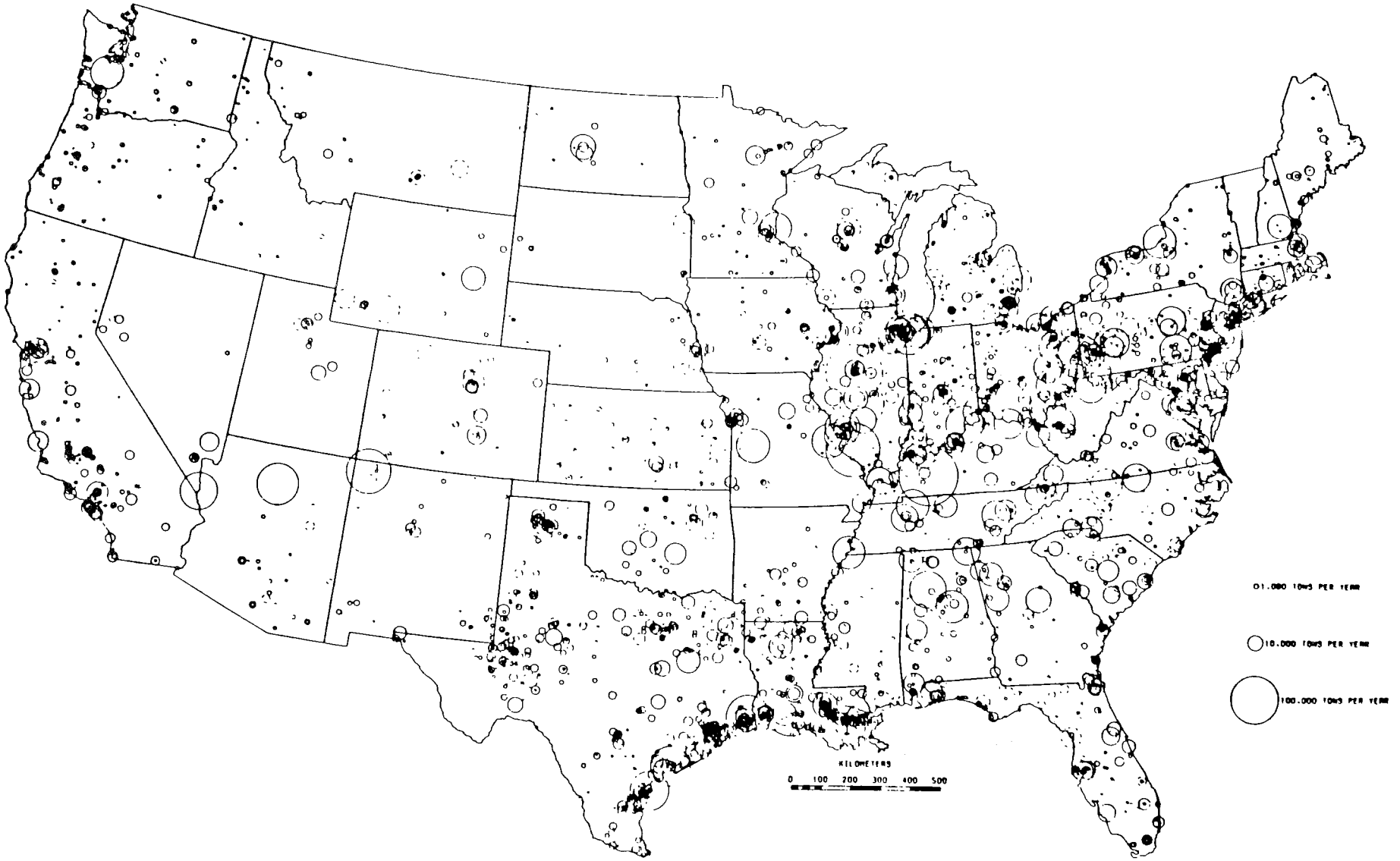


Figure 8-15b. NO_x emissions over 100 tons per year from NEDS.

large scale movements of pollutants within the United States and across national boundaries have been presented in the document, "The Long-Range Transport of Air Pollutants (LRTAP) in North America."[227]

> "The meteorological regime in eastern North America is conducive to long-range transport and transboundary transport in both directions across the Canada-United States border.
>
> The large-scale movement of pollutants does occur within the United States and within Canada, as well as across the Canada-United States border, and poses an environmental problem.
>
> The net flux of sulfur compounds is from south to north across the border. The northward movement of sulfur is comparable in magnitude to the internal emissions in Canada, whereas, the southward flux is substantially less than domestic United States emissions.
>
> The greater portion of total sulfur deposition in each country is probably the result of domestic emissions. The contribution of neighbour-country emissions is relatively greater in the case of United States emissions being deposited in Canada. However, the crucial aspect is the magnitude of deposition of acid species on sensitive ecosystems within the United States and Canada.
>
> Preliminary estimates suggest that two-thirds of the sulfur emitted into the atmosphere of eastern North America is probably deposited there with the remainder leaving the atmosphere of the region, primarily to the east."[226]

8.7.2 Formation and Composition

Precipitation is that portion of the global water cycle by which water vapor from the atmosphere is converted to rain or snow and then is deposited on earth.[2] Water by evaporation and transpiration (water vapor lost by vegetation) moves into the atmosphere. Once it reaches the atmosphere, the water vapor is cooled, then condenses on solid particles and soon reaches equilibrium with atmospheric gases. One of the gases is carbon dioxide. As carbon dioxode dissolves in water carbonic acid (H_2CO_3) is formed. Carbonic acid is a weak acid and in distilled water only dissociates slightly yielding hydrogen ions and bicarbonate ions (HCO_3^-). At normal atmospheric concentrations and pressures of carbon dioxide, the pH of rain and snow is 5.6.[176]

The pH of precipitation may vary and become more basic or more acidic depending on substances in the atmosphere. Dust and debris may be swept from the ground in small amounts and into the atmosphere where it can be involved in the rain. Soil particles are usually slightly basic in distilled water and release positive ions, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), and sodium (Na^{+}) into solution. Bicarbonate usually is the corresponding negative ion. Decay organic matter adds gaseous ammonia to the atmosphere. Ammonia gas in rain or snow forms ammonium ions (NH_4^{+}) and tends to increase the pH. In coastal areas sea spray plays a strong role in the chemistry of precipitation. The important ions entering into precipitation, sodium, magnesium, calcium, potassium, and the anions chloride (Cl^{-}) and sulfate (SO_4^{2+}) are the ones most abundant in the ocean.[176]

Other gases, in addition to CO_2, which enter precipitation are sulfur dioxide (SO_2), hydrogen sulfide (H_2S) the nitrogen oxides. The sulfur gases originate from such natural sources as volcanoes and swamps. In the atmosphere both of these gases can be oxidized to sulfuric acid. Nitrogen oxides in the atmosphere are converted to nitric acid.[176] If the two acids are present in significant amounts, the acidity of precipitation can go below a pH of 5.6. The acidity of precipitation, however, is a reflection not only of sulfuric, nitric, hydrochloric and organic acids but also of the total ionic balance between all cations and anions in precipitation.

The amounts of the various substances in the atmosphere originating from seawater, desert sands, volcanic islands or vegitated land influence the chemistry of natural precipitation. In regions with calcareous soils, calcium and bicarbonate may enter precipitation and presumably as a result of the dust being incorporates, the pH of rain or snow is usually above 6.0.[176]

The precipitation that fell before the Industrial Revolution and was preserved in glaciers and continental ice sheets has been analyzed, and it generally has a pH above 5.0. In Greenland, the pH of ice that had originated as snow approximately 180 years ago, was measured by Swiss scientists and found to have a pH ranging from 6.0 to 7.6[176]

Combustion of fossil fuels and the smelting of sulfide ores in the heavily industrialized and urbanized regions of the north temperate zone have changed the picture. Evidence exists that during the past two decades the emission of large amounts of sulfur and nitrogen oxides (See Chapter 4) have caused the strong inorganic acids, sulfuric (H_2SO_4) and nitric (HNO_3) to appear in increasing amounts in the precipitation in many of the areas surrounding the industrial regions of the world.[130,151,176-181] Strong acids dissociate completely in dilute aqueous solutions and lower the pH to less than 5.6 Acidic precipitation is rain or snow with a pH below 5.6[78,130,176]

Continuous sampling and analysis of precipitation over northern Europe since the mid-1950's have revealed that there has been a steady increase in acidity from a range in pH of 6.0 to 5.5 in 1956 to one of 4.5 to 4.0 in 1966.[130,176] The pH rainfall throughout southern Scandinavia is less than 4.5, and the hydrogen ion content of precipitation in some parts of Scandinavia has increased 200-fold (a change of 2.3 pH units) in the past two decades.[151,179-181] Studies to date in the northeastern United States have also demonstrated a trend toward a decrease in the pH of rain and snow as well as an expansion of the area receiving precipitation with a decreasing pH (Figures 8-16, 8-17).[98a,130,151,176,177,181-186]

The continuing occurrence of acidic rainfall and snow over large areas of the eastern United States, Canada and northern Europe has received increasing attention in recent years.[98a,130,151,176-186] Currently the average annual pH of precipitation in the northeastern United States is between 4.0 and 5.0. Average pH values around 4.5 have been reported as far south as northern Florida,[151,185] from Illinois,[187] the Denver area of Colorado,[188] the San Francisco Bay Area of California,[189,190] Pasadena, Ca.,[191] the Puget Sound area of Washington[192] and from eastern Canada.[98a,192,193]

It is clear from recent studies that acidic rainfall is a manmade problem (See Chapter 4 and 5). Such acidification has the potential for causing serious ecological effects over widespread geographic areas. Especially noteworthy in this connection are the observations showing the acidity of rainfall to be many times higher downwind from major industrial areas than elsewhere.[181,194-196] Several aspects of the problem, however, remain subject to debate because existing data are ambiguous or inadequate. Important issues include: (1) the rate at which rainfall is becoming more acidic and the rate at which the problem is becoming geographically more widespread; (2) the quantitative contributions of various acids to the overall acidity of rainfall; (3) the relative extent to which the acidity of rainfall in a region depends on local emissions of sulfur and nitrogen oxides versus emissions transported from distant sources; (4) the relative importance of changes in total mass emission rates compared to changes in the nature of the emission patterns (ground level versus tall stacks) in contributing to regional acidification of precipitation; and (5) the biological/ecological effects on terrestrial ecosystems.

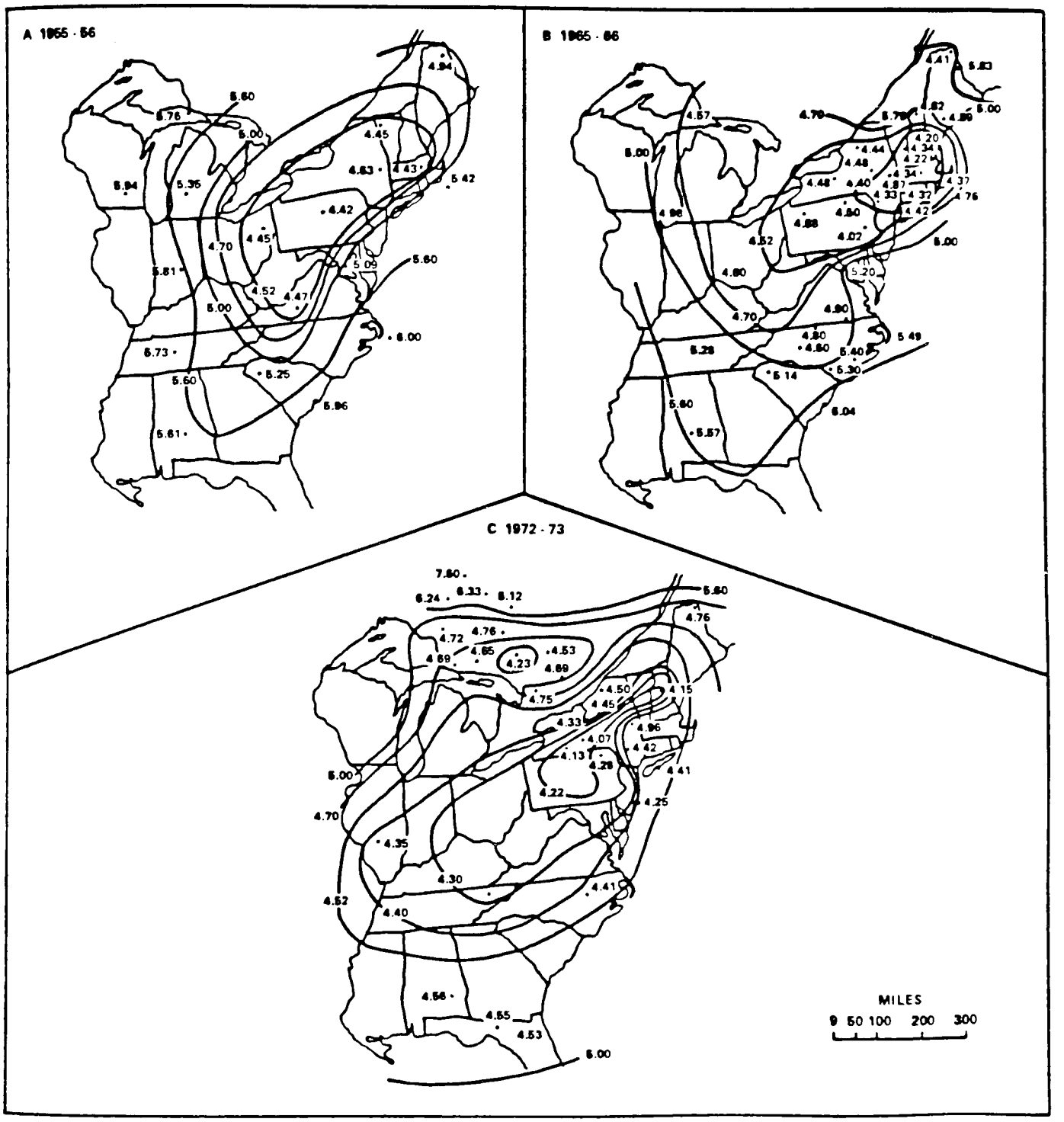


Figure 8-16. The weighted annual average pH of precipitation in the eastern U. S. in 1955-56, 1965-66, and 1972-73.[151]

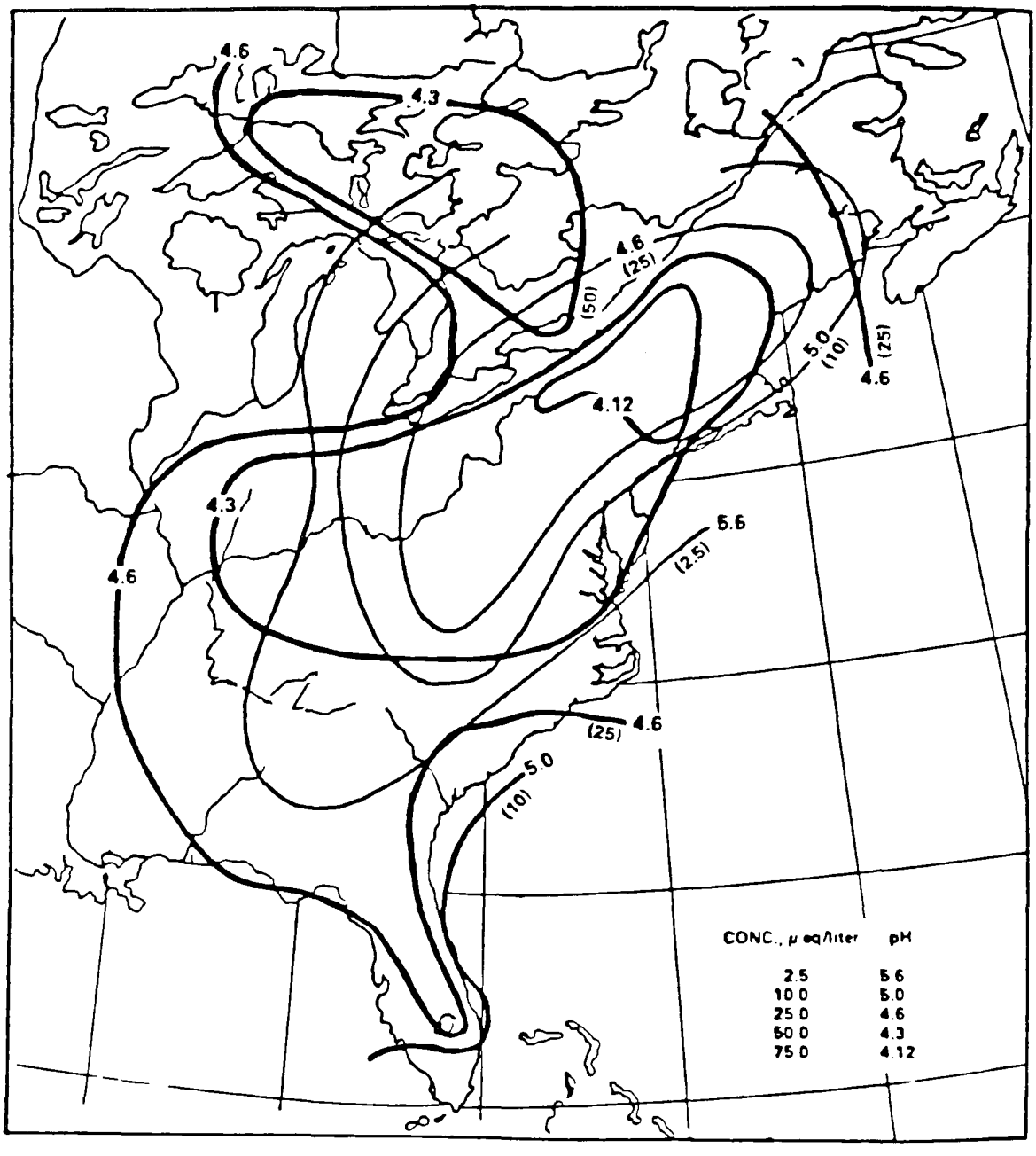


Figure 8-17. Spread of acid rain, 1975-76.[176]

The following sections discuss evidence related to the first four issues while the ecological effects have been discussed in the preceeding sections of this chapter. The emissions of sulfur oxides from both natural and man-made sources are set forth in Chapter 4, ambient concentrations of sulfates, SO_2 and nitrate aerosols are described in Chapter 5 while transformation of SO_2 and the transmission of particles are explained in Chapter 6. The ecological effects resulting from the acidification and the possibility of effects due to the long term acidification of terrestrial ecosystems if the present trends continue is cause for concern. An understanding of the factors involved in the formation of acidic precipitation is essential if the trends are to be ameliorated.

8.7.3 Long Term Trends

In northern Europe and the northeastern United States rainfall has become more acidic. For Europe the data obtained from long-term studies[15,16,179,180,181] shows conclusively that since the 1950's, the acidity of precipitation has increased. The United States is not so fortunate. Belatedly an atmospheric deposition network has been established to aid in determing trends in precipitation acidity as well as the composition.[78] Lacking such a system it has been necessary to extrapolate long-term trends from such data as are available.

The isopleth maps of rainfall pH presented in Figure 8-15 indicate that the acidity of rainfall over the eastern United States has increased during the past 20 years, but the rate of change at a given location is difficult to quantify, largely because historical data on the pH of rainfall are extremely rare. Even where fairly long-term records are available (e.g., measurements have been made since 1964 at Hubbard Brook, New Hampshire), values are

scattered over a wide range. Likens et al.,[197] reported that the weighted annual average pH ranged from 4.03 to 4.21 between the years 1965 and 1973-74. (A weighted average considers the amount of rain as well as its composition.) No statistically significant trend was noted, however, when concentrations were multiplied by the amount of precipitation to give areal deposition rates (equivalents of H^+/ha-yr), a trend of increasing H^+ deposition (a 36 percent increase over the decade) was noted [Figure 8-18 (A)]. Increases in the annual amount or frequency of precipitation will increase the rate of deposition in the same way that increases in acidic emissions will; and as Figure 8-16 (B) shows, the annual amount of rainfall at Hubbard Brook increased significantly over the decade. However, deposition rates for cations other than H^+ at the same site were not related to the annual amount of precipitation [Figure 8-16 (C)]. The amount of annual rainfall is one of the factors influencing H^+ deposition and may help to explain the increase in H^+ deposition over time. The acidity of pH in Florida has resulted in the isopleths for that state to move farther south (Figure 8-17) than in Figure 8-16(C). The change reflects the availability of more accurate data.

Cogbill[183] reviewed the temporal trends and the geographic distribution of rainfall acidity in the northeastern United States, and summarized the sparse information on rainfall pH available prior to the 1960s. He found that the acidity of rainfall at nine stations near the periphery of the central isopleth in 1955-1956 (see Figure 8-17) showed an average increase of 12 μg H^+/l by 1965-1966. Data for two of the stations near the northern limit of the acidic region showed an apparent stabilization in rainfall pH after the initial decrease in the 1960s. At Caribou, Maine, the pH values for 1955 to

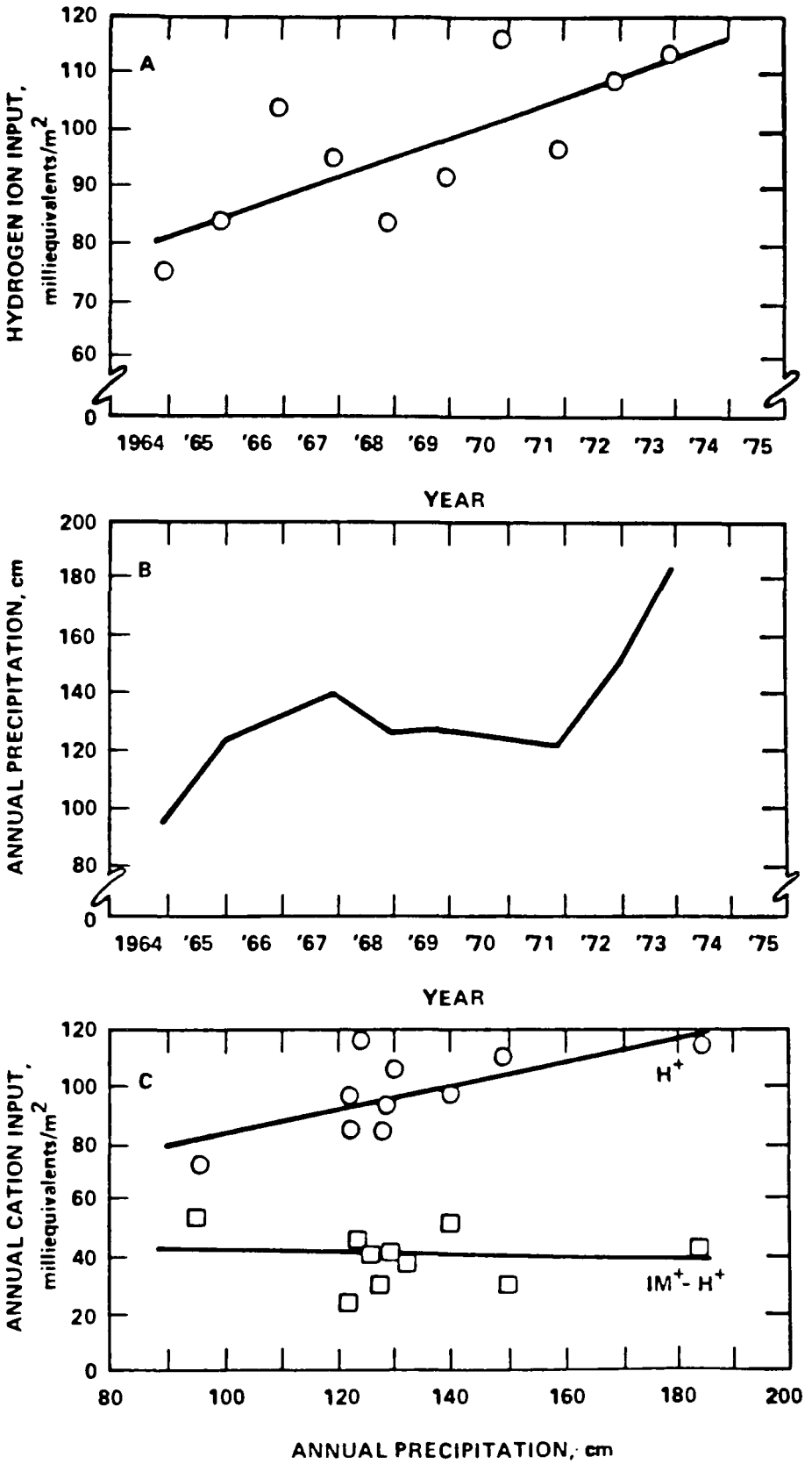


Figure 8-18. Cation inputs in precipitation at Hubbard Brook, New Hampshire. (A) Annual input of hydrogen ion, 1964-73; (B) Annual precipitation, 1964-1973; (C) Comparison of annual input of hydrogen ion and annual input of total cations less hydrogen ion plotted against amount of annual precipitation.[197]

1956, 1965-1966, and 1972-1973 were 4.94, 4.63, and 4.76, respectively, and at Sault Ste. Marie, Michigan, the pH values for the same years were 5.76, 4.76, and 4.69, respectively.[183] Other reviews of available data suggest that the average pH is decreasing in the most affected areas, from about 4.4 in the 1950s to 4.0 to 4.1 in the 1970s,[151,198] but quantitative inferences should be made cautiously.

Acidic precipitation has been a reality in New York State for an undetermined period of time. The data collected by the United States Geological Survey[199] over a ten year period which documents this statement is presented in Figure 8-19. These curves represent the pH of precipitation at eight different locations in New York State and one location in Pennsylvania. Each of these locations (Figure 8-20) represents an area within a given watershed, Table 8-14. Because the pH of precipitation has remained nearly at the same general average during the entire ten year period, it is obvious that precipitation was probably acidic in nature more than ten years before this fact was noted. Since data for the years prior to 1965 are lacking, it is difficult to determine when the pH in precipitation first began to decrease.[199]

8.7.4 Seasonal Variations in pH

Seasonal variations in pH measured at several sites in New York during 1970 to 1971[182] were erratic and site-specific, but pH values tended to be lower in summer than in winter.[182] Hornbeck et al.[200] reported that precipitation at nine stations in the northeastern United States was most acidic during the growing season (May to September) and least acid during winter (December to February). At Hubbard Brook, New Hampshire, the mean H^+

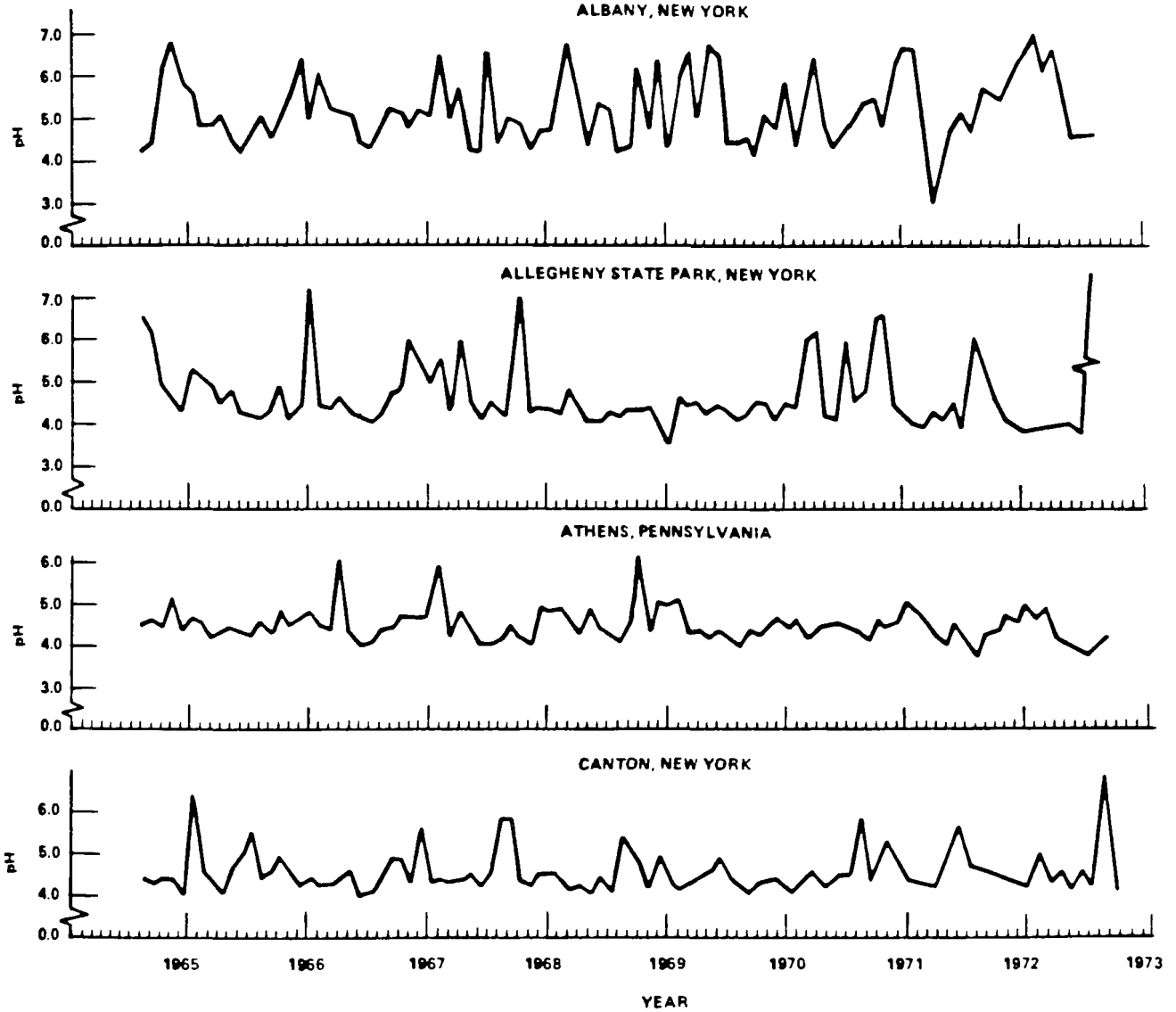


Figure 8-19. History of acidic precipitation at various sites in and adjacent to State of New York.[199]

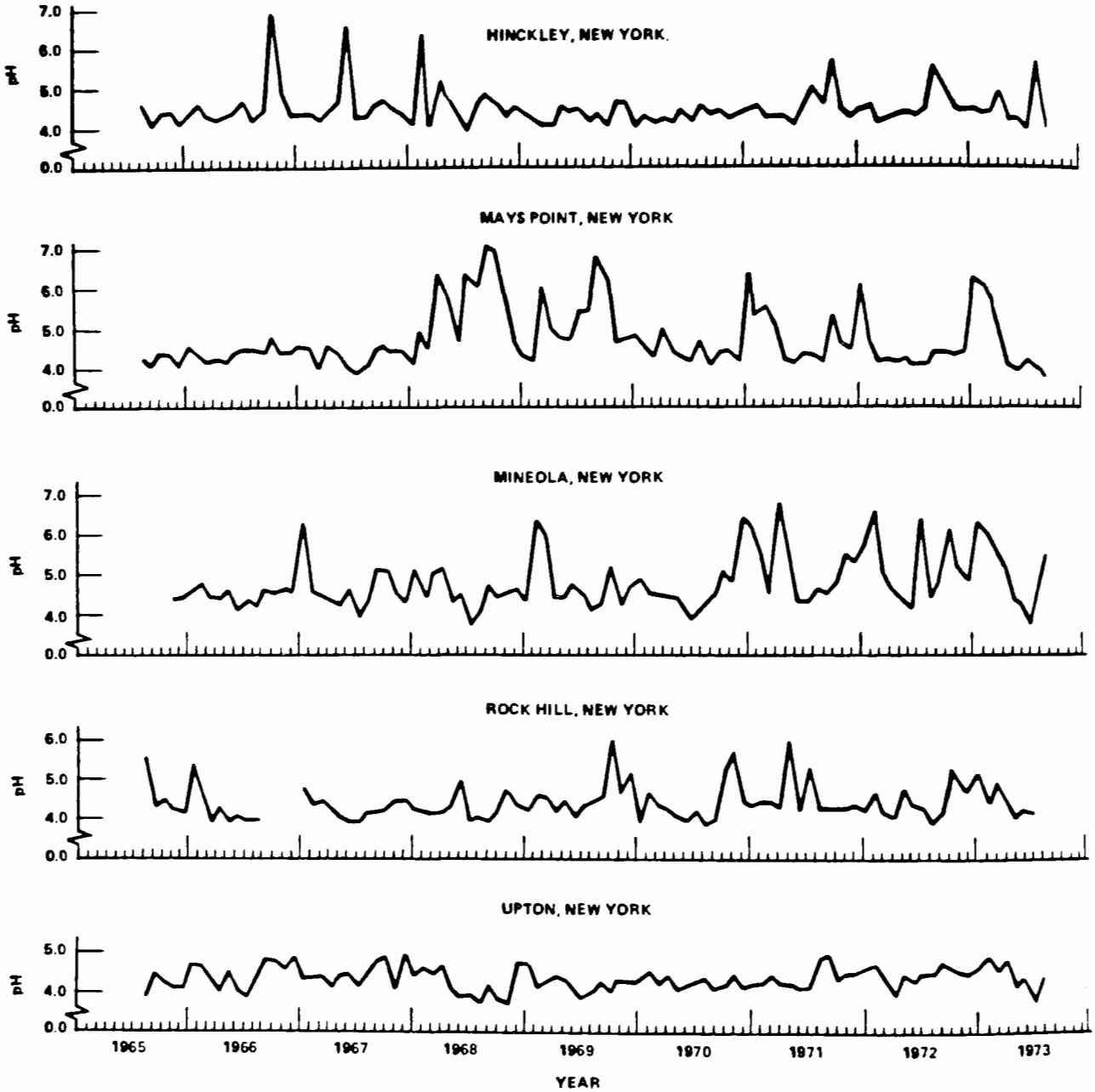


Figure 8-19 (cont'd). History of acidic precipitation at various sites in and adjacent to State of New York.[199]

1. Albany, N.Y.
2. Alleghany State Park, N.Y.
3. Athens, Pa.
4. Canton, N.Y.
5. Hinckley, N.Y.
6. Mays Point, N.Y.
7. Mineola, N.Y.
8. Rock Hill, N.Y.
9. Upton, N.Y.

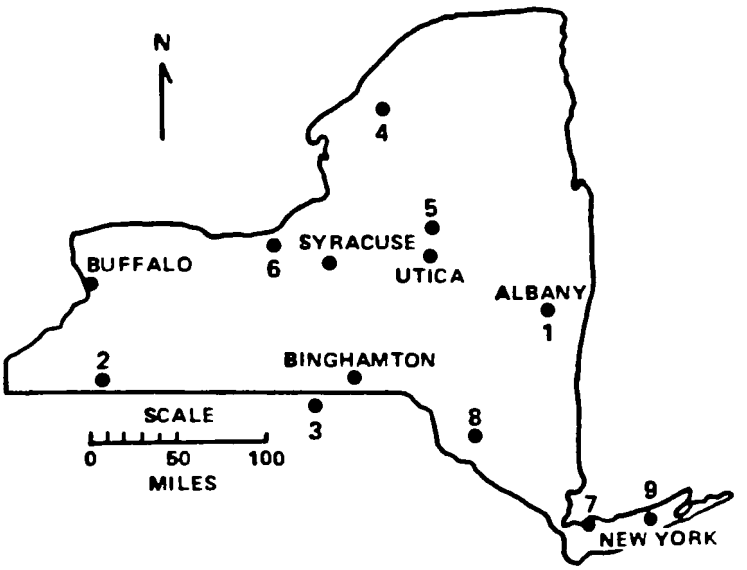


Figure 8-20. Location of acidic precipitation monitoring stations.[199]

TABLE 8-14. STATIONS IN THE PRECIPITATION pH MONITORING NETWORK

Station	Location	Watershed
1. Albany	Albany County	Hudson River
2. Alleghany State Park	Cattaraugus County	Alleghany River
3. Athens, Pennsylvania	Bradford County	Susquehanna
4. Canton	St. Lawrence County	St. Lawrence River
5. Hinckley	Oneida County	Upper Hudson River
6. Mays Point	Wayne County	Lake Ontario
7. Mineola	Nassau County	Long Island
8. Rock Hill	Sullivan County	Lower Hudson River
9. Upton	Suffolk County	Long Island

1. At U.S. Weather Bureau Station at Albany Municipal Airport, 0.5 mile north of new State Highway 155.

2. At U.S. Weather Bureau Station in Alleghany State Park, 100 feet west of Park Administration Building, 300 feet west of Park Highway 1 and 0.6 miles south of Salamanca, N.Y.

3. At U.S. Weather Bureau Station, 300 feet west of U.S. Highways 220 and 309, 0.6 mile west of the mouth of the Chemung River, 2.0 miles south of Athens, Pa. and 5.1 miles south of the New York-Pennsylvania state line.

4. At U.S. Weather Bureau Station at the Canton State University Farm on State Highway 68, 2.5 miles of U.S. Highway 11 and Canton, N.Y.

5. At U.S. Weather Bureau Station at Hinckley Dam on West Canada Creek on Cody Road in Hinckley, N.Y.

6. At U.S. Weather Bureau Station at Lock 25, Erie (Barge) Canal and State Highway 89 at Mays Point, 6.2 miles south of Savannah, N.Y.

7. At U.S. Weather Bureau Station 1 W on roof of U.S. Geological Survey office, at 1505 Kellum Place, Mineola, N.Y.

TABLE 8-14 (continued)

8. On North Shore Road, just north of Wanaksink Lake, 0.9 mile east of Rock Hill and 3.5 miles northwest of U.S. Weather Bureau, Rock Hill 35 W station and 6.5 miles southeast of Monticello, N.Y.

9. At U.S. Weather Bureau Station at Brookhaven National Laboratory weather tower about 2 miles east of main entrance at Upton, N.Y.

content of precipitation was 46 μg/l (pH = 4.34) in winter, and 102 μg/l (pH = 3.99) in summer. The seasonal trends in pH were mirrored by seasonal trends in sulfate content of precipitation, and the trends in both components could be explained by the lower efficiency of snow (compared to rain) in scavenging substances from the atmosphere. Analyses by Pack[201] of the MAP_3S (Multi-State Atmospheric Power Production Pollutant Study) data for 1976 to 1977 of H^+, SO_4^{2-} and NO_3^- concentrations in precipitation from five sites in the eastern United States between Virginia and upstate New York supports the seasonal variation of sulfates in precipitation (Figure 8-21) as does the study by Miller et al.[202] Pack[201] noted that the consistency of the SO_4^{2-} correlations over the network's entire range suggested that the SO_4^{2-} concentrations were the result of long range transport and mixing. Nitrates, however, showed a definite decrease with increasing distance. The H^+ ion was significantly correlated between sites out to 600 km site separation, a value which was intermediate between SO_4^{2-} and NO_3^-.

No significant seasonal trends were noted in pH of bulk precipitation rainfall at Gainesville, Florida, during 1976 to 1977, but wet-only deposition showed a trend of highest pH in fall and winter months and lowest pH in spring months (see Figure 8-22).[203]

The mean pH of precipitation falling on the New York Metropolitan Area during a 2-year (1975 to 1977) study was 4.28; however, a pronounced seasonal variation was observed (Figure 8-23). The minimum pH at all sites except Manhattan occurred during July to September while the maximum occurred during October to December. The minimum pH in Manhattan, however, occurred January to March and then gradually increased through the year. The lowest mean pH of 4.12 for the New York Metropolitan area occurred during the summer months.[204]

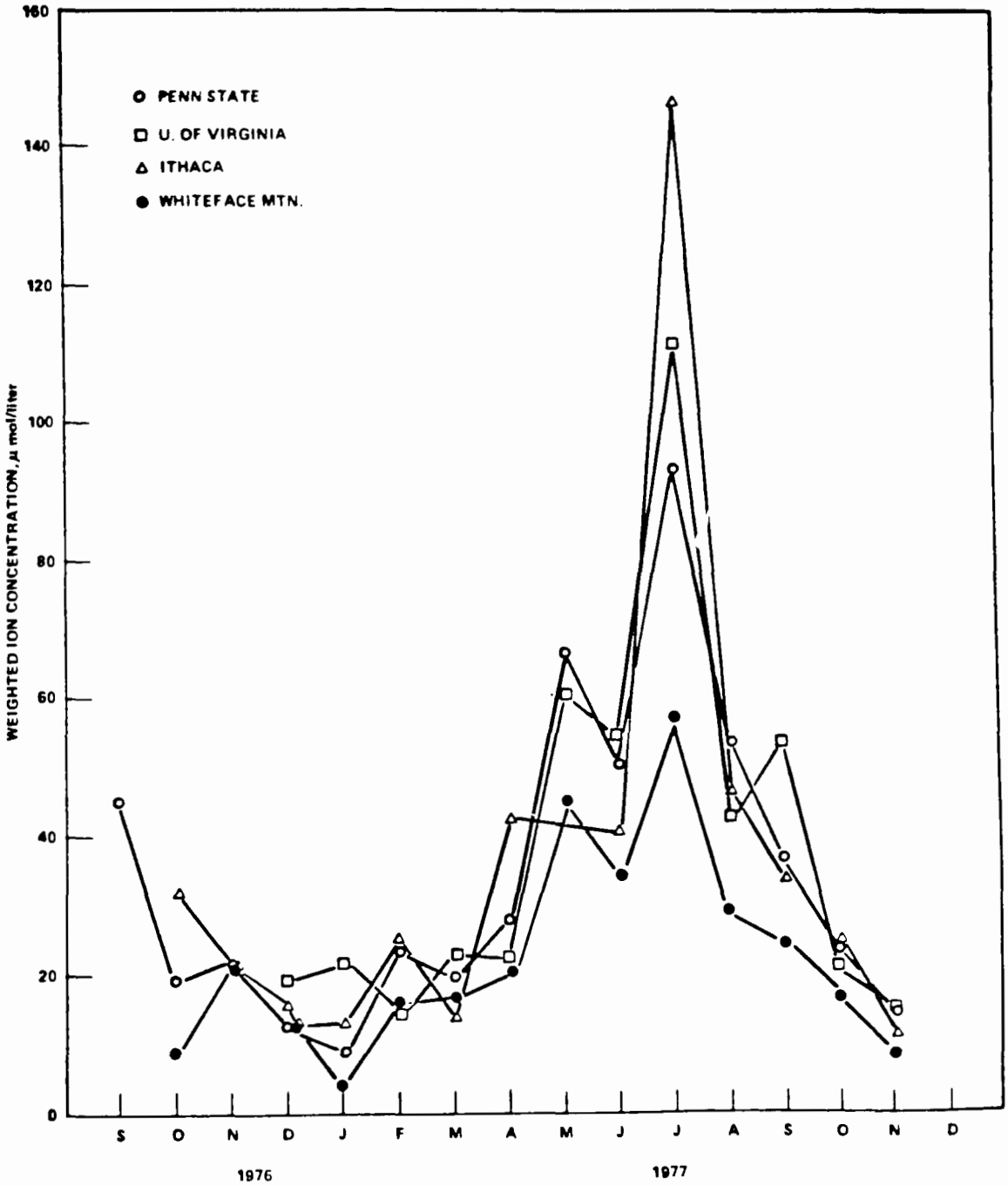


Figure 8-21. Sulfate monthly weighted ion concentrations.[201]

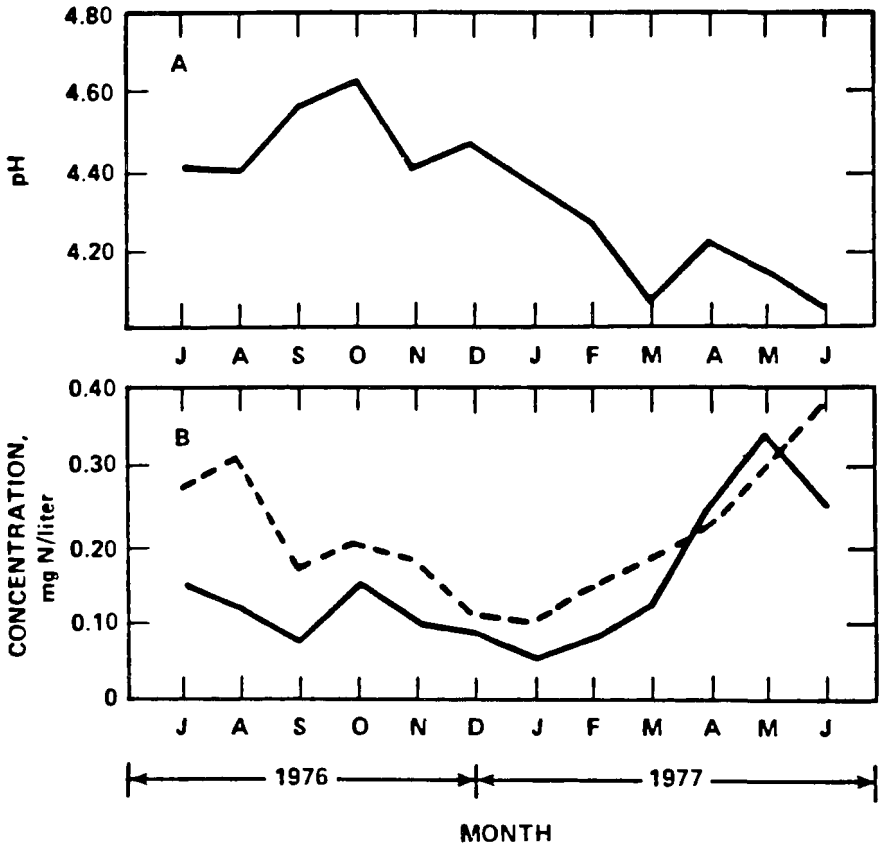


Figure 8-22. Seasonal variations in pH (A) and ammonium and nitrate concentrations (B) in wet-only precipitation at Gainesville, Florida. Values are monthly volume-weighted averages of levels in rain from individual storms.[202]

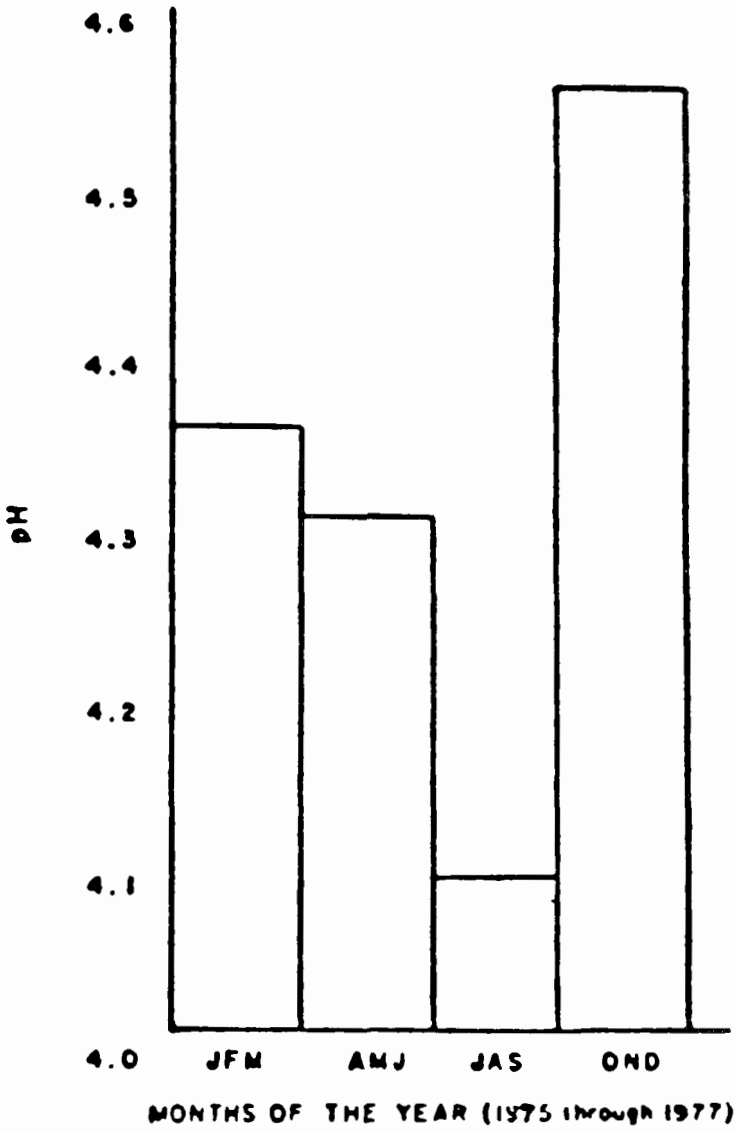


Figure 8-23. Seasonal variation of precipitation pH in the New York Metropolitan Area. 203

In general the pH of rain is usually lower in the summer than in the winter and is associated with the high summertime sulfate concentrations. In addition, the lowest pH's were associated with cold fronts and air mass type precipitation events. These events occur more frequently during the summer months. The lower pH's also occurred on west or southwest winds.

Precipitation associated with cold fronts generally occurs when the heaviest cold air behind the front lifts the warmer less dense air which precedes the front off the ground. The warmer air is usually the trailing edge of the backside of a high-pressure system. As a result, both the air mass and the frontal type events generally occur in a polluted air mass.[204]

8.7.5 Geographic Extent of Acidic Rain

As indicated earlier, there appears to be no published data dealing with precipitation chemistry that includes pH measurements for the northeastern United States prior to 1962.[205,206] However, data that shows measureable $CaCO_3$ alkalinity in precipitation is available from central New York and Tennessee prior to 1930.[182] Landsberg[207] in a 1954 publication mentions that the pH of individual raindrops 17 km west of Boston, Massachusetts, during 1952 to 1953 averaged approximately 4.0. Cogbill and Likens[182] point out that according to Granat,[208] a stoichiometric relationship exists for the major chemical ions in precipitation (Figure 8-24).

> "Certain cation equivalents come from sea-salt particles and are effectively neutralized by corresponding anions. We have used Na^+ as a basis for sea-salt measurement, since its dominant source is the ocean. Then the ratio of Na^+ to other ions in seawater [Granat,[208]] is used to predict the equivalent amounts of $SO_4^{=}$, Cl^-, Mg^{++}, Ca^{++}, and K^+ expected to orginate from the sea. When the ratio of Cl:Na is less than that of seawater, Cl^- is used as the basis [Junge and Werby[209]]. Such cases, however, are rare in recent samples in the northeastern United States.[182,183]

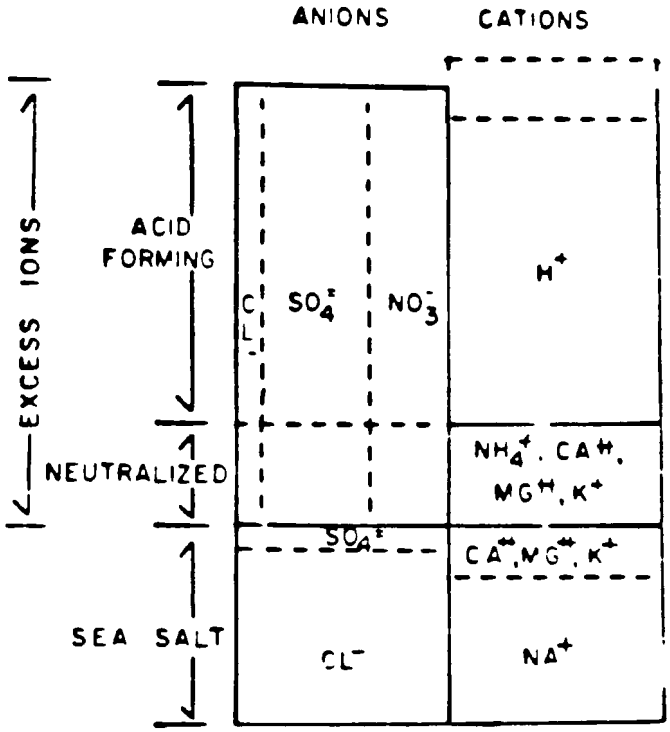


Figure 8-24. Theoretical relationship between major chemical ions in precipitation (see text). Any lack of equivalence between anions and cations can be envisioned to exist as a misestimate of H^+ concentration.[182]

Remaining anions ($SO_4^=$, NO_3^-, and sometimes Cl^-), commonly called 'excess' ions, are assumed to originate from terrestrial sources. A certain amount of this excess is neutralized by other cations (particularly Mg^{++}, Ca^{++}, K^+, and NH_4^+), which probably originate from soil or other particulate matter. Equal proportions of those remaining $SO_4^=$, NO_3^-, and Cl^- equivalents are associated with H^+, since the calculations are in equivalents. Each $SO_4^=$ is associated with two hydrogen ions, and each NO_3^- or Cl^- is associated with one. The sum of these hydrogen ion equivalents gives a predicted hydrogen ion concentration or pH (due to H_2SO_4, HNO_3, or HCl) that can be compared to the measured pH."

To substantiate the assumptions that a stoichiometric balance exists between ion equivalents as well as the association of H^+ with SO_4^{2-}, NO_3^- and Cl^- and the overall predictability of acidity, Cogbill and Likens[182] compared the weighted average precipitation chemistry of samples collected on a storm-by-storm basis with the predicted pH (see Table 8-15). A statistically significant relationship (correlation coefficient r = 0.96) between predicted and actual pH was observed based on actual storm-by-storm samples collected in the eastern United States. Measured and predicted values appeared to be within 0.1 of a pH unit.

Using the ionic relationship to predict pH, and the chemical data from Junge[210] and Junge and Werby[209] for 1955 to 1956, Cogbill and Likens[182] predicted the annual average pH for the eastern United States. Using the same method and data from Lodge et al.[211] for the U.S. during 1960 to 1966, Gambell and Fisher[205] for North Carolina and Virginia during 1962 to 1963 and Pearson and Fisher for New England and New York, 1965 to 1966, Cogbill and Likens[182] predicted the pH for 1965 to 1966. Based on the data obtained from their calculations, Cogbill and Likens[182] developed the maps shown in Figure 8-16 A and B.

The isopleth maps in Figure 8-16, based on the predicted annual average pH for 1955 to 1956 and 1962 to 1963, illustrates that a significant increase

TABLE 8-15. WEIGHTED PRECIPITATION CHEMISTRY AND PREDICTED pH FOR LOCATIONS IN EASTERN UNITED STATES DURING 1972 TO 1973

Location	Period	Water cm/area	$SO_4^{=}$, mg/l	NO_3^{-}, mg/l
Ithaca, N.Y.	Sep. 1972 to Aug. 1973	90.04	4.96	2.88
Aurora, N.Y.	Sep. 1972 to Aug. 1973	98.07	4.51	2.72
Geneva, N.Y.	Sep. to Aug. 1973	91.34	4.58	3.27
Hubbard Brook, N.H.	June 1973 to Aug. 1973	7.95	4.77	1.92
Gatlinburg, Tenn.	June 1973 to Aug. 1973	38.15	3.19	1.24

Location	Cl^{-}, mg/l	NH_4^{+}, mg/l	Na^{+} mg/l	K^{+}, mg/l	Ca^{++}, mg/l	Mg^{++}, mg/l	pH	Predicted pH
Ithaca, N.Y.	0.47	0.32	0.15	0.09	0.83	0.08	4.05	4.05
Aurora, N.Y.	0.47	0.40	0.08	0.07	0.45	0.07	4.05	4.02
Geneva, N.Y.	0.37	0.42	0.10	0.09	0.73	0.13	4.09	4.09
Hubbard Brook, N.H.	0.15	0.37	0.07	0.07	0.24	0.05	4.05	4.03
Gatlinburg, Tenn.	0.15	0.19	0.05	0.07	0.20	0.03	4.19	4.20

Ref. 182

in the area affected by acidic rainfall has occurred during the past 20 years and that it now covers nearly all of the United States east of the Mississippi River. Controversy exists over this apparent trend due to the fact that the pH values in the 1955 to 1956 and 1965 to 1966 maps are computed rather than measured and in addition it has been suggested that the number of sampling stations is too small for accurate placement of the isopleths in all of the maps. It has also been suggested that the accuracy of the method used by Cogbill and Likens[182] may overestimate the accuracy of data from most routine monitoring programs.

The controversy regarding the number of data points used to draw isopleths is illustrated by the fact that the pH 5.00 isopleth was drawn through the border between North and South Carolina in the first two maps in Figure 8-15, but in Likens'[151] map for the early 1970s the pH 5.00 line was moved to central Florida. This change was based on recent acquisition of data for two Florida cities, Tallahassee and Gainesville, in a region where pH measurements had not previously been made, and it does not necessarily imply a rapid expansion of the acidic rainfall area.

Despite the cautions mentioned above regarding the rate of expansion of acidic precipitation, as more and more evidence accumulates indications are that the area, both east and west of the Mississippi receiving acidic precipitation is increasing. Reports from both Minnesota[212] and Illinois[187] indicate precipitation events which are acidic. Data from the San Francisco Bay area indicate that precipitation has become more acidic in that region since 1957 to 1958.[189] The pH has decreased from 5.9 in 1957 to 1958 to 4.0 in 1974, and seems to be related to the NO_3^- concentration.[189] Another report, using data from the California Air Resources Board (CARB)[190] states that acidic precipitation has been reported from such widespread areas as Pasadena, Palo Alto,

Davis and Lake Tahoe. Due to the geological composition of the soil, the areas most likely to be affected by acidic precipitation are the national forests, state parks and preserves, Bureau of Land Management forested areas, many national parks and private forest holdings concentrated in the southern California mountains, the western slope of the Sierra Nevada and the Coast Range. All of the areas have acidic soils and are being adversely affected by photochemical oxidant air pollutants at the present time.[213,214]

The increasing acidity of precipitation has also been noticed in Colorado. Lewis and Grant,[188] based on the collection of bulk precipitation in Boulder County, Colorado, over a three year period, report a decline in pH of 0.80 units, from 5.43 to 4.63. The downward trend in pH appears to cut across seasons and across years with very different weather patterns. No evidence exists for the exclusive association of declining pH with upstate weather, as would be expected if the decline were caused exclusively by direct movements of pollutants from Denver over the station.[188]

Studies in the Great Smoky Mountain National Park[215] indicate a downward trend in pH has occurred there over the past twenty years. There has been a drop in pH from a range of 5.3-5.6 to 4.3 in 1979.

The absence of a precipitation monitoring network throughout the United States in the past makes determination of trends in pH extremely difficult and a controversial topic. This shortcoming has been rectified recently through the establishment of the National Atmospheric Deposition Program. Under the program, monitoring stations collect precipitation samples, determine their pH and then send the samples to the Central Analytical Laboratory to be analyzed. The network plans to have 75 to 100 collection sites throughout the U.S.

8.7.6 Sulfur and Nitrogen Oxides and the Formation of Acidic Precipitation

The generally held hypothesis is that sulfur and nitrogen compounds are largely responsible for the acidity of precipitation. Jacobson et al.[216] analyzed the contribution of the sulfate and nitrate anions to precipitation by collecting the wet deposition from 58 events from January through December 1971, in the area of Yonkers, New York. The sulfate anion was generally in greatest concentration, but in some samples the concentration of the nitrate anion was greater.

Likens[151] has pointed out that although sulfuric acid has been by far the dominant acid in precipitation at the Hubbard Brook Experimental Forest in New Hampshire for the past decade, the increased deposition of hydrogen ion has been due chiefly to an increase in the amount of nitric acid in the precipitation (rain and snow) falling there. The components in precipitation and their contribution to acidity in precipitation are listed in Tables 8-16 and 8-17.

The acidity of precipitation is a reflection of the balance of the major cations and anions in precipitation. The contribution of sulfate and nitrate anions has changed with time and analysis indicates that the nitrate anion ion makes up an ever-increasing fraction of the total negative ion equivalents. Following the reasoning of Granat,[208] Likens et al.[197] found, (assuming $2H^+$ per SO_4^{2-} ion as in H_2SO_4 or one H^+ ion per SO_4^{2-} as in NH_4SO_4) that the contribution of sulfate to acidity declined from 83 to 66 percent of the total acidity between 1964 to 1974 at Hubbard Brook, and the contribution of nitrate increased from 15 to 30 percent of the total during the same period. Furthermore, increased annual input of H^+ was closely correlated with increased input of nitrate, but there was little correlation between H^+ input and sulfate input (Figure 8-25). Hendry[203] found that sulfate contributed 69 percent,

TABLE 8-16. ACIDIC SULFATE AND NITRATE SALTS SOURCES OF ACIDITY IN PRECIPITATION

Substance	Concentration in precipitation (mg per liter)	Contribution to free acidity[a] (microequivalents per liter)	Contribution to total acidity[b] (microequivalents per liter)
H_2CO_3	0.62[c]	0	20
NH_4	0.92	0	51
Al, dissolved	0.05[d]	0	5
Fe, dissolved	0.04[d]	0	2
Mn, dissolved	0.0005[d]	0	0.1
Total organic acids	0.34	2.4	4.7
HNO_3	4.40	39	39
H_2SO_4	5.10	57	57
TOTAL		98	179

[a]At pH 4.01.
[b]In a titration to pH 9.0.
[c]Equilibrium concentration.
[d]Average value for several dates.

Note: Data from a sample of rain collected at Ithaca, N.Y., on Oct 23, 1975. Ref. 151.

TABLE 8-17. HYDROCHLORIC, SULFURIC, AND NITRIC ACIDS ARE STRONGEST OF SEVERAL POTENTIALLY IMPORTANT PROTON DONORS IN RAIN AND SNOW

Acid	Relative strength (pK_a)
HCl	~-3
H_2SO_4	~-3
HNO_3	-1
$SO_2 \cdot H_2O$	1.9
HSO_4	2.0
$Fe(H_2O)_6^{+3}$	2.2 to ~3
FH	3.2
Organic acids	3 to 7
$Al(H_2O)_6^{+3}$	4.9
H_2CO_3	6.3
HSO_3	7.2
HN_4^+	9.3
HCO_3^-	10.3

Ref 151.

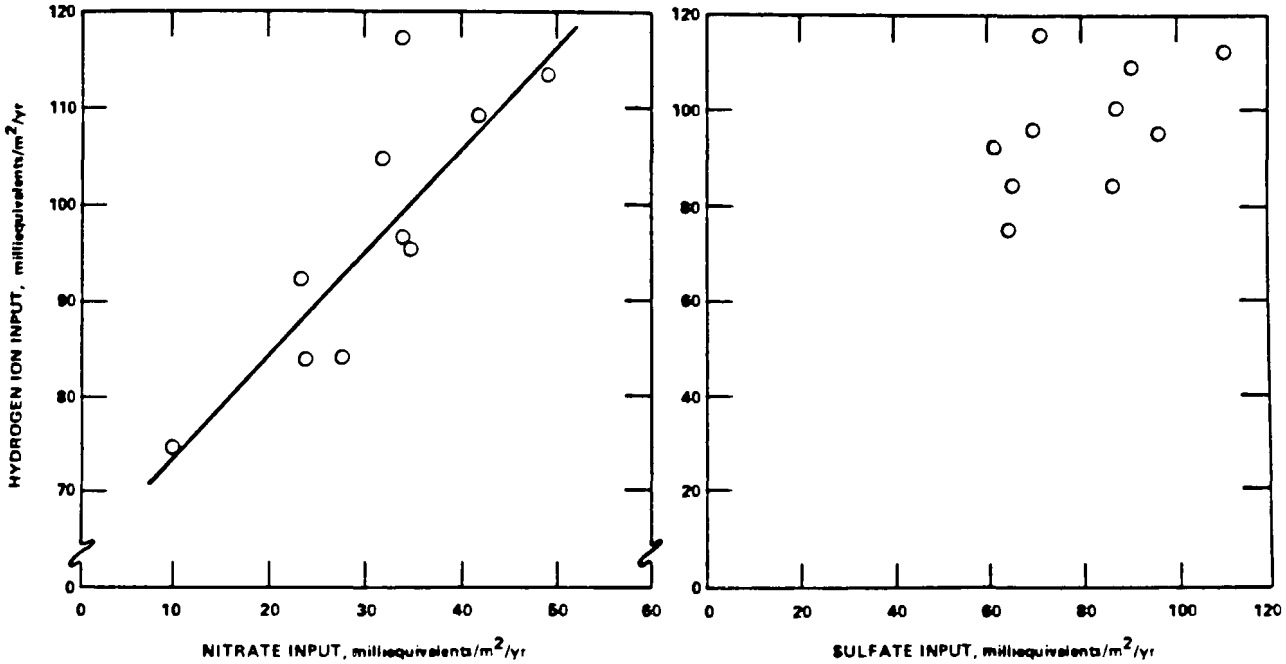
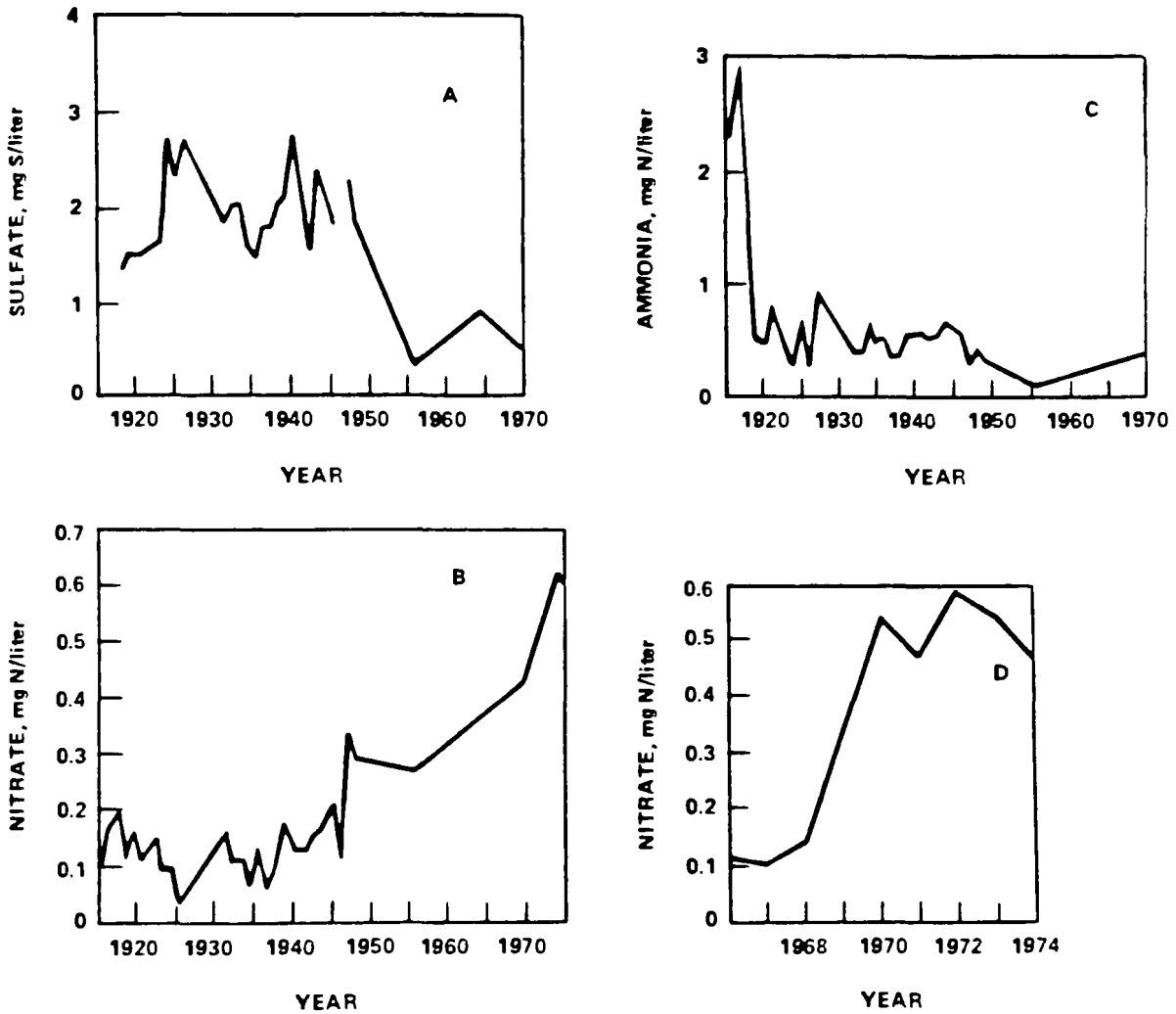


Figure 8-25. Hydrogen ion deposition in precipitation plotted against (A) nitrate deposition and (B) sulfate deposition. Data from Hubbard Brook, New Hampshire, 1964-1973.[197]

nitrate 22 percent, and chloride 6 percent of the free acidity in rainfall at Gainesville, Florida, during 1976. On the other hand, Gorham[216,217] reported that hydrochloric acid was the dominant acid in urban precipitation in Great Britain. Coal used in Great Britain is high in chloride, but low in sulfur. Data for nitrate, ammonia and sulfate in rain at Ithaca and Geneva, New York, constitute the longest record of precipitation chemistry in the United States according to Likens.[184]

Data are available from 1915 to the present, but long gaps exist in the measurements, especially at the Geneva site. Figures 8-26 (A) to (C) show that marked changes in composition have occurred at Ithaca: a gradual decline in ammonia, an increase in nitrate beginning around 1945, and a marked decrease in sulfate starting between 1945 and 1950. Early data for Ithaca showed higher concentrations of sulfate in winter than in summer, presumably because of greater local burning of coal in winter. Data for 1971 showed the reverse trend, however, with nearly half the annual sulfate input occurring during the months of June to August. Likens[184] concluded that, despite deficiencies in the historical data and questions concerning their reliability, the trends are real and can be explained by changes in fuel consumption patterns; i.e., natural gas began to replace coal for home heating near the time of the shifts in precipitation chemistry. Likens[151] reported a sharp increase in nitrate concentrations in New York state during the past decade (Figure 8-26 [D]), on the basis of United States Geological Survey data for nine stations.

Data for eastern North America indicate a roughly three-fold increase in nitrate in rainfall since 1955, whereas sulfate in rain has roughly doubled in this period. According to Nisbet,[198] sulfate/nitrate ratios in rainfall averaged about 4 in the eastern United States in 1955-1956, but the average ratio had fallen to about 3 in 1972-1973. Nisbet calculated that the fraction



SOURCE: (A), (B), and (C) modified from Likens;[183] (D) modified from Likens.[151]

Figure 8-26. Trends in mean annual concentrations of sulfate, ammonia, and nitrate in precipitation. (A), (B), and (C) present long-term data for Ithaca, New York; (D) presents data for eight years averaged over eight sites in New York and one in Pennsylvania. One point in (A), for 1946-47, is believed to be an anomaly (see Likens[183] for discussion).

of H^+ deposition attributable to nitrate assuming nitric acid rose from 19 percent in 1955-1956 to 24 percent in 1972-1973 (Table 8-18). He also projected trends in acid deposition for 1970 to 1980 for a number of scenarios assuming continued control of SO_2 emissions, but no controls on projected NO_x emissions. Even if SO_2 emissions were held constant by source controls on new power plants, a small increase in acidity would be likely because of increase in NO_x emissions.

Lindberg et al.[219] noted that SO_4^{2-} and H^+ were by far the dominant constituents of precipitation at the Walker Branch Watershed, Tennessee. Comparison with the annual average concentration of major elements in rain at the Walker Branch Watershed on an equivalent basis, indicates that H^+ constitutes approximately 50 percent of the cationic strength and trace elements account for only 0.2 percent. SO_4^{2-} constituted approximately 65 percent of the anionic strength and on an equivalent basis was 3.5 times more concentrated than NO_3^-, the next most abundant anion. The incident precipitation for the 2 year (1976-1977) period was described "as a dilute mineral acid solution," primarily H_2SO_4, at a pH approximating 4.2 and containing relatively minor amounts of various trace salts.[219]

It is becoming increasingly clear that there are significant spatial and temporal variations and differences in the chemistry of rain in the United States. The pH of rain varied from 4.2 to a high of 7.5 in central Minnesota during 1976 and 1977.[212] The following parameters were quantified in samples without dead volume, and obtained during individual rain falls: free, total, strong and non-volatile weak acids as well as NH_4^+, SO_4^{2-}, and NO_3^-. No chloride was detected in any of these samples. Statistical analyses of the data indicated no single parameter to be dominant in predicting free acid concentrations. All the parameters quantified in the study has some influence on the rain pH.

TABLE 8-18. DEPOSITION OF SULFURIC AND NITRIC ACIDS IN PRECIPITATION IN EASTERN NORTH AMERICA

	1955-56	1972-73	Percent change 1956-73
Total deposition of acid (as H^+)	4.0	10.8	+170
Estimated deposition as sulfuric acid (percent of total) expressed as sulfate	3.2 (80)[b]	7.9 (73)[b]	+150
Estimated deposition as nitric acid (percent of total) expressed as nitrate	0.76 (19)[b]	2.60 (24)[b]	+240
Total deposition of sulfates	16.4	31.8	+94
Sulfuric acid as % of sulfates	19.7	24.8	+27

[a]Deposition rates are expressed as multiples of the chemical equivalent weight, so that rates for different chemical species can be compared directly. 1 ton H^+ is equivalent to 49 tons sulfuric acid or to 63 tons nitric acid.

[b]A small but increasing fraction of the acid in precipitation is attributable to hydrochloric acid.

SOURCE: Modified from Ref. 198.

Table 8-19 shows correlation coefficients between the different parameters measured. Based on these results it can be concluded that on a comparative basis sulfate and nitrate are more highly correlated with ammonium ion than with the hydrogen ion. This is consistent with the results of Weiss et al.[220] who reported that a significant portion of the sulfate aerosol in the midwest is associated with the ammonium ion. This may be more true for nitrate [($NH_3 + HNO_3 \rightarrow NH_4NO_3$)] in certain geographic areas of the United States such as Minnesota. The averate μ equivalents of ammonium ion could account for 83 percent of the average μ equivalents of $SO_4 + NO_3$.

The pH of rainfall varies from event to event, from locality to locality and from storm to storm.[204] Wolff et al.[204] noted that there was some site to site variability among the eight sites they studied in the Manhattan area (Table 8-20). They also noted that the pH varied according to storm type (Table 8-21). Storms with a continental origin have a lower pH than storms originating over the ocean. The storms with trajectories from the south and southwest had the lowest pH's, while those from the north and east had the highest pH's. The lowest pH's were associated with cold front air mass type precipitation and high summertime sulfate concentrations.[204]

Hendry[203] and Seymour et al.[221] have also studied variations in the content of elements in single precipitation events. Hendry collected 5-minute segments within three individual rain storms. The temporal variations of constituents in rain storms at Gainesville, Florida in 1976 are listed in Table 8-22. Seymour et al.[221] sampled rain water during five rainfall events during July and August, 1977 in Tucson, Arizona. Variations in H^+, SO_4^{2-}, NO_3^-, and NH_4^+ concentrations were observed. Initially the concentration of ions was low, then increased rapidly as a function of time until a maximum was reached, and then fell off. The ionic strengths were noted to attain maximum

TABLE 8-19. CORRELATION COEFFICIENTS FOR VARIOUS PARAMETERS QUANTIFIED AS μ EQUIVALENTS IN INDIVIDUAL RAINFALL SAMPLES IN CENTRAL MINNESOTA DURING 1976 AND 1977.

Dependent Variable	Independent Variable	Correlation Coefficient
$SO_4 + NO_3$	NH_4	0.746
NO_3	NH_4	0.723
$SO_4 + NO_3$	$FA + NH_4$	0.708
SO_4	NH_4	0.532
SO_4	NO_3	0.469
FA	NH_4	0.343
NO_3	FA	0.282
$SO_4 + NO_3$	HT	0.252
SO_4	HT	0.245
HT	NH_4	0.221
$SO_4 + NO_3$	FA	0.215
NO_3	HT	0.197
SO_4	FA	0.054

FA = Free acid, HT = total acid

Where SO_4^{2-} concentrations were below the limits of detection, they were assumed to be half of the minimum limit of quantification.
Cation/anion balance was achieved in these samples.

From Ref. 219.

TABLE 8-20. MEAN pH VALUES IN THE NEW YORK METROPOLITAN AREA (1975-1977)

Site	Mean pH	SD	No. obsd	Range
Caldwell, N.J.	4.32	0.26	50	3.35-5.60
Piscataway, N.J.	4.25	0.36	64	3.57-5.50
Cranford, N.J.	4.34	0.34	48	3.44-5.95
Bronx, N.Y.	4.31	0.37	57	3.42-5.75
Manhattan, N.Y.	4.29	0.25	39	3.80-5.50
High Point, N.J.	4.25	0.30	25	3.74-4.90
Queens, N.Y.	4.63	0.35	20	3.98-5.28
Port Chester, N.Y.	4.60	0.19	21	4.00-5.10
All sites	4.28	0.32	72	3.50-5.16

From Ref. 204

TABLE 8-21. STORM TYPE CLASSIFICATION

Type	Description of dominant storm system	No. obsd	Mean pH
1	Closed low-pressure system which formed over continental N. Amer.	22	4.35
2	Closed low-pressure system which formed in Gulf of Mexico or over Atlantic Ocean	21	4.43
3	Closed low which passed to W or N of N.Y.C.	26	4.39
4	Closed low which passed to S or E of N.Y.C.	17	4.39
5	Cold front in absence of closed low	16	4.17
6	Air mass thunderstorm	5	3.91
7	Hurricane Belle	1	5.16
8	Unclassified	6	4.31

From Ref. 204.

TABLE 8-22. TEMPORAL VARIATIONS OF CONSTITUENTS IN RAIN STORMS IN GAINESVILLE, FLORIDA, 1976

Date	Collection (min)	TKN	NH_4-N	NO_3-N	Ortho P	Total P	Na	K	Ca	Mg	Cl	SO_4	pH
Sept. 19	0-5	1.09	0.23	0.60	0.060	0.125	0.88	0.23	1.50	0.30	1.95	5.15	4.38
	5-10	1.10	0.11	0.22	0.030	0.082	0.31	0.20	0.75	0.04	1.10	2.50	4.19
	11-15	0.63	0.07	0.14	0.030	0.035	0.14	0.19	0.55	0.01	0.95	1.90	4.15
	15-end	0.60	0.03	0.07	0.005	0.010	0.04	0.20	0.36	0.01	0.60	1.25	4.29
Oct. 16	0-5	1.35	0.44	0.75	0.024	0.160	1.03	0.28	1.95	0.38	1.95	5.80	4.65
	5-10	1.11	0.16	0.25	0.016	0.095	0.28	0.21	1.23	0.10	1.23	4.03	4.42
	10-15	1.02	0.07	0.16	0.006	0.050	0.21	0.17	0.84	0.09	0.84	2.88	4.51
	15-20	0.80	0.05	0.15	0.003	0.009	0.11	0.11	0.72	0.09	0.72	2.60	4.32
	20-25	0.69	0.01	0.11	0.005	0.005	0.08	0.08	0.43	0.06	0.43	1.68	4.49
	25-end	0.41	0.01	0.10	0.005	0.805	0.07	0.07	0.30	0.03	0.30	1.60	4.37
Oct. 26	0-5	1.41	0.24	0.55	0.045	1.215	1.45	0.35	1.55	0.45	2.40	7.35	4.68
	5-10	1.03	0.09	0.50	0.008	0.150	1.05	0.10	1.90	0.35	1.65	5.43	4.45
	10-15	0.83	0.12	0.31	0.005	0.075	0.85	0.15	0.95	0.13	1.55	4.23	4.27
	15-20	0.65	0.03	0.24	<.005	0.680	0.30	0.14	0.65	0.00	1.05	2.34	4.36
	20-end	0.70	0.02	0.11	<.005	0.040	0.35	0.10	0.70	0.10	0.90	1.45	4.38

All values in mg/l except pH.

values in the course of a single precipitation event. The variations in the concentrations of H^+ and NH_4^+ were observed to be closely followed by changes in the concentrations of the anions, NO_3^- and SO_4^{2-}. H^+, NH_4^+, SO_4^{2-} and NO_3^- were the principal ionic constituents of a single precipitation event. Dissolved CO_2 from the atmosphere was also noted.[221]

Stensland[221a] has compared the precipitation chemistry for 1954 and 1977 at a site in central Illinois. The precipitation samples for 1954 were more basic than those of 1977, due mainly to high concentrations of sulfate and nitrate. The corrected pH for 1954 was 6.05. The pH for 1977 was 4.1. The author suggests that the higher pH in 1954 is due to atmospheric dust because of drought in the area. He also concludes that further data is needed to determine the effect of sample handling on the calcium and magnesium values.

Scavenging by rainfall produces large changes in atmospheric contaminant concentrations during a given rainfall event. The decline in constituent levels is usually rapid, at least in localized convective showers, and low, steady-state concentrations are usually reached within the first half hour of a rain event.

The variability of rainfall volume within small geographic areas over short periods of time and on a year-to-year basis for larger geographic regions is well known. Variations of up to 50 percent of the long-term average amount of precipitation are relatively common for any given year. Large annual differences in rainfall amounts can also occur within small geographic regions of 10 to 50 km^2, but this variability is probably more pronounced in areas where convective rain showers predominate.

Nearly all of the nitrate in rainfall is formed in the atmosphere from NO_x, and little is derived from wind erosion of nitrate salts in soils. Similarly, nearly all of the sulfate in rainfall is formed in the atmosphere from SO_2. The reactions that produce nitrate and sulfate from NO_x and SO_2 are

generally known and result in the production of equivalent amounts of hydrogen ion, regardless of the reaction mechanism:

$$OH + NO_2 \rightarrow HNO_3, \text{ or}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3, \text{ and}$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4.$$

Thus, all atmospherically derived nitrate and sulfate contribute to the acidification of rainfall, since H^+ is associated stoichiometrically with the formation of each. A second stoichiometric process that affects the acidity of rain is the reaction of nitric and sulfuric acids with ammonia or other alkaline substances (e.g., dust particles) in the atmosphere to form neutral nitrate and sulfate aerosols. To the extent that such neutralization occurs, the free acidity of rainfall will be reduced.[222] Reuss[223] noted, however, that even ammonium (NH_4^+)in rain can contribute to the acidification of soil, since ammonium that enters the soil may be oxidized, resulting in the formation of nitric acid.

8.7.7 Seasonal Variations in Sulfate and Nitrates

Many workers have reported that the sulfur content as well as the pH of precipitation shows seasonal fluctuations. In general SO_4^{2-} and H^+ concentrations in precipitation in the eastern United States are higher in the summer than in the winter. Wolff et al.[204] found this to be true for the New York Metropolitan Area. Hornbeck[200] and Miller et al.[202] both stated that a summer maximum for sulfate for pH exists in upstate New York, the Hubbard Brook Experimental Forest in New Hampshire and in portions of Pennsyvania. Pack,[201] using data from the four original MAP3S (Multistate Atmospheric Power Production Pollution Study) precipitation chemistry network, plotted the weighted monthly sulfate ion concentrations (Figure 8-21). Maximum sulfate concentrations occurred from June through August. Lindberg et al.[219] studying wetfall deposition of

sulfate in the Walker Branch Watershed also noted summer maxima for SO_4^{2+} and H^+. Using the same MAP3S data as did Pack they plotted weighted mean concentrations of sulfate in rain collected from November, 1976 through November 1977. This information is depicted in Figure 8-27. The concentrations at Walker Branch Watershed, Tennessee, are lower than all of the stations except remote Whiteface Mountain, New York. The regional nature of the wet deposition of sulfate is apparent. Reasons for the existence of the high summer maxima of sulfate for the eastern United States is discussed in some detail in Chapter 5, Section 5.2.2.1 (Ambient Sulfates). Ambient nitrate aerosols also are discussed in Chapter 5, Section 5.2.2.2. Information concerning nitrates in the atmosphere is limited. Data from studies prior to 1977 are in doubt because of artifact formation on filters. Aerosol nitrate is now believed to be in the form of ammonium nitrate.

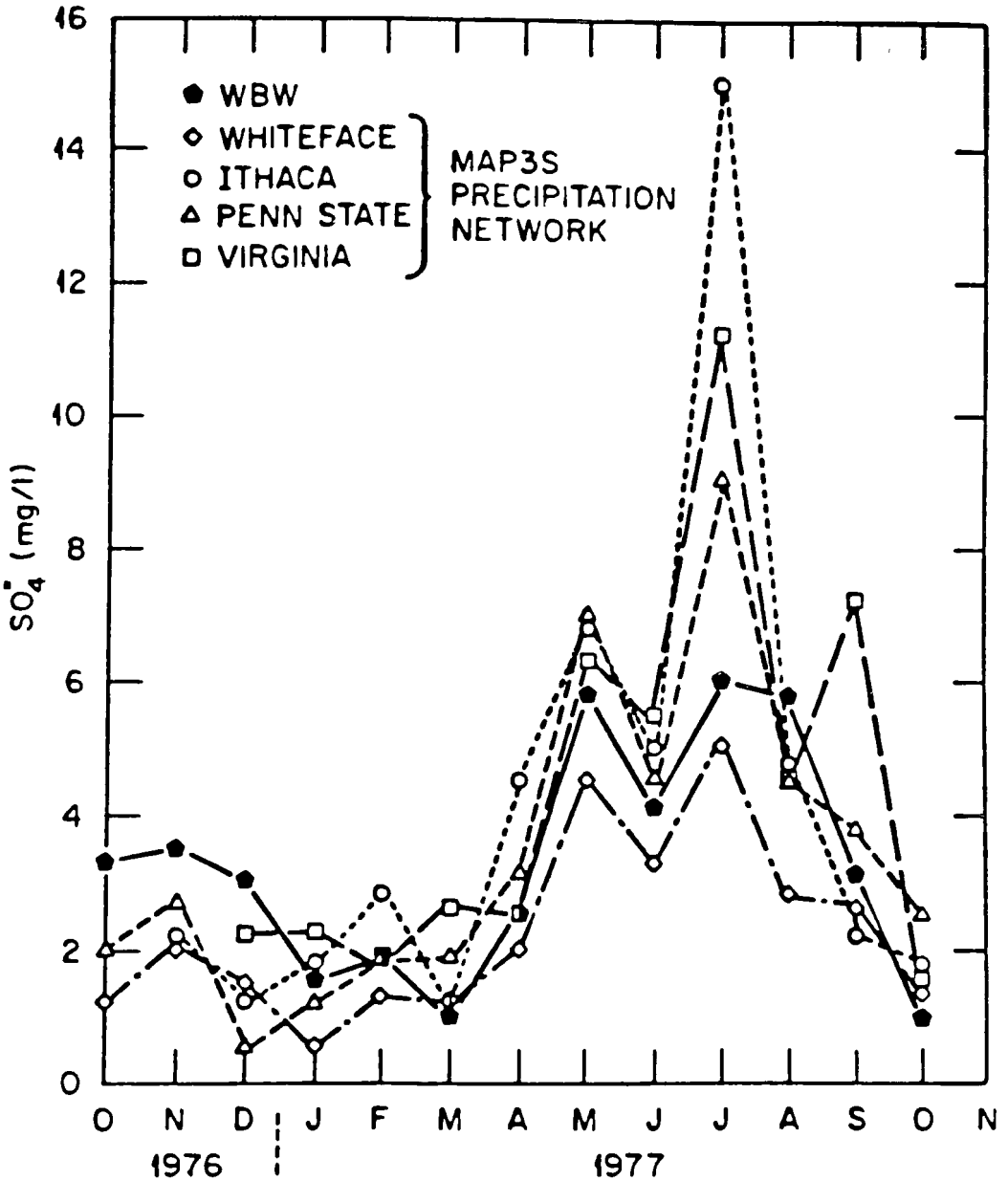


Figure 8-27. Comparison of weighted mean monthly concentrations of sulfate in incident precipitation collected in Walker Branch Watershed, Tenn. (WBW) and four MAP3S precipitation chemistry monitoring stations in New York (◇, 0), Pennsylvania (△), and Virginia (□).[219]

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9. EFFECTS ON VISIBILITY AND CLIMATE

9.1 INTRODUCTION

Haze particles are the most conspicuous trace constituents of the atmosphere; their presence can be detected from afar by the unaided eye. Particles scatter and absorb visible radiation, redirecting a portion of it to form "air light," which obscures distant objects. Section 9.2 of this chapter discusses the effects of particles on visibility.

Particles also indirectly affect the properties of the atmosphere. For example, essentially all water vapor condensation occurs by nucleation, that is, water deposition onto cloud condensation nuclei or ice nuclei. Addition of such particles to the atmosphere therefore affects cloudiness, which in turn influences insolation. Section 9.3 of this chapter discusses the effects of particles on solar radiation.

The incorporation of aerosols into cloud and fog droplets can change the quality as well as the quantity of precipitation. The mechanisms and effects of acid precipitation are discussed in chapter 8.

In 1977, the National Science Foundation Workshop on Inadvertent Weather Modification (Robinson, 1977) identified five major areas in which effects on the atmosphere can be attributed to presence of particles: visibility, solar radiation/sunshine, cloudiness, precipitation quantity, and precipitation quality. On the basis of current scientific knowledge, weather phenomena were assessed to determine the likelihood and qualitative scale of their inadvertent modification by human activities. Major inadvertent effects are considered scientifically established for changed precipitation quality, increased haze, and increased cloudiness. Moderate inadvertent effects are established for decreases in solar radiation and sunshine and for urban-scale increases in

quantity of precipitation and thunderstorms. Probable but not yet firmly established inadvertent changes include mesoscale increases in cloudiness and thunderstorms.

9.2 EFFECTS ON VISIBILITY

The term "visibility" is used colloquially to refer to various characteristics of the optical environment, such as the clarity with which distant details can be resolved and the trueness of their apparent coloration. These and other aspects of visibility are addressed in an EPA report to Congress (U.S. Environmental Protection Agency, 1979). Daytime visibility is normally taken to mean visual range, or the greatest distance at which a large black object can be distinguished against the daytime horizon sky. The National Weather Service (NWS), however, uses the term prevailing or horizontal visibility, which is the greatest visability which is attained or surfaced throughout at least half of the horizon circle not neccessarily continuous.

An insight into general visibility conditions in the United States can be obtained by examining available regional airport visibility data. Figure 9-1 (Trijonis and Shapland, 1978) shows isopleths of median visibility, a statistic that is insensitive to the site-specific availability of markers as long as the farthest markers consistently reported lie beyond the median visibility. The data represent midday visual ranges for 1974-76 from 100 suburban/nonurban locations. Visibilities at 93 of the locations were determined from airport observations, usually by NWS. Instrumental visibility measurements from seven sites in the Southwest are also included. Although some uncertainties arise from the use of airport visibility observations, there is reasonably good consistency among airport observations within regions and between airport and instrumental results in the Southwest.

The best visibility (70+ miles, 110+ km) occurs in the mountainous Southwest. Visibility is also quite good (45-70 miles, 70-110 km) north and south of that

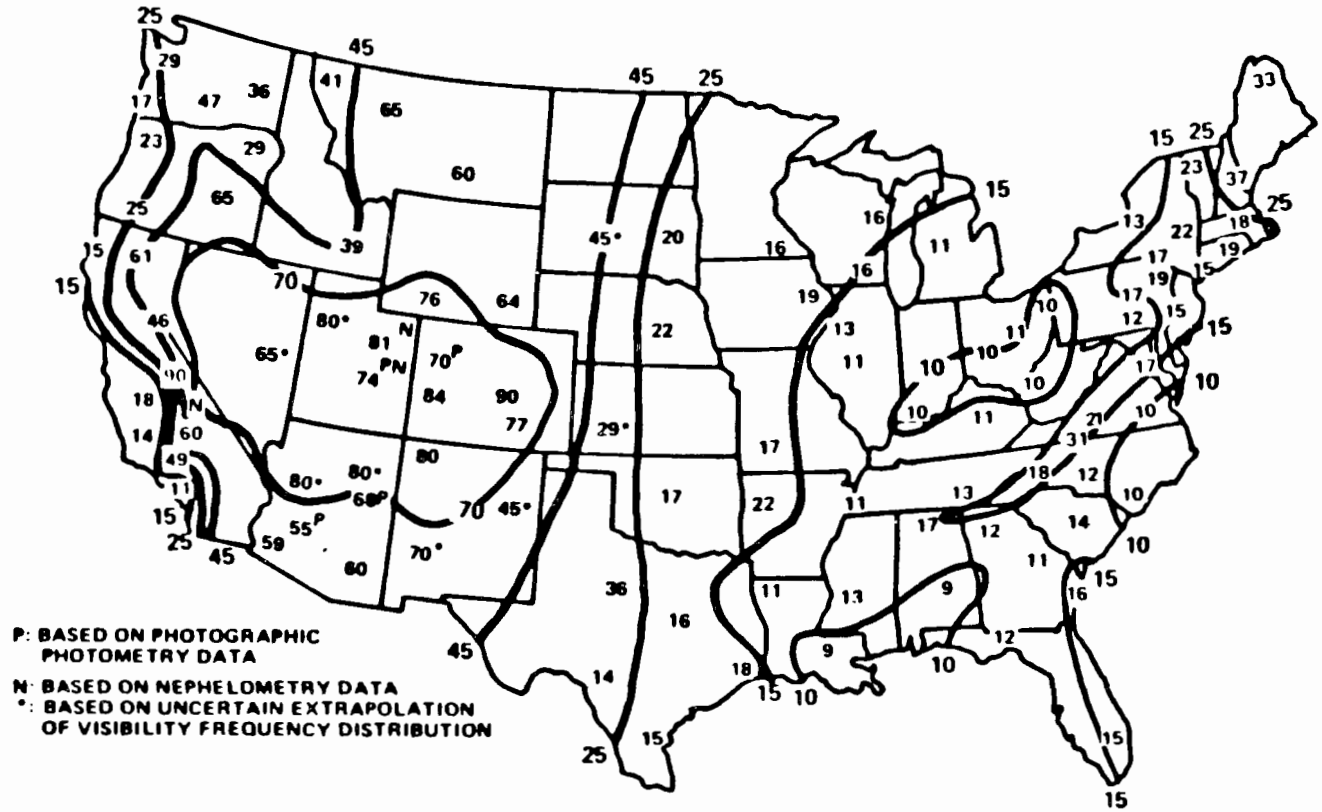

Figure 9-1. Map shows median yearly visual range (miles) and isopleths for suburban/nonurban areas, 1974-76.

Source: Trijonis and Shapland (1978).

region, but sharp gradients occur to the east and west. Most of the area east of the Mississippi and south of the Great Lakes has a median visibility of less than 15 miles (24 km). Within the East, the lowest visibilities occur along the heavily industrialized Ohio River Valley.

Although natural sources of visibility impairment are undoubtedly an important factor in producing these geographical and seasonal patterns, analysis of visibility trends and other information discussed in later sections suggests that manmade air pollution has a significant impact. It is also important to note that the regions with the best existing visibility levels are the most sensitive to additional impairment and most responsive to incremental pollution reductions. The reasons for this are discussed in the next section.

9.2.1 Fundamentals of Atmospheric Visibility

The effect of the intervening atmosphere on the visual properties of distant objects (e.g., the horizon sky, mountains, and clouds) can be determined if the concentration and characteristics of air molecules, aerosols, and nitrogen dioxide along the line of site are known. The rigorous treatment of visibility requires a mathematical description of the interaction of light with the atmosphere, known as the radiative transfer equation. The description presented here is intended to provide a qualitative understanding of the underlying theory. Detailed treatments are available in a number of publications (Middleton, 1952; Chandrasekhar, 1960).

Figure 9-2a shows the simple case of a beam of light (e.g., from the sun or a searchlight) transmitted horizontally through the atmosphere. The intensity of the beam in the direction of the observer, $I(x)$, decreases with distance from the source as light is absorbed or scattered out of the beam. Over a short interval, this decrease is proportional to the length of the interval and to the intensity of the beam at that point:

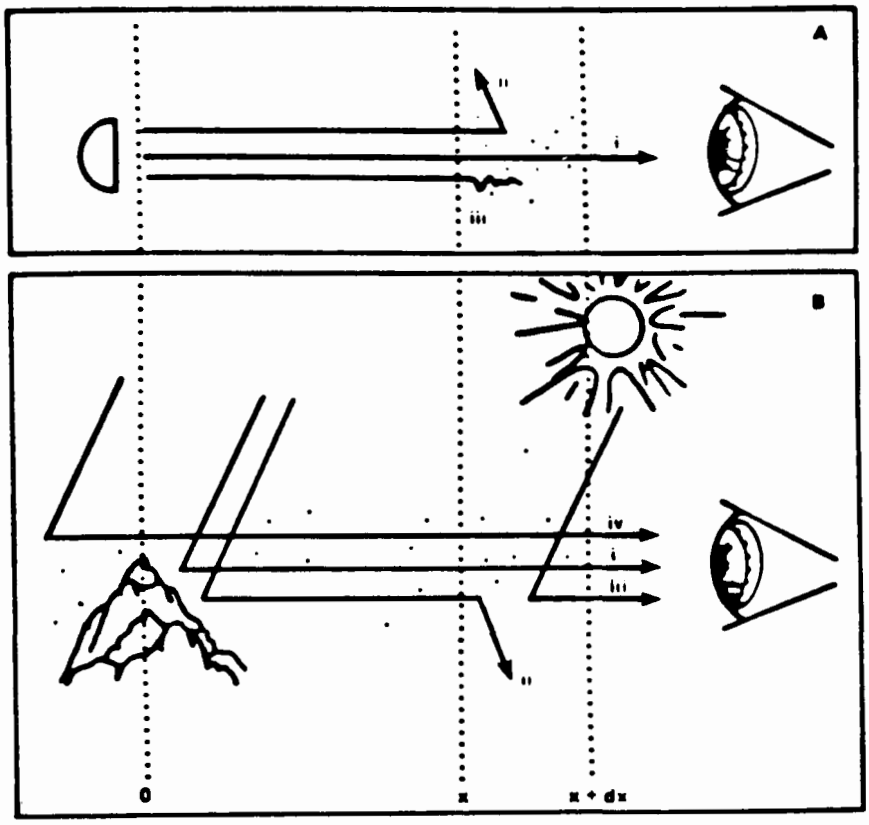

Figure 9-2. (A) A schematic representation of atmospheric extinction, illustrates (i) transmitted, (ii) scattered, and (iii) absorbed light. (B) A schematic representation of daytime visibility illustrates: (i) residual light from target reaching observer, (ii) light from target scattered out of observer's line of sight, (iii) air light from intervening atmosphere, and (iv) air light constituting horizon sky. (For simplicity, "diffuse" illumination from sky and surface is not shown.) The extinction of transmitted light attenuates the "signal" from the target at the same time as the scattering of air light is increasing the background "noise."

$$-dI = b_{ext} I dx$$

where dI is the decrease in intensity, b_{ext} is the extinction coefficient, I is the original intensity of the beam, and x is the path length. The extinction coefficient b_{ext} has units of inverse distance. The extinction coefficient is determined by the scattering and absorption of particles and gases and varies with pollutant concentration and wavelength of light.

Consider an observer looking at a distant target in the daytime (Figure 9-2b). Just as a beam is attenuated by the atmosphere, the light from the target reaching the observer is also diminished by absorption and scattering. The reduced brightness of distant objects is not usually the primary factor limiting their visibility, however; if it were, the stars would be visible around the clock, since their light must traverse the same atmosphere night and day. In addition to light originating at the target, the observer receives extraneous light scattered into the line of sight by the intervening atmosphere. It is this air light that we describe as haze.

The effect of extinction and added air light on the perceived brightness of visual targets is shown graphically in Figure 9-3. At increasing distances, both bright and dark targets are "washed out" and approach the brightness of the horizon. Thus, the contrast of an object relative to the horizon (and other objects) decreases.

The limiting distance at which a target can be distinguished from the horizon sky is the distance at which its apparent contrast (target brightness minus horizon brightness, divided by horizon brightness) drops to the observer's threshold of detection. In a uniform atmosphere, the apparent contrast between a target and the horizon sky decays exponentially with observer-target distance x (Middleton, 1952):

$$C = C_0 \exp(-b_{ext} x) \qquad (9\text{-}1)$$

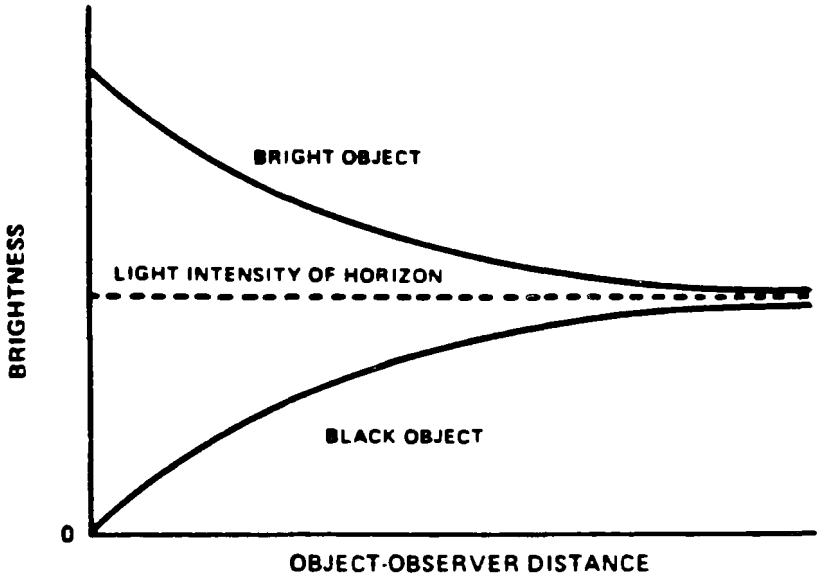

Figure 9-3. The apparent contrast between object and horizon sky decreases with increasing distance from the target. This is true for both bright and dark objects.

where C_0 is the initial contrast at x = 0. The maximum distance at which a given large target can be distinguished from the horizon is therefore inversely proportional to the extinction coefficient:

$$x_{max} = \frac{\log |C_0| - \log |\varepsilon|}{b_{ext}} \tag{9-2}$$

where ε is the observer's contrast threshold.

The proportionality factor, $\log |C_0| - \log |\varepsilon|$ in equation 9-2, depends on the target's intrinsic contrast with the horizon and on the observer's contrast threshold. For a black target, $C_0 = -1$, so that $\log |C_0| = 0$ and the proportionality factor reduces to $-\log |\varepsilon|$. The visual range (V) in a uniform atmosphere is thus given by the Koschmieder formula:

$$V = \frac{-\log |\varepsilon|}{b_{ext}} \tag{9-3}$$

The observer's contrast threshold, ε, is of course no universal constant. It varies with apparent target size and overall illumination, and it varies with observer (Figure 9-4; Middleton, 1952). However, it enters equation 9-3 only logarithmically, so that the relationship of visual range to extinction is not unduly sensitive to the psychophysiology of the observer. A sevenfold increase in ε, for example, does not quite double $-\log |\varepsilon|$. The conventional choice of $|\varepsilon|$ for a "standard" observer is 0.02, which yields $V = 3.9/b_{ext}$.

Little error is introduced into the determination of visual range by using as targets such nonblack features as dark forests and deep shadows. For a target whose intrinsic brightness is as much as 30 percent that of the horizon sky, for example, the limiting distance given by equation 9-2 is within 10 percent of the visual range. On the other hand, the intrinsic brightness of sunlit objects can approach that of the horizon sky, in which case their use as targets can lead to large underestimates of visual range.

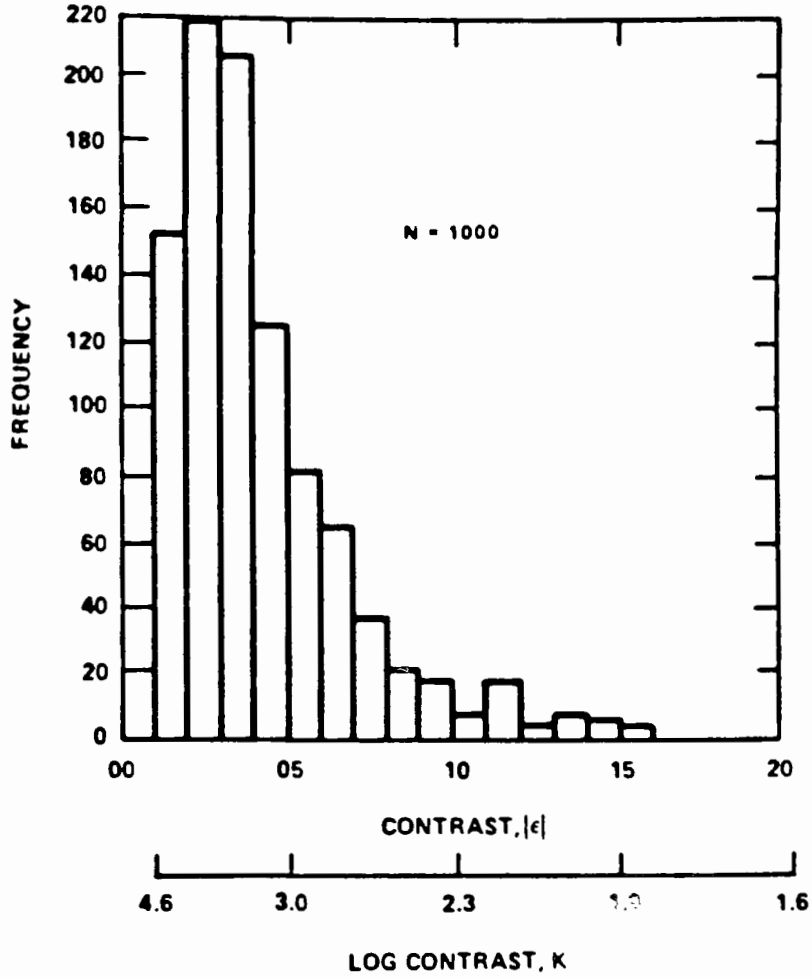

Figure 9-4. Measured apparent contrast of farthest visibility marker was identified in 1000 determinations of visual range by 10 observers. Scatter is due to both the variability of observer thresholds and the discrete nature of the marker set. The corresponding value for the Koschmieder constant, $K = -\log \epsilon$, is 3.2 ± 0.6.

Source: From Middleton (1952).

The Koschmieder formula's neglect of pollution gradients and the earth's curvature limits its applicability near sources of primary particulate matter and in very clean air. Where visibility is restricted by diffuse haze, however, equation 9-3 performs well. Comparisons of daytime visual range, as measured by a human observer, and extinction from scattering, as measured instrumentally at a single point, show visual range to correlate with the reciprocal of extinction, as illustrated in Figure 9-5 (Horvath and Noll, 1969; Samuels et al., 1973). The correlation coefficients are commonly in the neighborhood of 0.9, which is quite good considering that the point measurement of extinction is being extrapolated along a sight path several kilometers long.

9.2.1. Summary--Visibility is inversely proportional to the atmospheric extinction coefficient.

9.2.2 Measurement Methods

The extinction coefficient introduced in section 9.2.1 represents a summation of contributions from scattering and absorption by air and by pollutants: $b_{ext} = b_{Rg} + b_{ag} + b_{scat} + b_{abs}$, where b_{Rg} is Rayleigh scattering by air molecules; b_{ag} is absorption by nitrogen dioxide gas; b_{scat} is scattering by particles; and b_{abs} is absorption by particles. There are several methods for measuring total extinction and its various components, as discussed below.

9.2.2.1 Observer (Total Extinction)

9.2.2.1.1 Method. Contrast of an object is reduced as range increases as:

$$C = C_0 \exp(-b_{ext}\, x) \qquad (9\text{-}4)$$

For a black object viewed against the horizon, $C_0 = -1$ and a 0.02 contrast detection limit for the observer.

$$V = \frac{3.91}{b_{ext}} \qquad (9\text{-}5)$$

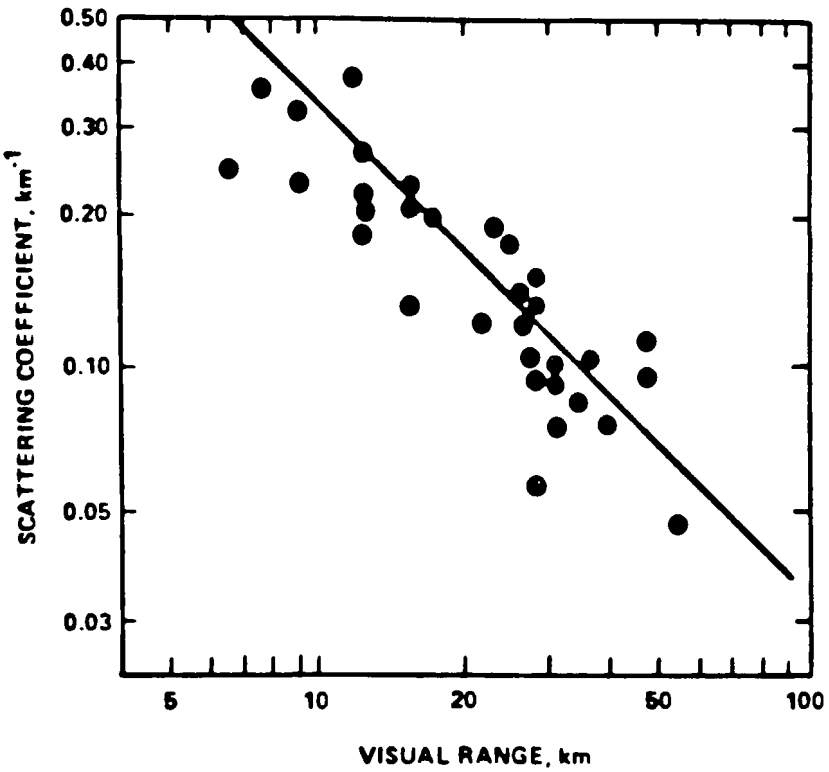

Figure 9-5. Inverse proportionality between visual range and the scattering coefficient, b_{scat}, was measured at the point of observation. The straight line shows the Koschmieder formula for nonabsorbing ($b_{ext} = b_{scat}$) media. $V = 3.9/b_{scat}$ The linear correlation coefficient for V and $1/b_{scat}$ is 0.89.

Source: Horvath and Noll (1969).

For the ideal case of a large black object and spatially uniform aerosol and illumination, V will be independent of sun angle. Prevailing visibility is normally observed over half of the horizon circle. A somewhat different V will result if the observation is based on detecting fine spatial contrast detail instead of a large black object (Henry, 1977).

9.2.2.1.2 Problems. This method is labor intensive and requires black objects at several distances to provide gradation in measured visibility as b_{ext} changes.

Few sites are suited for visibility observations over a visual range greater than 50 km. For reflecting targets, such as snow-covered mountaintops, the distance at which they can be detected under constant extinction can change from the visual range or somewhat greater under clear skies and high sun elevations to less than one-fourth the visual range for evenly overcast skies. The contrast between the horizon and the target is a function of sun angle except for ideal black targets.

To detect changes in visual range, targets are required at a range of distances. For example, Tombach and Chan (1977) reported on a visibility measurement program consisting of about 1 year of weekly observations. In all observations, the most distant target at 120 km was visible. The site used was not well suited because targets were not available at various distances near the mean visual range. In some places, topography or earth curvature prevent the establishment of appropriate markers at $V \approx 250$ km.

9.2.2.2 Contrast Telephotometry (Total Extinction)

9.2.2.2.1 Method. The brightness (usually luminance or radiance at various wavelengths) of a black object at a distance much less than the visual range is measured and expressed as ratio to the same brightness of the nearby horizon.

Either photographic or photoelectric sensing is used. The extinction coefficient is obtained from equation 9-4, which gives

$$\frac{1}{x} \ln \left(\frac{C}{C_0}\right) = -b_{ext} \tag{9-6}$$

Black targets must be used unless C_0 is known for other targets, and the wavelength of operation must be chosen. The obvious choice of photopic response to match an observer is probably not the best choice in clean sites. Tombach and Chan (1977) and Trijonis and Yuan (1978a) have shown that visual range or extinction is at times largely determined by the molecular (Rayleigh) scattering in the atmosphere. Therefore, there will be a color shift between the horizon and the air light that is detected by looking at a nearby black object (Middleton, 1952). Measurements should be made by using narrowband radiance rather than broadband luminance detectors to avoid errors in measurement of extinction.

Telephotometers may be useful for characterizing plumes in terms of their brightness or contrast relative to sky or terrain background. Simple contrast measurement of distant visible objects may be useful even if it is not possible to reduce the observations to extinction.

9.2.2.2.2 Problems. At some sites there may be relatively few days on which telephotometers are useful because clouds (on the horizon or above the path to the nearby black object) introduce errors. The use of equation 9-6 to reduce contrast measurements to extinction coefficients requires uniform illumination of both measurement paths and assumes that the horizon is optically thick horizontally. This means that visual range is limited by optical extinction and reduced contrast and not by the earth's curvature. This last assumption is not true in clean locations where visual range is largely limited by molecular scatter. The error from this assumption will increase calculated extinction, particularly at longer wavelengths.

Although it is possible to design automatic, low-maintenance telephotometers that can scan selected targets, no instrument of this type is now available. Therefore this measurement is labor intensive, requiring an operator. Even with an automated instrument, accuracy requires that the sight path and horizon be cloud-free, and this check may be difficult to automate. Photographic measurements minimize capital investment but increase operator cost and decrease accuracy.

9.2.2.3 Long-Path Extinction (Total Extinction)

9.2.2.3.1 Method. The most direct way to measure extinction is simply to measure the decrease in intensity of a beam of light as a function of range:

$$\frac{I}{I_0} = \exp(-b_{ext}\, x)$$

$$\frac{1}{x} \ln \frac{I}{I_0} = b_{ext}$$

This method has great appeal in that no assumptions are involved and it measures average extinction over the path.

Experimentally, a source (either incoherent or laser) is observed at a large distance by using collecting optics plus a photomultiplier light detector and an optical band-limiting filter. The source and detector may be at opposite ends of the path or at the same end, with a distant mirror used to reflect the beam.

9.2.2.3.2 Problems. The calibration of a long-path transmissometer is difficult for these reasons: (1) the outgoing optical energy is usually not well known; (2) the distant mirror or other retroreflector has unknown divergence and reflectivity; (3) the receiver sensitivity, including the collecting optics and filter transmissions, is unknown; and (4) 1 through 3 can change with time.

Hall and Riley (1976) have measured extinction by observing the same source at two ranges. Any decrease in intensity with range in excess of the inverse-square decrease is due to extinction. This method avoids any need for absolute calibration, since only the ratio of intensities at two ranges need be measured. This method as used by Hall and Riley is labor intensive but has been demonstrated in clean and urban environments during night operation. A mercury arc light probably would allow daytime operation.

Systems that do not use multiple path lengths require another calibration method that must be stable over long periods and be accurate enough to permit aerosol extinction comparable to or less than Rayleigh scattering to be quantified. It is not clear how this can be done.

9.2.2.4 Nephelometer (Scattering)

9.2.2.4.1 Method. The integrating nephelometer was developed around 1943 as a simple means of measuring visual range, and the principle has been used widely for about 25 years (Middleton, 1952). The configuration of this instrument gives an integration-over-scattering angle such that the scattering component of the extinction, b_{scat}, can be measured. By subtracting the Rayleigh scattering, b_{Rg}, a measurement of b_{sp} is possible with an accuracy in most cases of about 10 percent of the reading (Ensor and Waggoner, 1970; Rabinoff and Herman, 1973). This measurement is made at a point in an internal sample volume. This closed system allows both humidity control and the calibration with particle-free gases such as carbon dioxide or Freon-12. Since these gases are widely available and are inexpensive, calibration is simple. The instrument is commercially available from both U.S. and foreign manufacturers. The U.S. version was developed under Federal Government support (Public Health Service, National Air Pollution Control Administration, Environmental Protection Agency, and National Science Foundation). Other versions are available that differ in sensitivity and

wavelength response. The most sensitive instruments are capable of measuring aerosol particle scattering extinction, b_{sp}, at or below 10 percent of Rayleigh scatter (i.e., at $b_{sp} \approx 0.1\ b_{Rg}$). Thus, adequate sensitivity is available for class I regions.

The nephelometer can be used to measure the scattering coefficient at the same point where samples are taken for mass or chemical determination. Most of the data relating cause and effect (i.e., particle concentration or composition and optical effect) have been acquired with the integrating nephelometer. Agreement between the nephelometer and the long-path transmissometer has been demonstrated (Waggoner and Charlson, 1976; Weiss, 1978).

9.2.2.4.2 Problems. The instrument measures optical properties at a point, which may limit its application to cases where there is spatial uniformity of atmospheric optical properties. There may be errors introduced by differences in humidity inside the instrument relative to ambient conditions. The instrument will have two types of error if atmospheric optical properties are controlled by particles larger than 3 μm such as in fog or dust storms: (1) coarse particles will be excluded by impaction on the sampling ductwork; and (2) the angular integration suffers from truncation at low scattering angles and in fog will underestimate the actual scattering coefficient by as much as a factor of 2.

9.2.2.5 Light Absorption Coefficient--Without doubt, the absorption component of extinction, b_{ap}, is the most difficult to measure. As yet, no single method has proven to be the most effective. Were it not for the fact that graphitic carbon as soot is a dominant species in cities and industrial regions, b_{ap} would be inconsequentially small. However, even a few percent of the submicron mass as soot produces a significant effect on b_{ap} or b_{ext}. The methods that have so far been used to evaluate b_{ap} include: (1) determining the difference

between b_{ext} and b_{sp} by combining long-path transmissometer with nephelometer (Weiss, 1978); (2) determining absorption on Nuclepore filters with scattered light removed by an integrating plate of opal glass (Weiss, 1978); (3) determining absorption on Millipore filters (Rosen et al. 1980 ~~and Novakov, 1979~~); (4) determining the reflectivity of a white powder with aerosol mixed into it, called the Kubelka-Monk method (Lindberg and Lande, 1974); (5) determining absorption of light by a sample of particles inside a white sphere (integration sphere) (Fischer, 1975); (6) estimating an imaginary refractive index from regular scattering or polarization and size distribution (Eiden, 1971); (7) measuring the amount of graphitic carbon and its size distribution and then calculating b_{ap}.

To date, none of these methods has been characterized well enough to permit making a clear-cut choice.

9.2.3 Role of Particulate Matter in Visibility Impairment

As noted in section 9.2.2, the extinction coefficient comprises contributions from gas and aerosol scattering and absorption:

$$b_{ext} = b_{Rg} + b_{ag} + b_{scat} + b_{abs}$$

This section discusses the relative magnitudes of these contributions.

9.2.3.1 Rayleigh Scattering--The particle-free molecular atmosphere at sea level has an extinction coefficient of about $12 \times 10^{-6}\ m^{-1}$ for green light (wavelength 0.55 μm), limiting visual range to about 320 km. The coefficient b_{Rg} decreases with altitude. In some areas of the Western United States, the extinction of the atmosphere is at times essentially that of the particle-free atmosphere (Charlson et al., 1978). Rayleigh scattering thus amounts to a simply definable and measurable background level of extinction with which other extinction components (such as those caused by manmade pollutants) can be

compared. Rayleigh scattering decreases with the fourth power of wavelength, and contributes a strongly wavelength-dependent component to extinction. When Rayleigh scattering dominates, dark objects viewed at distances over several kilometers appear behind a blue haze of scattered light, and bright objects on the horizon (such as snow, clouds, or the sun) appear reddened at distances greater than about 30 km.

9.2.3.2 Nitrogen Dioxide Absorption--Of all gaseous air pollutants, only nitrogen dioxide has a significant absorption band in the visible part of the spectrum. Nitrogen dioxide absorbs strongly in the blue and can color plumes red, brown, or yellow. The effects of nitrogen dioxide on visibility are discussed in the criteria document for oxides of nitrogen. Its contribution to total extinction is in general minor.

9.2.3.3 Particle Scattering--As the particle concentration increases from very low levels, where Rayleigh scattering dominates, the particle scattering coefficient, b_{scat}, increases until eventually b_{scat} is greater than b_{Rg}. At 40-km visibility, for example, Rayleigh scattering contributes about one-eighth of the total extinction. At this point, the visual quality of air is controlled by particle scattering. Two principal problems in understanding the degradation of the visual quality of air have been: (1) defining the size range and other physical characteristics of particles most effective in causing scatter; and (2) defining the chemical composition and thus identifying the source of particle in this size range (Charlson et al., 1978).

Size, refractive index, and shape are the most important parameters in relating particle concentration and particle-related extinction coefficients, b_{scat} and b_{abs}. If these properties are established, the light scattering and absorption can be calculated. Alternatively, the extinction coefficient associated with an aerosol can be measured directly.

From the point of view of aerosol optics, a key question is whether an aerosol particle is spherical. For such particles, rigorous Mie theory (Mie, 1908) is applicable, and the optical properties can be readily calculated from their size and refractive index. Measurements in St. Louis by Allen et al. (1978) show that in the fine mode less than 5 percent of the aerosol population is nonspherical. Pueschel and Wollman (1978) found that spherical particles also dominate fine-mode aerosols near Cedar Mountain.

Coarse particles are almost exclusively nonspherical; using the Mie theory to calculate their optical properties will therefore give only a crude approximation. There is, however, an extensive body of experimental data on the optical properties of the nonspherical particles (e.g., Pinnick et al., 1976).

Charlson et al. (1978) used Mie theory to calculate the light-scattering and absorption efficiency per unit volume of particles for a typical aerosol containing some light-absorbing soot (Figure 9-6). As illustrated in the figure, particles of 0.1 to 1 μm are the most efficient light scatterers. The remarkably high scattering efficiencies of these particles are illustrated by the following examples: a given mass of aerosol of 0.5-μm diameter scatters about a billion times more light than the same mass of air; a 1-mm-thick sheet of transparent material, if dispersed as 0.5-μm particles, would be sufficient to scatter 99 percent of the incident light, that is, to completely obscure vision across such an aerosol cloud.

Atmospheric particles or aerosols are made up of a number of chemical compounds. All of these compounds exhibit a peak scattering efficiency in the same diameter range (0.1 to 1.0 μm) calculated to be optically important for the typical aerosol in Figure 9-6. However, because of differences in refractive index, the values of the peak efficiency and the particle size at which it occurs vary considerably among the compounds (Figure 9-7; Faxvog, 1975).

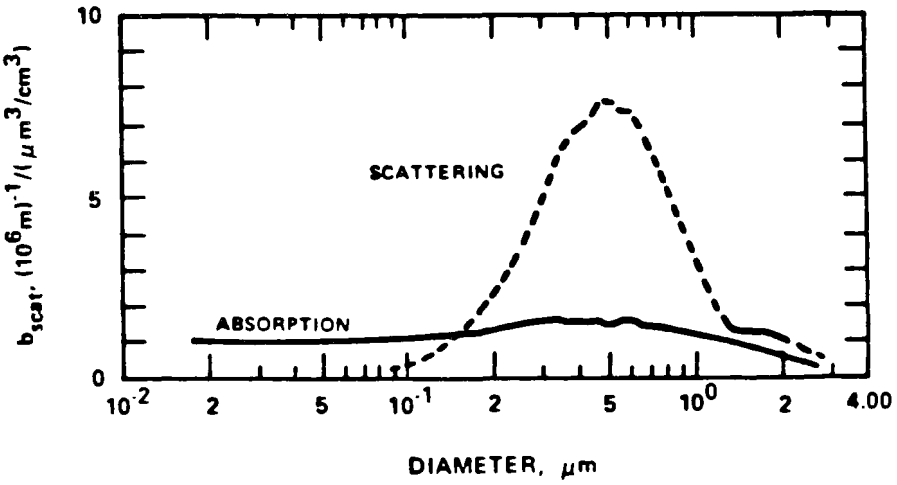

Figure 9-6. For a light-scattering and absorbing particle, the scattering per volume has a strong peak at particle diameter of 0.5 μm (m = 1.5 − 0.05i; wavelength = 0.55 μm). However, the absorption per aerosol volume is only weakly dependent on particle size. Thus the light extinction by particles with diameter less than 0.1 μm is primarily due to absorption. Scattering for such particles is very low. A black plume of soot from an oil burner is a practical example.

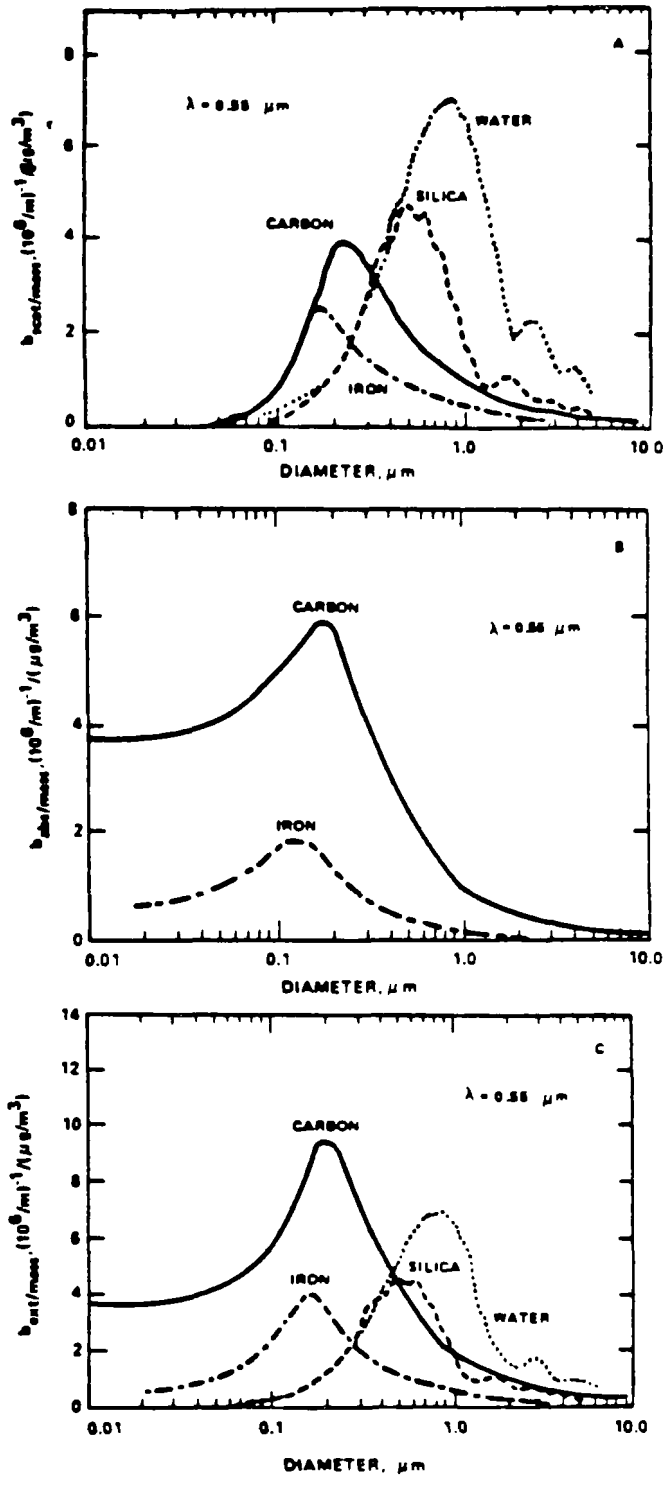

Figure 9-7. (A) Calculated scattering cross-section per unit mass at a wavelength of 55 μm for absorbing and nonabsorbing materials is shown as a function of diameter for single-sized particles. The following refractive indices and densities (g/cm³) were used: carbon (m = 1.96-0.66i, d = 2.0), iron (m = 3.51-3.95i, d = 7.86), silica (m = 1.55, d = 2.66), and water (m = 1.33, d = 1.0). (B) Calculated absorption cross-section per unit mass at 0.55 μm for single-sized particles of carbon and iron. (C) Calculated extinction cross section per unit mass at 0.55 μm for single-sized particles of carbon, iron, silica, and water.

(Source: (a) Faxvog (1975), (b and c) Faxvog and Roessler (1978).

Measured particle size distributions can be used in conjunction with Mie theory calculations for single particles to determine the contribution of different size classes to extinction. The results of this kind of calculation are shown in Figure 9-8. The peak in single-particle scattering per unit volume is at 0.3 μm, so that the fine particles dominate extinction in almost all cases.

Because the peak and shape of the bimodal particle mass distribution curve can vary, the light-scattering characteristics of a given particle mass might also be expected to vary. However, as noted by Charlson et al. (1978), for the observed range of atmospheric particle distributions, the calculated scattering coefficient per unit mass is relatively uniform. Latimer et al. (1979) have determined the scattering efficiency per unit volume for several aerosol distributions. The calculated coefficient changes by no more than 40 percent in the size range of 0.2 to 1.0 μm (Figure 9-9; Latimer et al., 1979).

The relative consistency of calculated light scattering per unit mass over a range of particle distributions and the dominant influence of fine particles suggest that reasonably good approximations of light-scattering coefficients can be obtained by measurements of fine-particle mass. Indeed, agreement from simultaneous monitoring of the two parameters at a number of sites has been found by several investigators. Measurements by Weiss (1978), Patterson and Wagman (1977), Macias et al. (1975), and Samuels et al. (1973) at various sites showed scattering per unit mass ratios of 3-5 x 10^{-6} $m^{-1}/(\mu g/m^3)$. Correlations between the fine-particle mass and b_{scat} are consistently high (Table 9-1). Figure 9-10 (Macias ~~et al.~~ and Hasan 1976, ~~1975~~) shows the relationship for St. Louis. The high correlations indicate that at the sites studied, fine-particle mass dominates particle scattering.

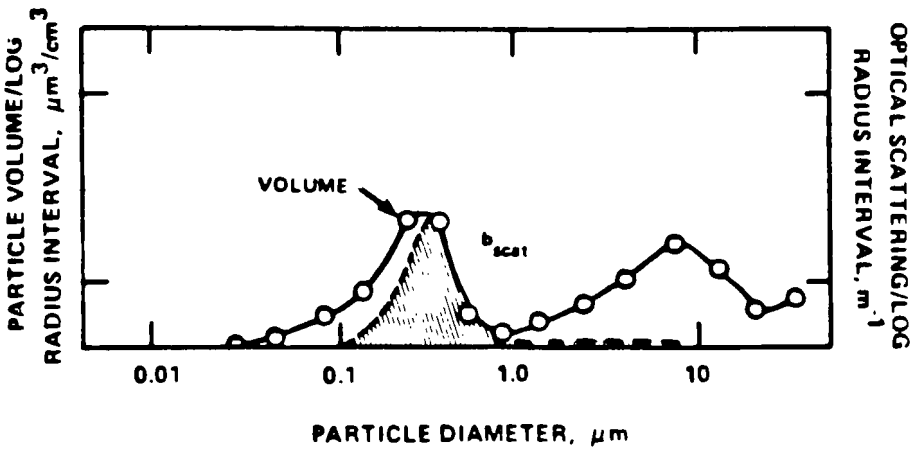

Figure 9-8. For a typical aerosol volume (mass) distribution, the calculated light-scattering coefficient is contributed almost entirely by the size range 0.1-1.0 μm. The total b_{scat} and total aerosol volume are proportional to the area under the respective curves.

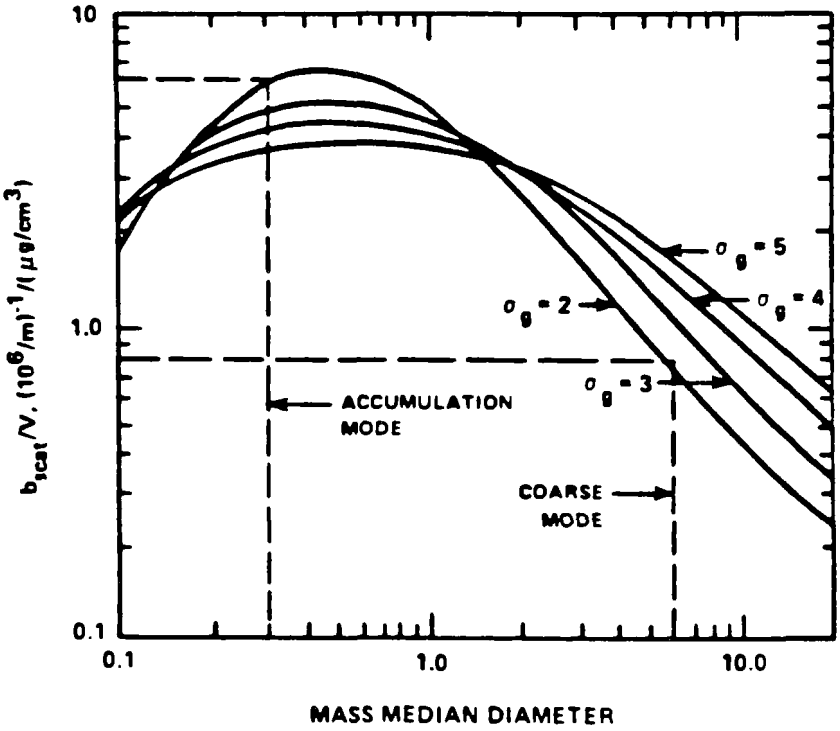

Figure 9-9. Scattering-to-volume ratios are given for various size distributions.

TABLE 9-1. LIGHT SCATTERING PER UNIT MASS OF FINE AEROSOL

Location	b_{scat}/mass, $10^6 m^{-1}/(\mu g/m^3)$	r	N	Reference[a]
Mesa Verde, CO	2.9	--	5	1
Seattle, WA (residential)	3.1	0.95	58	1
Seattle, WA (industrial)	3.2	0.97	64	1
Puget Island, WA	3.0	0.97	26	1
Portland, OR	3.2	0.95	108	1
New York, NY	5.0	--	--	2
St. Louis, MO	5.0	0.96	72	3
Los Angeles, CA	3.7	0.83	39	4
Oakland, CA	3.2	0.79	20	4
Sacramento, CA	4.4	0.98	6	4

[a]1, Waggoner and Weiss (~~1979~~ 1980); 2, derived by Charlson et al. (1978) from Patterson and Wagman (1977); 3, Macias et al. (1975); 4, Samuels et al. (1973).

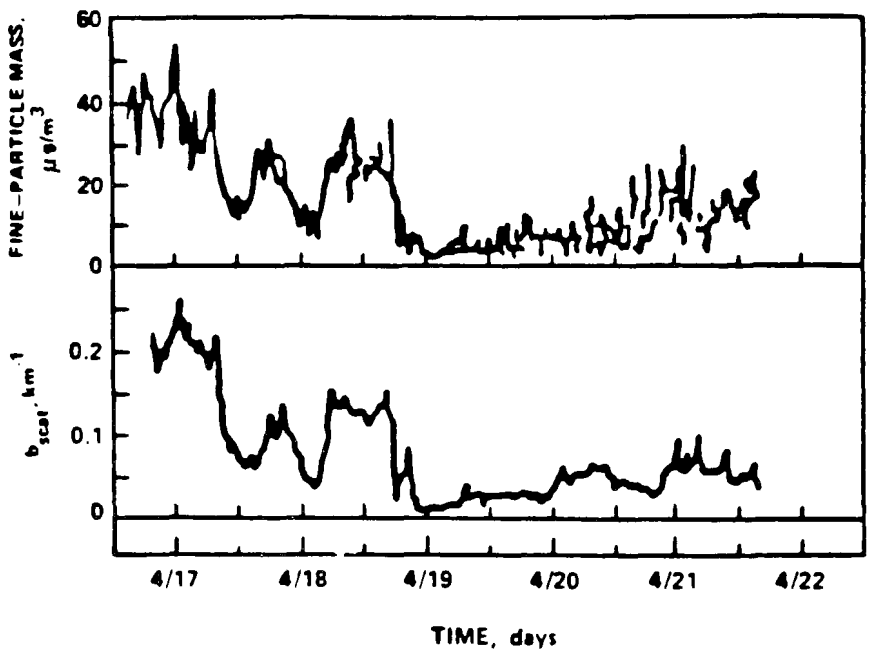

Figure 9-10. Simultaneous monitoring of b_{scat} and fine-particle mass in St. Louis in April 1973 showed a high correlation coefficient of 0.96, indicating that b_{scat} depends primarily on the fine-particle concentration.

Source: Macias et al. (1975).

This was documented in an experiment conducted by Patterson and Wagman (1977), who monitored the ambient aerosol size distribution by a set of four cascade impactors in the New York metropolitan area. The first impactor was operated only when the light-scattering coefficient was between 0 and 0.15 km^{-1}. Impactor A was operated at 0.15-0.3; impactor B at 0.3-0.45; and impactor C at 0.45. The measured mass distributions (Figure 9-11; Patterson and Wagman, 1977) show that at good background visibility levels, the mass concentration was largely (70 percent) contributed by coarse particles. At the low visibility level C, however, over 60 percent of the total mass was contributed by fine particles. Thus, visibility in the New York metropolitan area was found to be lowest when the concentration of fine particles reached a maximum.

It is conceivable that in the arid West the aerosol refractive index and relative amounts of coarse and fine particles are so different that the scattering mass ratios quoted above would not be applicable. However, preliminary results from project VISTTA (Macias et al., 1978) suggest that b_{scat}/fine mass ratios in the Southwest are $3 \times 10^{-6} m^{-1}/(\mu g/m^3)$, as measured elsewhere.

In clean areas where fine-particle levels are low, coarse particles may contribute to light scattering. Coarse dust particles are much less efficient scatterers per unit mass (Figure 9-6; Charlson et al., 1978), however, so that much higher mass concentrations are required to produce a given optical effect. In windblown dust, for example, Patterson and Gillette (1977) reported values of the ratio of light scattering to mass that were more than an order of magnitude lower than those noted above for fine particles.

The wavelength dependence of light scattering ranges from the very strong blue scattering of air molecules (Rayleigh particles < 0.05 μm) to wavelength-independent or "white" scattering for coarse particles of >5 μm.

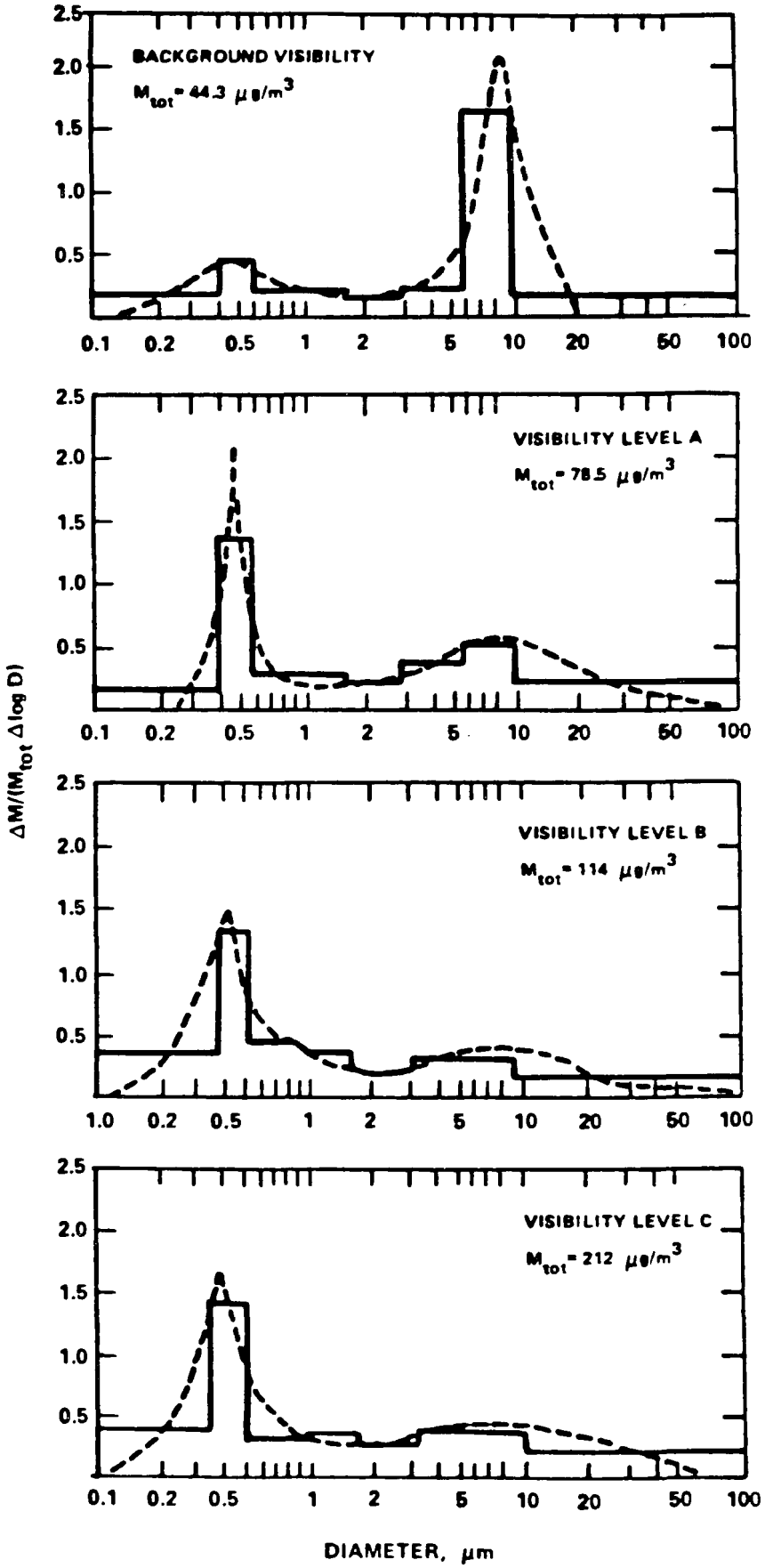

Figure 9-11. Aerosol mass distributions, normalized by the total mass, for New York aerosol at different levels of light-scattering coefficient show that at high background visibility, the fine-particle mass mode is small compared with the coarse-particle mode. At the low visibility level, ϵ, 60 percent of the mass is due to fine particles.

Source: Patterson and Wagman (1977).

In pristine areas, when Rayleigh scattering dominates ($b_{Rg} = 2 \times 10^{-6}\ m^{-1}$), addition of about 4 $\mu g/m^3$ of fine particles ($b_{scat} = 13 \times 10^{-6}\ m^{-1}$) would cause substantial "whitening" of the natural blue Rayleigh haze and the horizon sky (Charlson et al., 1978). At a fine-particle level of 30 $\mu g/m^3$ (0.1 km^{-1}), the wavelength-dependent scatter would be controlled by the aerosol itself.

9.2.3.4 Particle Absorption--Particle absorption (b_{abs}) appears to be on the order of 10 percent of particle scattering (b_{scat}) in low-background areas such as Bryce Canyon (Weiss, 1978). Its contribution may rise to 50 percent of b_{scat} in urban areas such as Phoenix, although values of 10 to 25 percent would be more typical (Weiss, 1978). The amount of absorption per unit mass depends on chemical composition and particle size distribution (Waggoner, et al 1973; Bergstrom, 1973). The most important contributor to this absorption in cities appears to be graphitic carbon in the form of soot (Hansen et al., 1978). The source of this highly absorbing submicron soot appears to be the combustion of liquid fuels, particularly in diesel engines; coal combustion may not be a major contributor (Charlson et al., 1978).

9.2.3.5 Summary--The extinction of light in polluted air is generally dominated by particle scattering. On a regional scale, almost all of the particle scattering is contributed by fine particles. Extinction due to scattering is roughly proportional to the fine-particle mass concentration, with extinction/mass ratios in the range of 3-5 x $10^{-6}\ m^{-1}/(\mu g/m^3)$.

9.2.4 Chemical Composition of the Light-Scattering Aerosol

The preceding section showed that identifying the sources of light-scattering aerosols largely reduces to determining the sources of fine-particle mass. In this regard, a critical observation is that sulfates (sulfate and associated cations) often account for 40 to 60 percent of the mass in the fine-particle mode.

Separate chemical mass balances for fine and coarse particles in Charleston, WV, were conducted by Lewis and Macias (1979) (Figure 9-12). Of the fine-particle mass (33 $\mu g/m^3$), about 30 percent was sulfate, 13 percent was ammonium, 18 percent was carbonaceous material, and the rest consisted of trace constituents and undetermined species (including water). Thus, sulfate accounted for a substantial part of fine-particle mass, with over 80 percent of the total aerosol sulfate residing within the fine-particle mode.

A more detailed size-chemical composition distribution was reported by Patterson and Wagman (1977) for the New York metropolitan area aerosol (Figure 9-13). Sulfate and ammonium ions, alone among the species measured, were concentrated in the size range between 0.2 and 0.7 μm. Comparison with Figure 9-6 (Charlson et al., 1978) shows that the size range in which sulfate and ammonium occur is also the window of peak light-scattering efficiency per unit mass. Consistent with their distribution with respect to particle size, sulfates appear to contribute disproportionately to the degradation of visibility. Sulfates have been found to be strongly associated with reduced visibility and increased light scattering in Europe and the United States (Rodhe et al., 1972; Eggleton, 1969; Barnes and Lee, 1978; Husar et al., 1979; Waggoner et al., 1976).

Sulfates correlate with reduced visibilities even when the remainder of the aerosol is taken into account. White and Roberts (1977) used multivariate analysis to estimate the relative contributions of sulfates, nitrates, organic compounds, and the remainder of the particulate mass to the measured light-scattering coefficient in the Los Angeles area. Sulfates appeared to contribute about twice as much extinction per unit mass as the average for the aerosol. Similar findings have been reported by Cass (1979), Trijonis and Yuan (1978a,b),

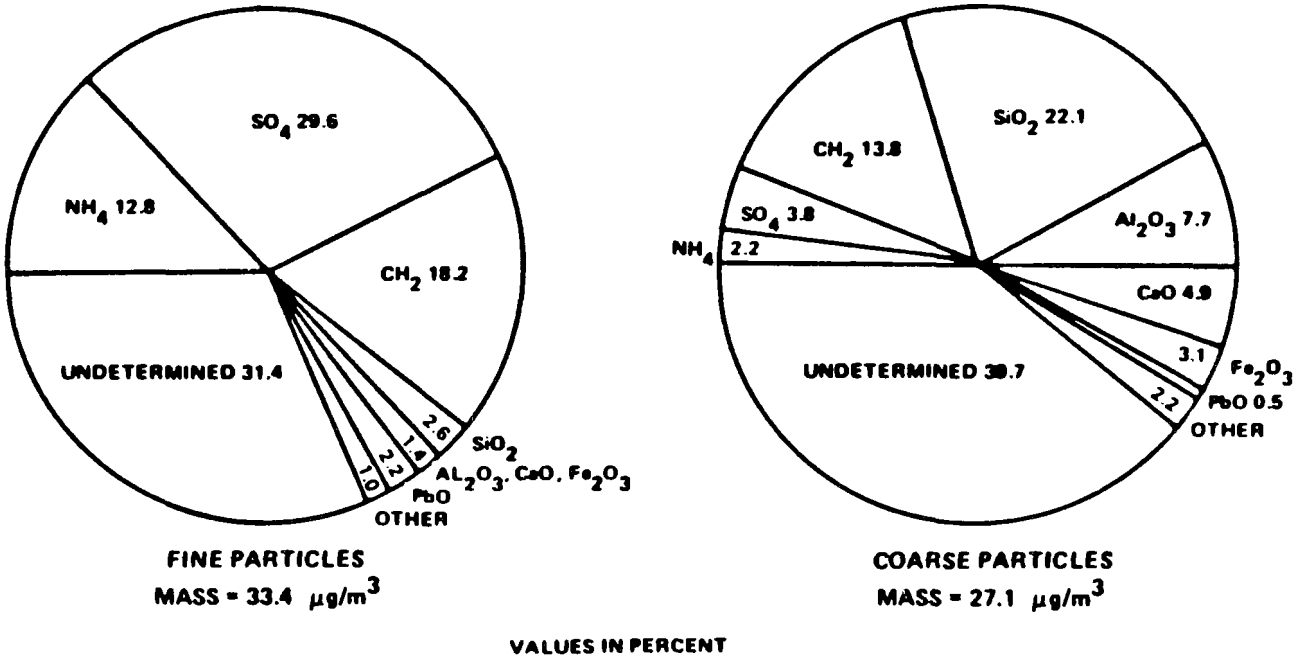

Figure 9-12. Chemical-mass balance was determined for fine and coarse particles collected in Charleston, WV.

Source: Lewis and Macias (1979).

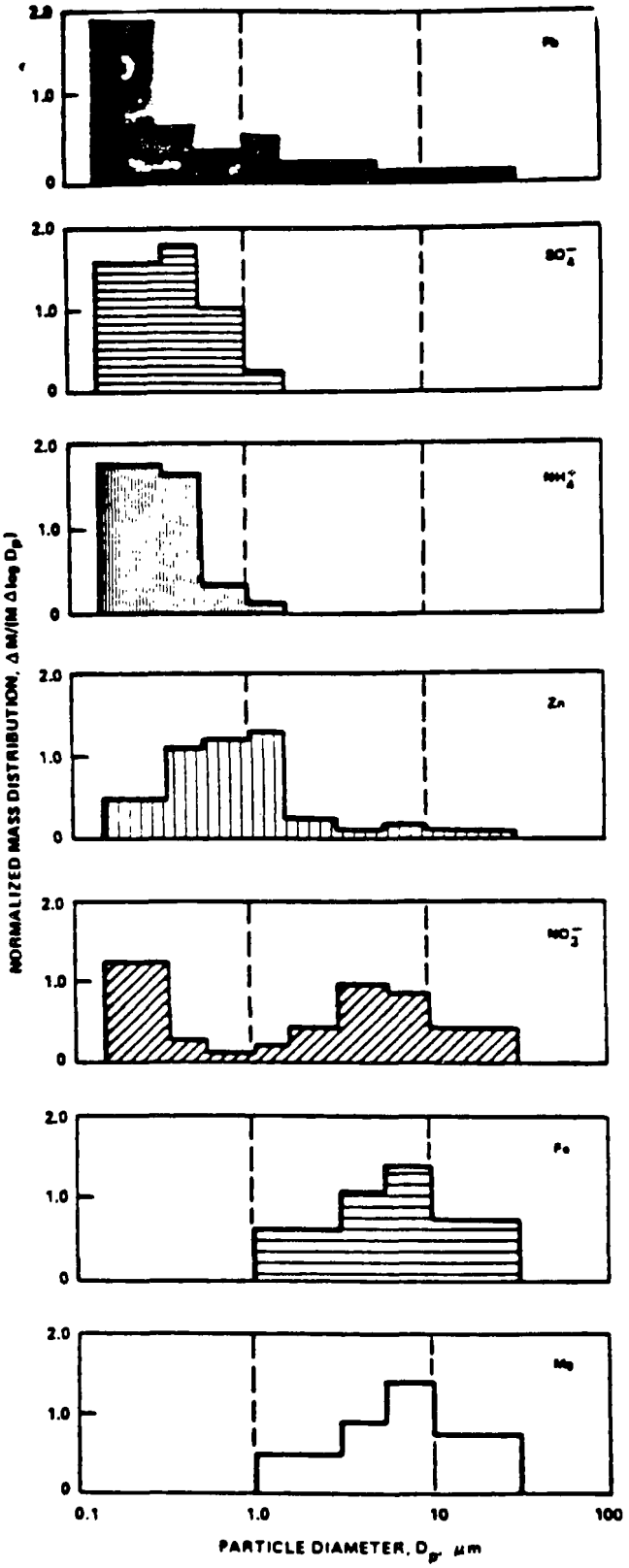

Figure 9-13. Normalized mass distribution functions of some species found in New York City aerosol show that sulfate and ammonium were found in the most efficient light-scattering size range (0.2-0.7 μm).

Source: Adapted from Patterson and Wagman (1977).

Grosjean et al. (1976), and Leaderer et al. (1978). As summarized in Table 9-2, empirically derived extinction/mass ratios for sulfate compounds are typically 7±1 [10^{-6} $m^{-1}/(\mu g/m^3)$] at 70 percent relative humidity. In the Los Angeles basin, Cass (1979) has further shown that the periods of highest light scattering per unit sulfate occur on days of high sulfate mass concentration.

Researchers (Charlson et al., 1974, Figure 9-14) recognize that the major atomspheric sulfate species are hygroscopic and their light-scattering-to-dry-mass ratio is a function of relative humidity. The light scattering of some sulfate species (e.g. H_2SO_4 and NH_4HSO_4) increases smoothly with increasing humidity; other species (e.g. $(NH_4)_2SO_4$) exhibit sudden particle size growth at or above certain relative humidities and a subsequent two-to-three fold increase in light scattering. The light scattering to humidity response of atmospheric sulfate aerosols in highly dependent on size distribution and molecular composition, which are difficult or almost impossible to measure with sufficient resolution and accuracy. Thus, visibility cannot always be accurately predicted using measurements of sulfate loadings or fine particle mass loadings.

To the extent that particulate nitrates are secondary aerosols formed in the size range of 0.2 to 1.0 μm, it is to be expected that they, too, are efficient light scatterers. Since ammonium nitrate is hygroscopic, the scattering/mass ratio for particulate nitrate could be comparable to that for sulfates. As Table 9-2 shows, there is some statistical support for this hypothesis. However, even if nitrates scatter efficiently, their absolute contributions to extinction may be small because concentrations of particulate nitrates in most locations may be low. As discussed in chapter 5, these conjectures cannot be satisfactorily tested with the existing data on particulate nitrate.

TABLE 9-2. EMPIRICAL EXTINCTION EFFICIENCIES OF SPECIFIC AEROSOL FRACTIONS

Efficiency, $10^{-6}m^{-1}/(\mu g/m^3)$[a]	Los Angeles, CA[b]	Phoenix, AZ[c]	Salt Lake City, UT[c]	Columbus, OH[d]	Charlotte, NC[d]	Lexington, KY[d]	Cleveland, OH[d]	Newark, NJ[d]
Sulfates								
30% RH		3.3	3.1	5.8	5.8	3.0	3.3	3.3
50% RH			4.3	8.2	8.2	4.3	4.6	4.6
70% RH	6.2		7.1	13.6	13.6	7.1	7.7	7.7
Nitrates								
30% RH	2.7	4.5	7.2	2.8				
50% RH	3.5		10.1	3.9				
70% RH	4.7		16.9	6.5				
Other, all RH	2.2		0.3			1.7		1.2
Fraction of variance accounted for (r^2)	0.93	0.76	0.66	0.81	0.53	0.52	0.52	0.50

[a]Efficiencies represent statistical increment in total scattering or extinction coefficient ($10^{-6}m^{-1}$) per increment in individual compound (including cation) concentration ($\mu g/m^3$). Efficiencies not differentiated by RH are entered nearest the average RH for the data set.
[b]White and Roberts (1977), from 2-hr average nephelometer and total filter data.
[c,d]Trijonis and Yuan (1978a,b), from 9-hr daytime airport visibilities and 24-hr high-volume-filter data. Visibilities are converted to extinction coefficients here via Koschmieder formula (see section 9.2.1) with contrast threshold of 0.031 (Figure 9-4).

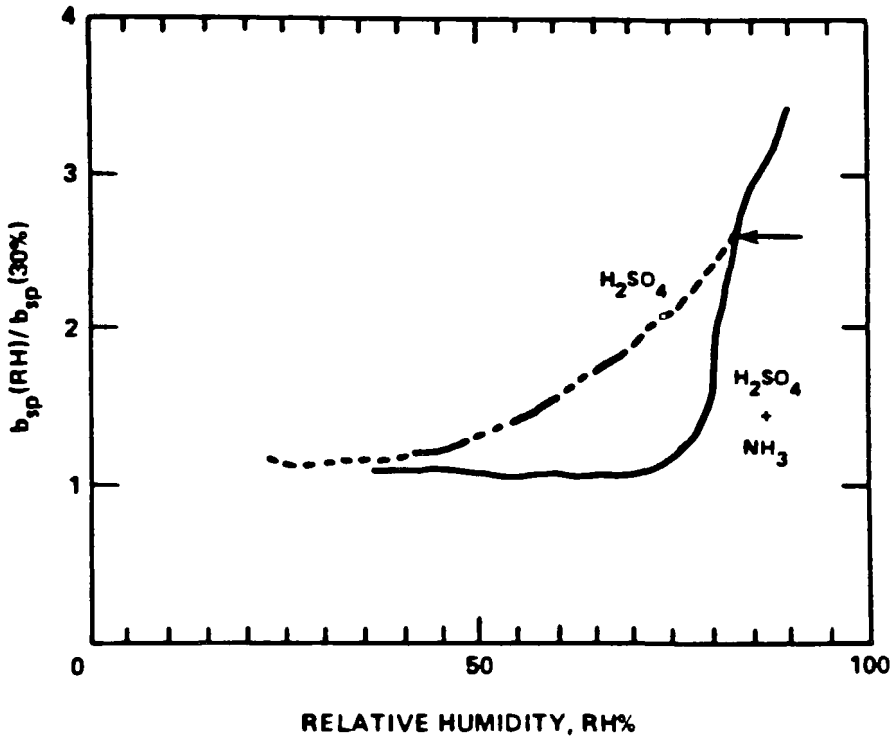

Figure 9-14. In this humidogram for laboratory H_2SO_4 aerosol and for the reaction product of this H_2SO_4 and NH_3, the ordinate is the ratio of light-scattering coefficient due to particulate matter at the given relative humidity [b_{sp} (RH)] to the light-scattering coefficient at 30 percent.

Source: Charlson et al. (1974).

9.2.5 Historical Patterns of Visibility

Records of visual range can be used to gain insight into the effects of changing emission patterns on visibility. As one example Marians and Trijonis (1978) have derived statistical relationships between light extinction (computed from visibility data) and historical emission trends. Yearly values of extinction from four Arizona airports were regressed against statewide emissions of smelter SO_x, nonsmelter SO_x, NO_x, and RHC. Smelter SO_x was found to be the most significant variable. Particularly close relationships between Arizona smelter SO_x and visibility at Tucson and Phoenix are shown in Figure 9-15.

Table 9-3 summarizes the results of the correlation/regression analysis between yearly airport extinction (visibility) data and Arizona smelter SO_x emissions. The correlation coefficients and Student's t-statistics indicate significant statistical relationships at high confidence levels. The regression (extinction/emission) coefficients of 0.04 ± 0.005 $(10^4\ m)^{-1}$/(1000 tons per day of SO_x) are remarkably consistent from site to site and represent the change in yearly median extinction associated with a given change in SO_x emissions; that is, adding 1000 tons per day of SO_x tended to increase yearly median extinction by approximately 0.04 $(10^4\ m)^{-1}$.

Perhaps the best example of changed emission patterns is a strike that shut down the copper industry over a 9-month period in 1967-68. In the Southwest at this time, copper production accounted for over 90 percent of the SO_x emissions, less than 1 percent of the NO_x emissions, and less than 10 percent of the conventional particulate emissions (Marians and Trijonis, 1978), and should therefore have affected visibility primarily through its contribution to sulfate loadings. Substantial decreases in sulfate occurred at five locations (Tucson, Phoenix, Maricopa County, White Pine, and Salt Lake City) within 12 to 70 miles of copper smelters as shown in Figure 9-16. More notably, sulfates

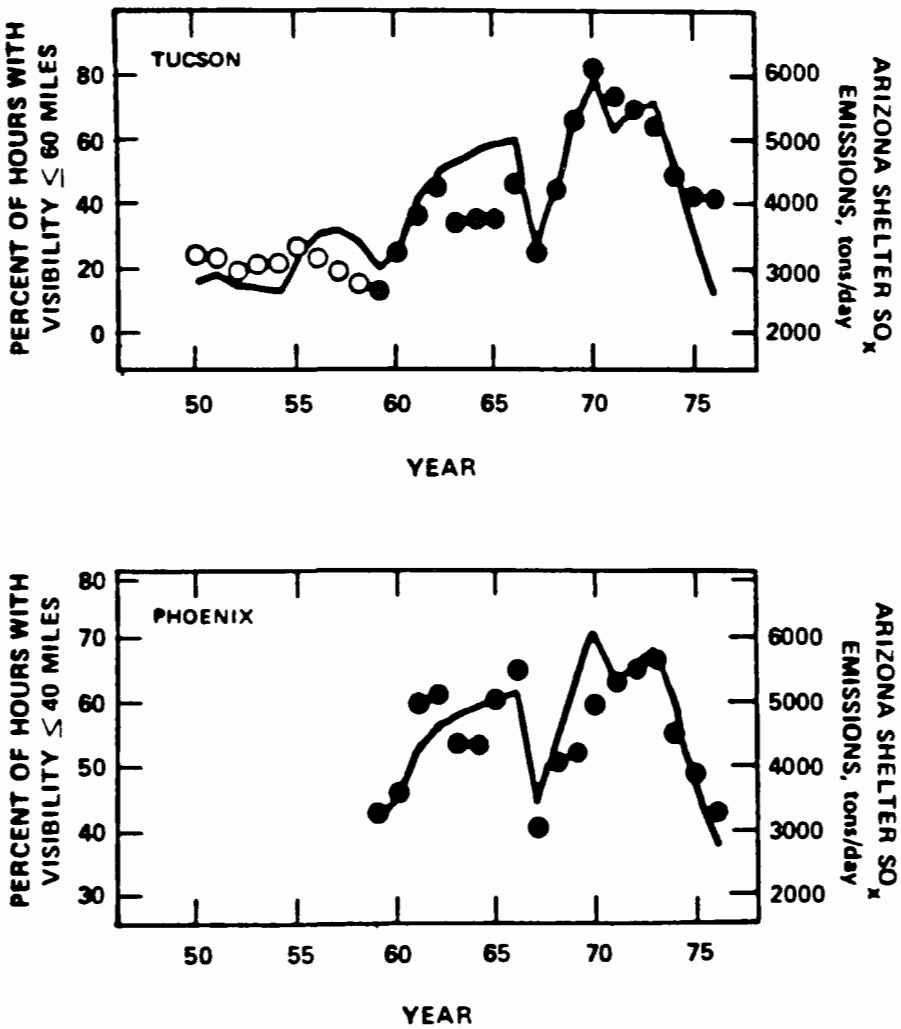

Figure 9-15. Historical trends in hours of reduced visibility at Phoenix and Tucson are compared with trends in SO_x emissions from Arizona copper smelters. Data points represent yearly percent of hours with reduced visibility. The Tucson observation site moved in 1958; although this move did not produce a statistically significant change in reported visibilities, open dots are used to distinguish data prior to 1958. Lines represent yearly SO_x emissions from Arizona copper smelters.

Source: Marians and Trijonis (1979).

TABLE 9-3. CORRELATION/REGRESSION ANALYSIS BETWEEN AIRPORT EXTINCTION AND COPPER SMELTER SO_x EMISSIONS

Data set		Correlation coefficient	Regression coefficient extinction/emissions, $(10^4\ m)^{-1}/(1000\ TPD)$	t-statistic ($t \approx 1.7$ for 95% confidence) ($t \approx 2.5$ for 99% confidence)
Tucson	(1950-75)	0.91	0.035	11.1
Tucson	(1959-75)	0.88	0.038	7.2
Phoenix	(1959-75)	0.81	0.041	5.4
Winslow	(1948-73)	0.68	0.047	4.5
Prescott	(1948-75)	0.70	0.031	5.0
Prescott	(1948-69)	0.70	0.039	4.4

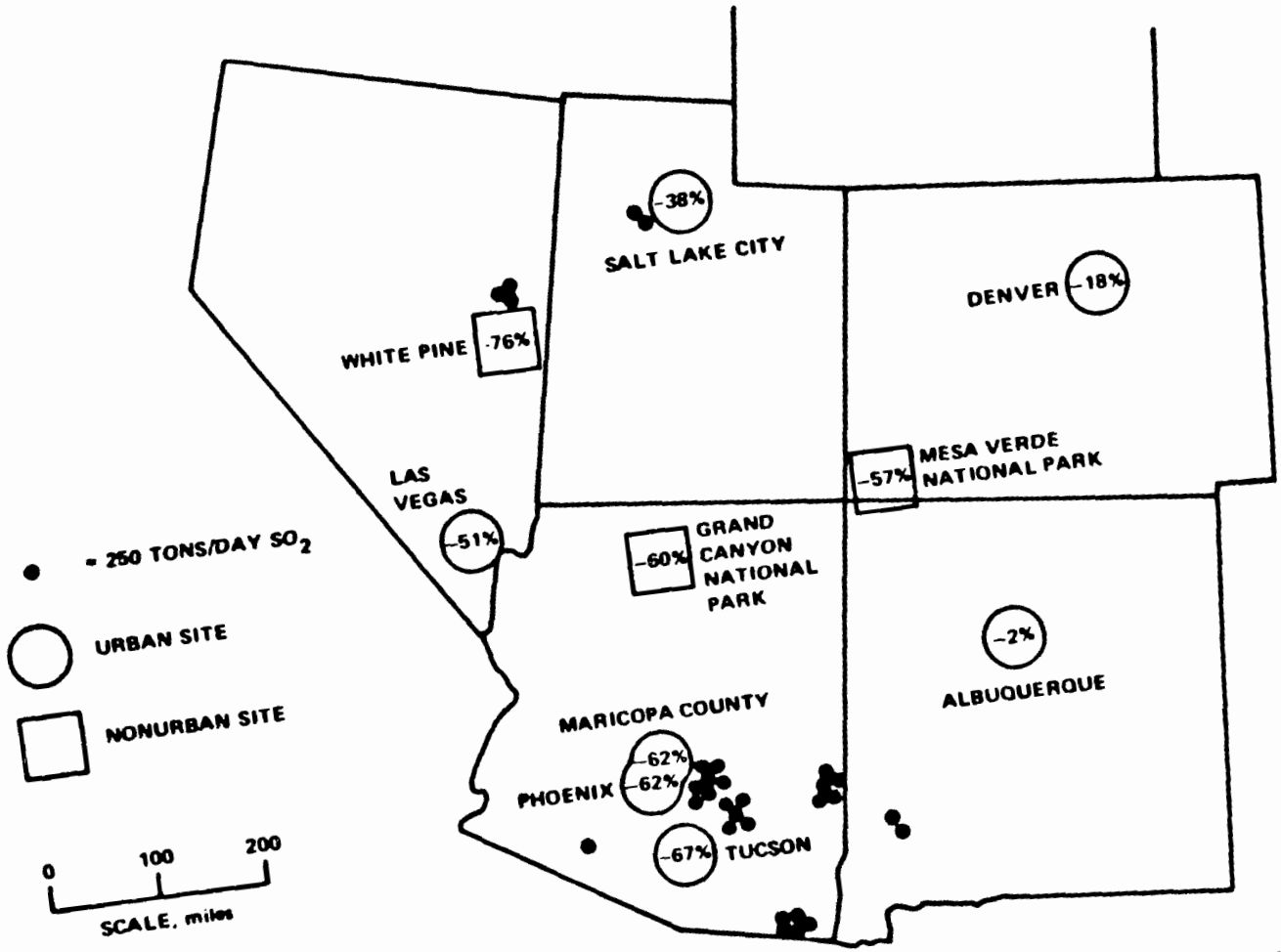

Figure 9-16. Seasonally adjusted changes in sulfate during the copper strike are compared with the geographical distribution of smelter SO_x emissions.

Source: Trijonis and Yuan (1978a).

dropped by about 60 percent at Grand Canyon and Mesa Verde; these remote sites are located 200 to 300 miles from the main smelter area in southeast Arizona. Comparing measurement during the strike with those during the surrounding 4 or 6 years, Trijonis and Yuan (1978a) found a large decrease in Phoenix sulfate loadings, accompanied by a substantial improvement in visibility (Figure 9-17).

Visibility improved at almost all locations during the strike, with the largest improvements occurring near and downwind (north) of the copper smelters in southeast Arizona and near the copper smelters in Nevada and Utah. The nine locations showing statistically significant improvements are all within 150 miles of a copper smelter. Attributing the improvement in visibility entirely to the drop in sulfate levels yields an estimated extinction efficiency of $3.9 \times 10^{-6}\ m^{-1}/(mg/m^3)$.

Altshuller (1973) has noted an increase over the past decade in sulfate concentration at nonurban sites in the Eastern United States, which is not inconsistent with the decreasing trend in nonurban site median visibilities noted by Trijonis and Yuan (1978b). Unfortunately, the historical record of sulfate concentrations extends back only to the mid-1960's. Within the Eastern United States, over 90 percent of the SO_x emissions are associated with the combustion of coal and oil. One apparent conclusion is that visibility reduction is currently due in large part to sulfate aerosol, which is formed primarily from coal combustion-related SO_2 emissions, than examination of the trends and changing spatial distributions of coal use should be similar the light extinction coefficient.

Air pollutants emitted over the Eastern United States result mainly from the combustion of fossil fuels--coal, oil products, and gas. The great spatial and seasonal variability of haziness (inverse of visibility) prompted Husar et al. (1979) to examine the patterns of coal consumption in the Eastern United States over the past few decades.

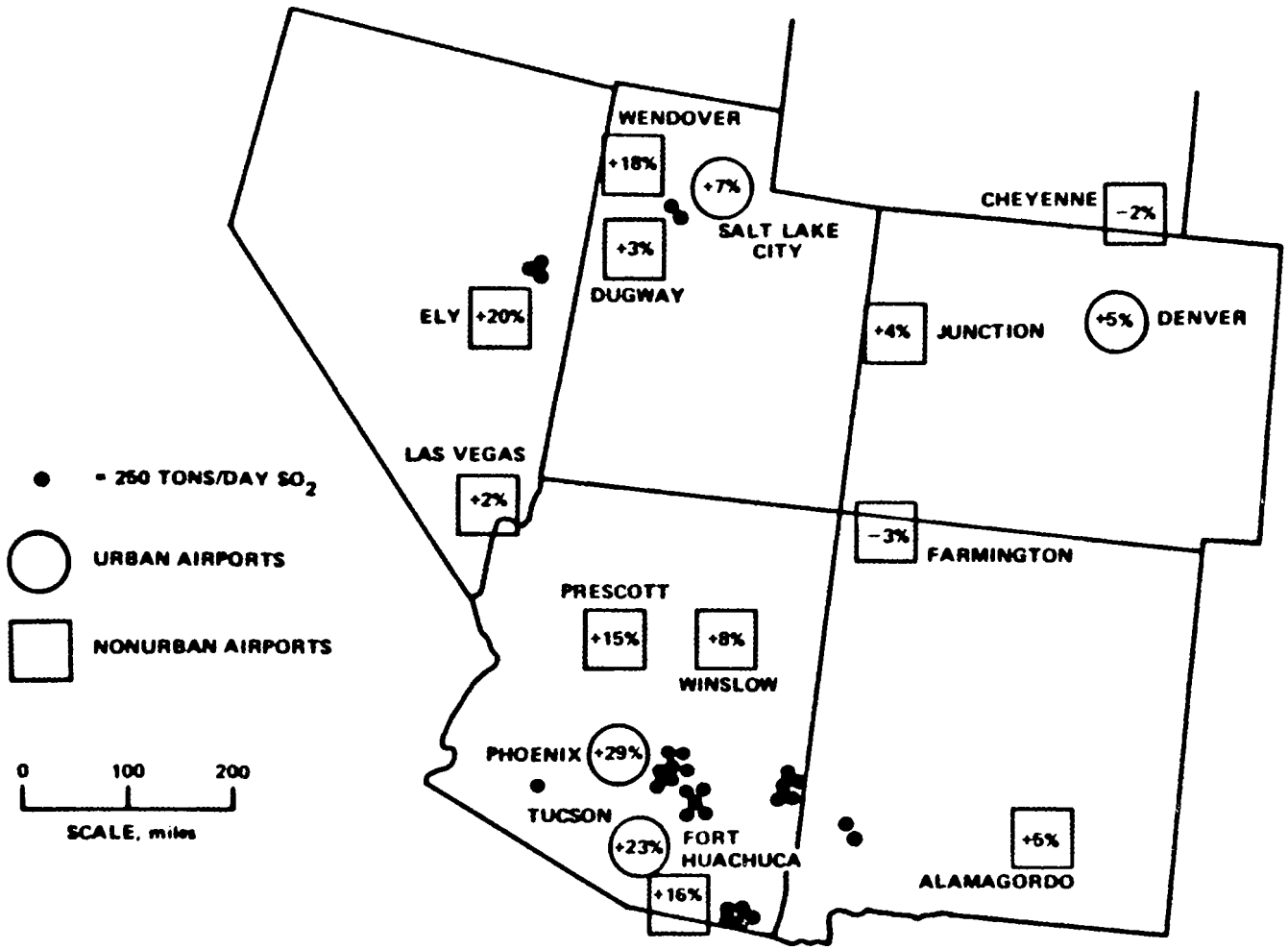

Figure 9-17. Seasonally adjusted percent changes in visibility during the copper strike are compared with the geographical distribution of smelter SO_x emissions.

Source: Trijonis and Yuan (1978a).

Figure 9-18 (U.S. Bureau of Mines, 1933-74) illustrates the striking similarity between summertime average haziness and coal use within the Eastern United States over the past three decades.

Further support for the relationship between coal consumption and haziness is given in Figure 9-19.

For comparison with coal consumption estimates, visibility data are expressed in terms of a light extinction coefficient, b_{ext}, via the Koschmieder formula: $b_{ext} = 3.92/VR$.

As shown in Figure 9-19, in 1951 the haziness was most pronounced in the wintertime, when the coal consumption was the highest. By 1974, there was a shift toward a summer peak, coincident with the increasing summer use of coal. Such coincident behavior alone cannot establish cause-effect relationships. It is nevertheless instructive to examine the more detailed spatial and temporal patterns of coal use and haziness.

Since 1940, the trend in coal consumption has been more pronounced in the summer than in the winter (Figure 9-16; U.S. Bureau of Mines, 1933-74); since 1960 summer coal use has grown by about 5.8 percent per year compared with 2.8 percent per year for winter coal demand. The monthly coal combustion peaked in the winter in the early 1950's, but the seasonal pattern had shifted to a summer peak by 1974 (Figure 9-20).

More instructive is examination of the State-by-State spatial trend of yearly coal consumption (Figure 9-21; U.S. Bureau of Mines, 1933-74). The corresponding regional trends of haziness in the Eastern United States (Figure 9-22; Husar et al., 1979) exhibit changes similar to those of coal combustion.

In the Ohio River Valley region, the winter (quarter 1) average extinction decreased slightly, whereas the spring (quarter 2) average increased. The summer (quarter 3) haziness increased from roughly 2.5 in the 1950's (a visibility of 10 miles) to about 4 in the 1970's (a visibility of less than 6 miles). Fall (quarter 4) haziness remained essentially unchanged. The summer average

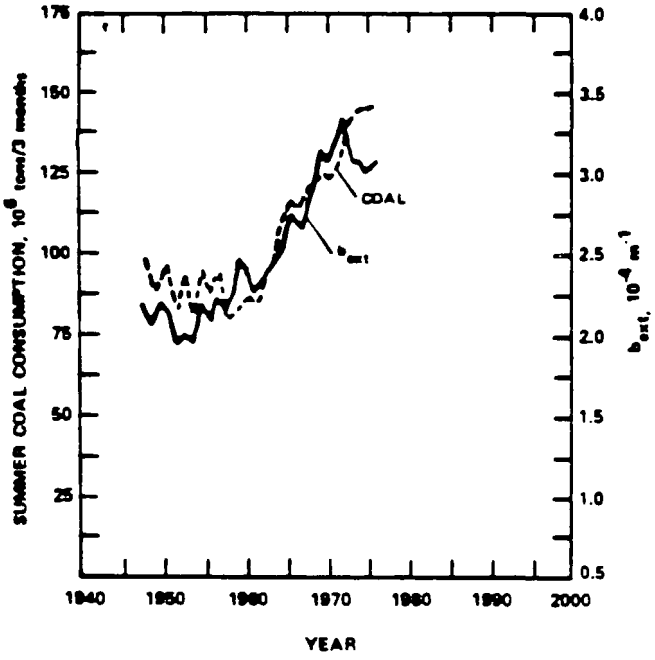

Figure 9-18. Compared here are summer trends of U.S. coal consumption and Eastern United States average extinction coefficient.

Source: Adapted from Husar et al. (1979).

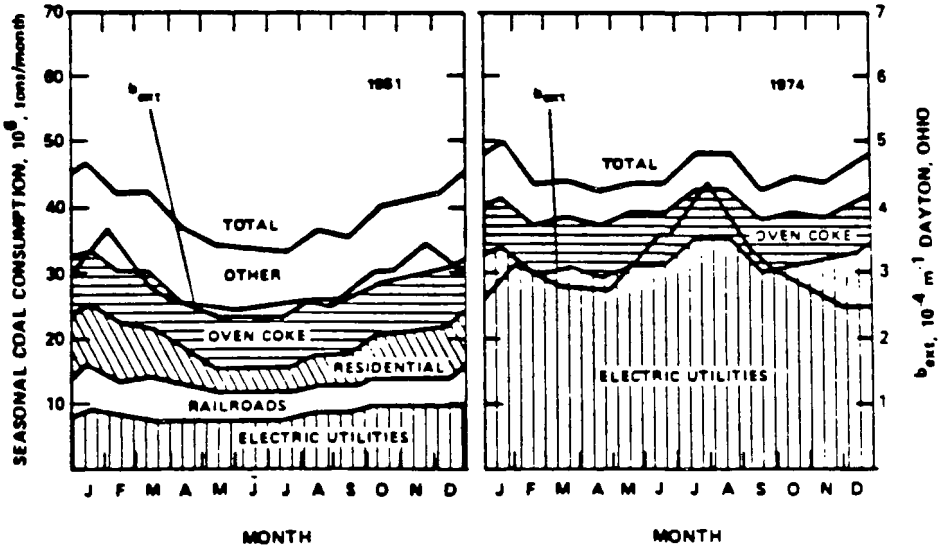

Figure 9-19. In the 1950's the seasonal coal consumption peaked in the winter primarily because of increased residential and railroad use. By 1974, the seasonal pattern of coal usage was determined by the winter and summer peak of utility coal usage. The shift away from a winter peak toward a summer peak in coal consumption is consistent with a shift in extinction coefficient from a winter peak to a summer peak in Dayton, OH, for 1948-52.

Source: U.S. Bureau of Mines Yearbooks 1933-74.

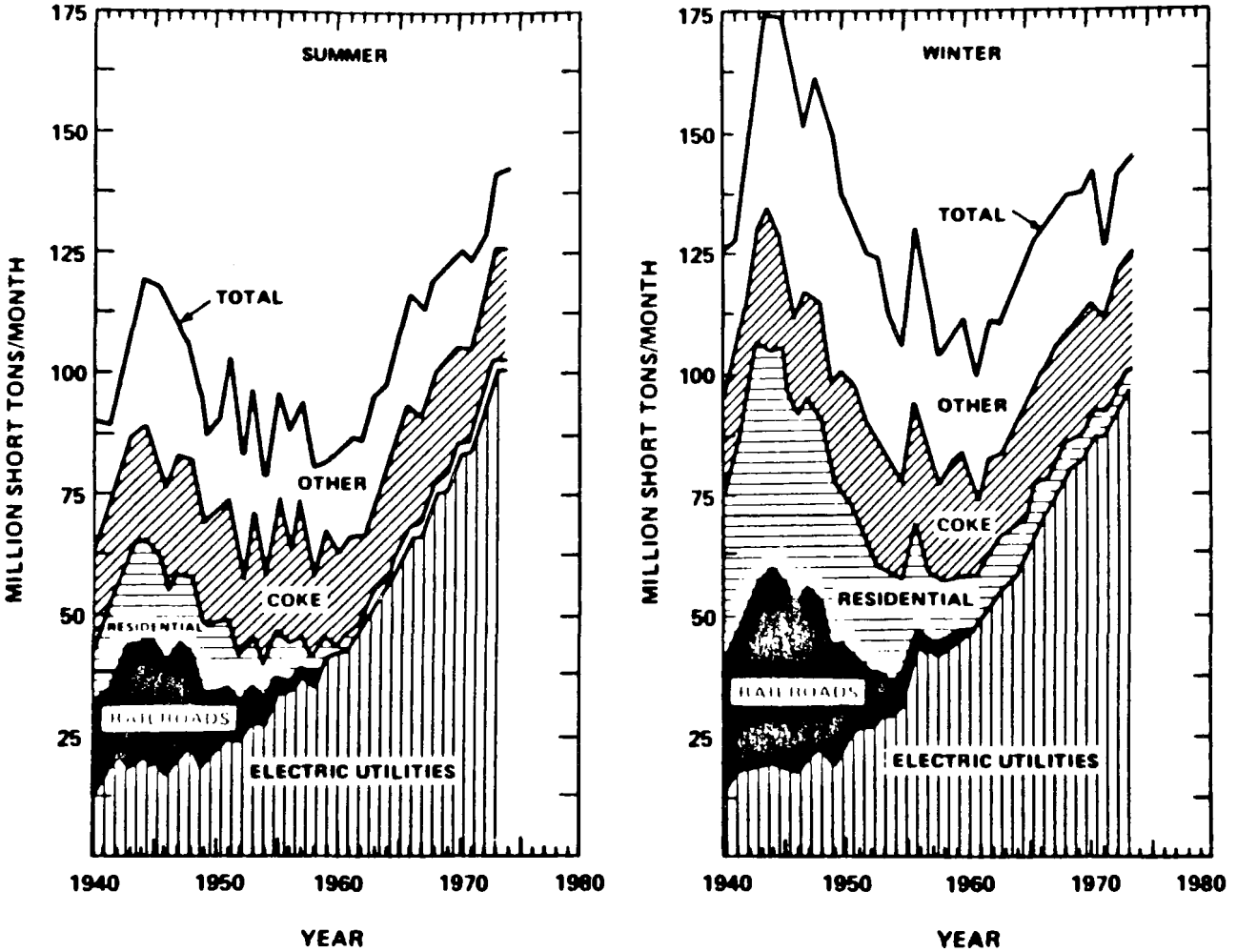

Figure 9-20. In 1974, the U.S. winter coal consumption was well below, while the summer consumption was above, the 1943 peak. Since 1960 the average growth rate of summer consumption was 5.8 percent per year, while the winter consumption increased at only 2.8 percent per year.

Source: U.S. Bureau of Mines, Minerals Yearbooks 1933-1974.

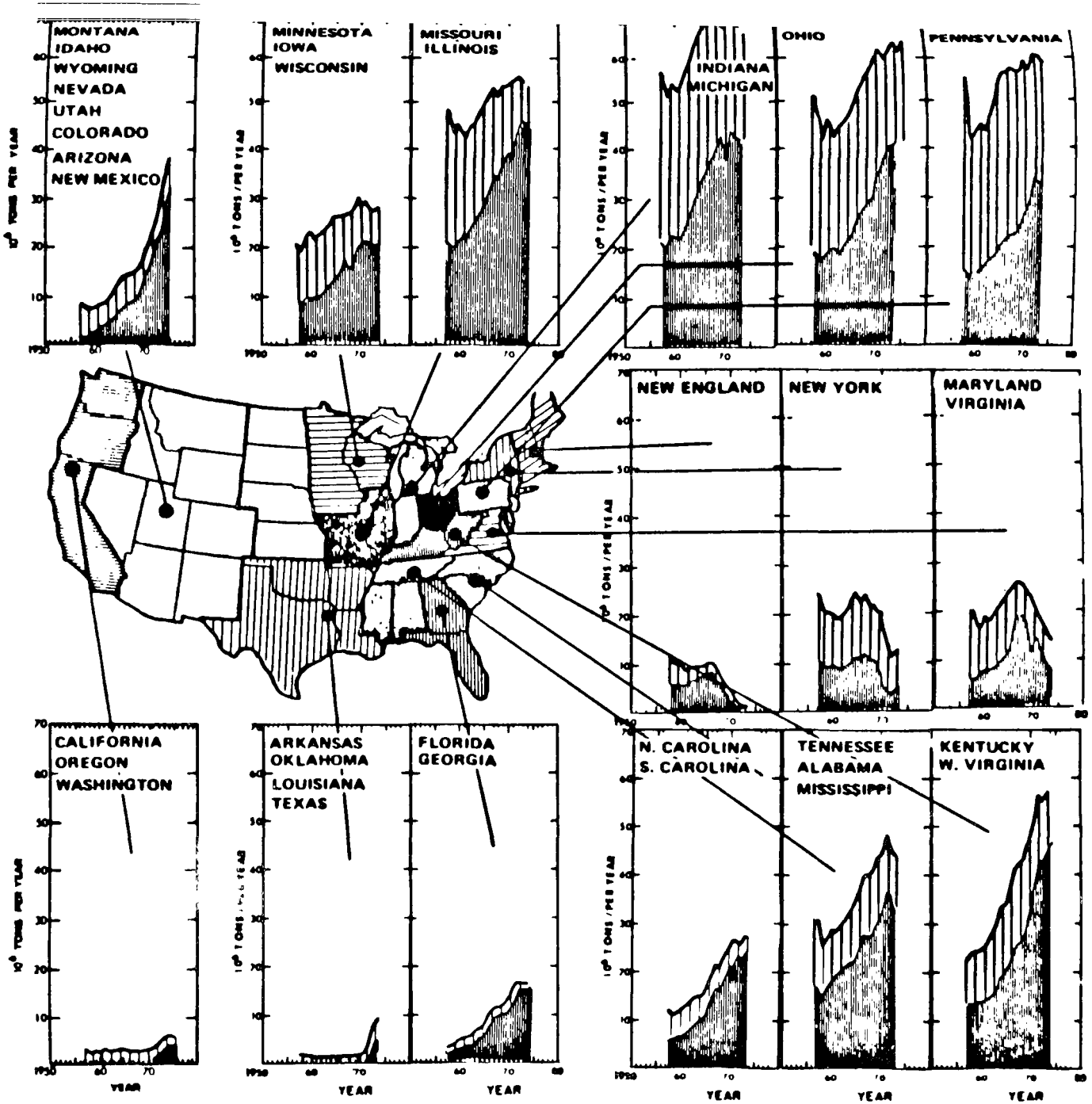

Figure 9-21. Trends in coal consumption in the continental United States are shown by region.

Source: U.S. Bureau of Mines, Minerals Yearbooks 1933-1974.

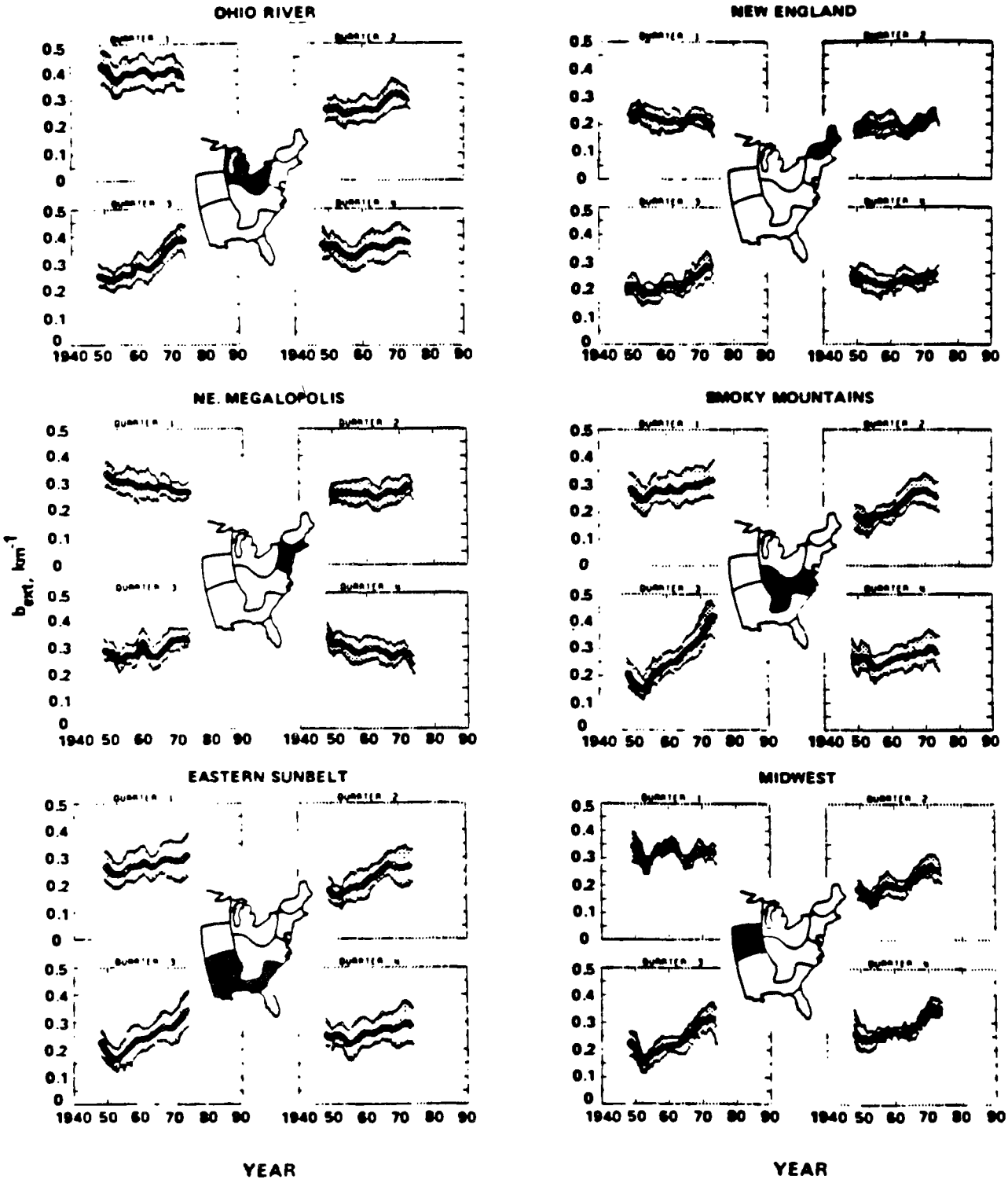

Figure 9-22. Trends in the light extinction coefficient (b_{ext}) in the Eastern United States are shown by region.

Source: Husar et al. (1979).

increased was from about 2 to 3, corresponding to a reduction in visibility from 12 to 8 miles. The Northeast megalopolis region shows a general decline in haziness during quarters 1 and 4, whereas quarters 2 and 3 display a slight increase from b = 2.7 (9 miles) to 3 (8 miles). The Smoky Mountain region displays a strong increase in the average summer quarter extinction coefficient from about 1.6 to 4, corresponding to visibility deterioration from 15 to 6 miles. Smaller but still pronounced increases are noted for quarters 2 and 4. Evidently the Smoky Mountains have become appreciably "smokier" over the past 20 summers. The Eastern Sunbelt region has an increased haziness for all quarters, most pronounced being the summer quarter, with an increased from 2 (12 miles) to 3.5 (7 miles). Midwest quarter-1 extinction fluctuated slightly with no discernible trend. The spring and fall quarters have increased appreciably, but summer values have nearly doubled, from 1.5 to 3 (16 to 8 miles).

The spatial shifts of Eastern United States haziness are displayed in greater detail in Figure 9-23 (Husar et al., 1979).

9.2.5.1 Summary--The impact of sulfates in reducing visual air quality in individual plumes and on the regional scale of 1000 km is no longer a matter of dispute. Considerable evidence from chemical mass balance methods indicates that sulfates, which make up approximately 50 percent of the fine-aerosol mass, contribute considerably more to visibility degradation than do other chemical species. Finally, the 30-year record of the spatial and temporal trends of coal combustion and visibility suggest that the increasing emissions of SO_x since the 1950's have in fact been associated with similar increased in haziness.

9.3 SOLAR RADIATION

Incoming solar radiation is composed of the direct beam and the diffuse skylight arising from the light-scattering atmosphere (Figure 9-24; Gates, 1966). The relative contribution of the skylight is least at noon and greatest at sunrise and sunset. At sea level, and for a clean atmosphere, skylight contributes at least 10 percent of the total radiation.

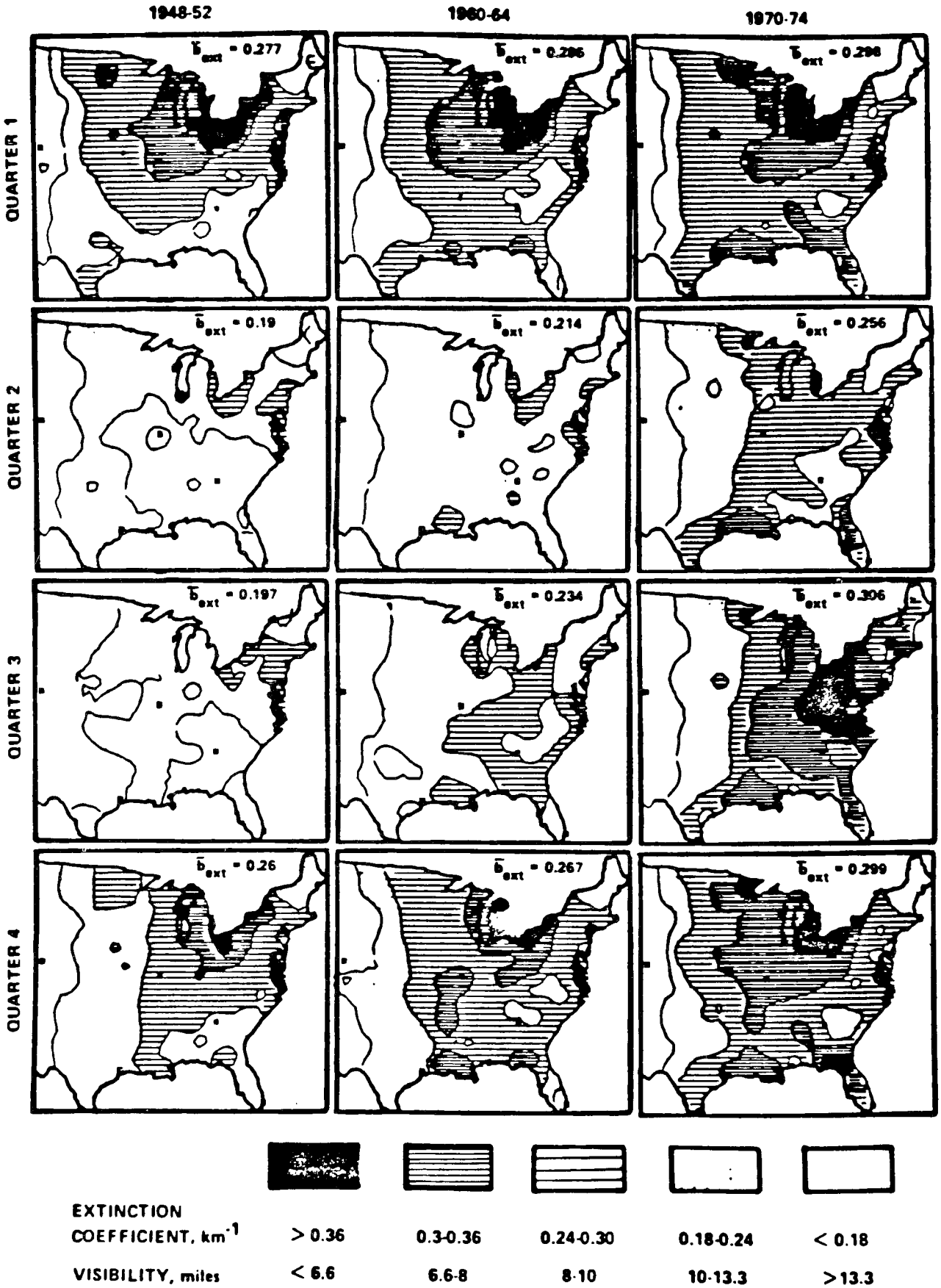

Figure 9-23. The spatial distribution of 5-year average extinction coefficients shows the substantial increases of third-quarter extinction coefficients in the Carolinas, Ohio River Valley, and Tennessee-Kentucky area. In the summers of 1948-52, a 1000-km size multistate region centered around Atlanta, GA, had visibility greater than 15 miles; visibility has declined to less than 8 miles by the 1970's. The spatial trend of winter (first quarter) visibility shows improvements in the Northeast megalopolis region and some worsening in the Sunbelt region. Both spring and fall quarters exhibit moderate but detectable increases over the entire eastern United States. Husar et al., 1979

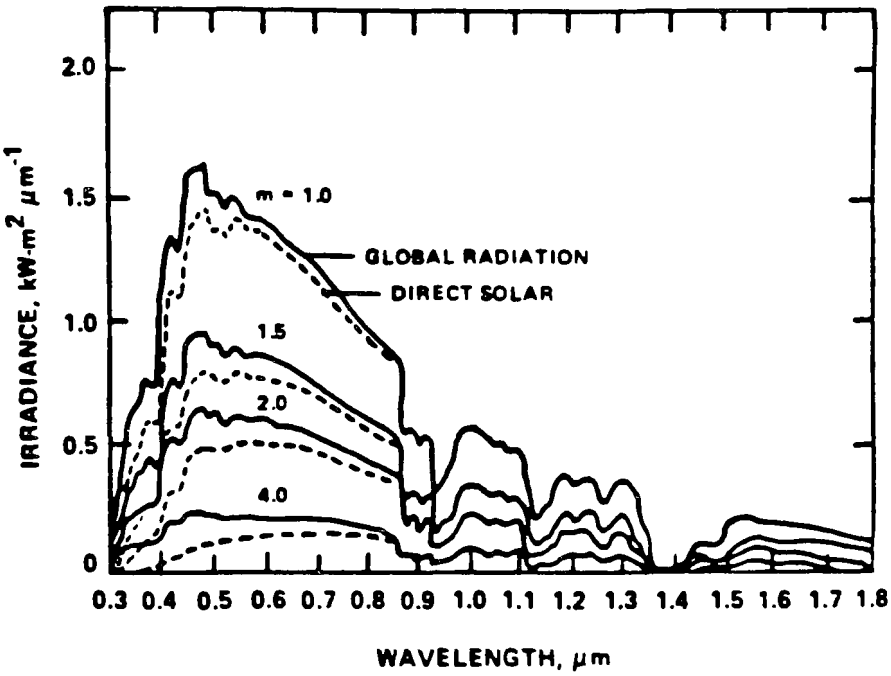

Figure 9-24. Solar radiation intensity spectrum at sea level in cloudless sky peaks in the visible window, 0.4-0.7 μm wavelength range, shows that in clean remote locations, direct solar radiation contributes 90 percent and the skylight 10 percent of the incident radiation on a horizontal surface. The airmass, m, is a measure of the amount of air the direct solar beam has to pass through.

Source: Gates (1966).

Aerosol layers in the atmosphere scatter and absorb solar radiation (Figure 9-25). Some of the scattered radiation is directed upwards and lost to space; some is directed downwards to the earth's surface. Most of the solar radiation eventually reaches the surface, but its spectral and directional composition, that is, the "quality" of the solar radiation, may be changed by atmospheric haze. A small fraction of the scattered radiation may also be lost back to space, in which case the amount of energy reaching the surface is reduced, contributing to the cooling at the earth's surface. A fraction of the radiation may also be absorbed by aerosols, further reducing the amount of radiation reaching the surface but at the same time heating the aerosol layer itself.

It should be noted that because aerosols are not uniformly distributed in the atmosphere, their effects are spatially nonhomogeneous. First, the horizontal spatial scale encompassing aerosol source, transport, and removal in the lower troposphere is variable but often about 1000 km. The vertical spatial scale of noninfluenced aerosols is also quite variable, but often the particles are concentrated in a layer from 500 to 2000 m deep. Hence, the aerosol effects should be concentrated in the lowest layers of the atmosphere, especially in industrial regions.

Global-scale effects might also occur. If the effects in industrial regions are strong enough, then the heat balance of the entire earth could be influenced. On the other hand, effects from long-lived aerosol, for example, in the stratosphere, might lead to direct physical effects on a global scale.

9.3.1 Spectral and Directional Quality of Solar Radiation

The spectral quality of solar radiation on a clear day and on a hazy day in Texas is shown in Figure 9-26 (McCree and Keener, 1974). On the hazy day, the direct solar radiation is reduced to about one-half of that on a clear day, but

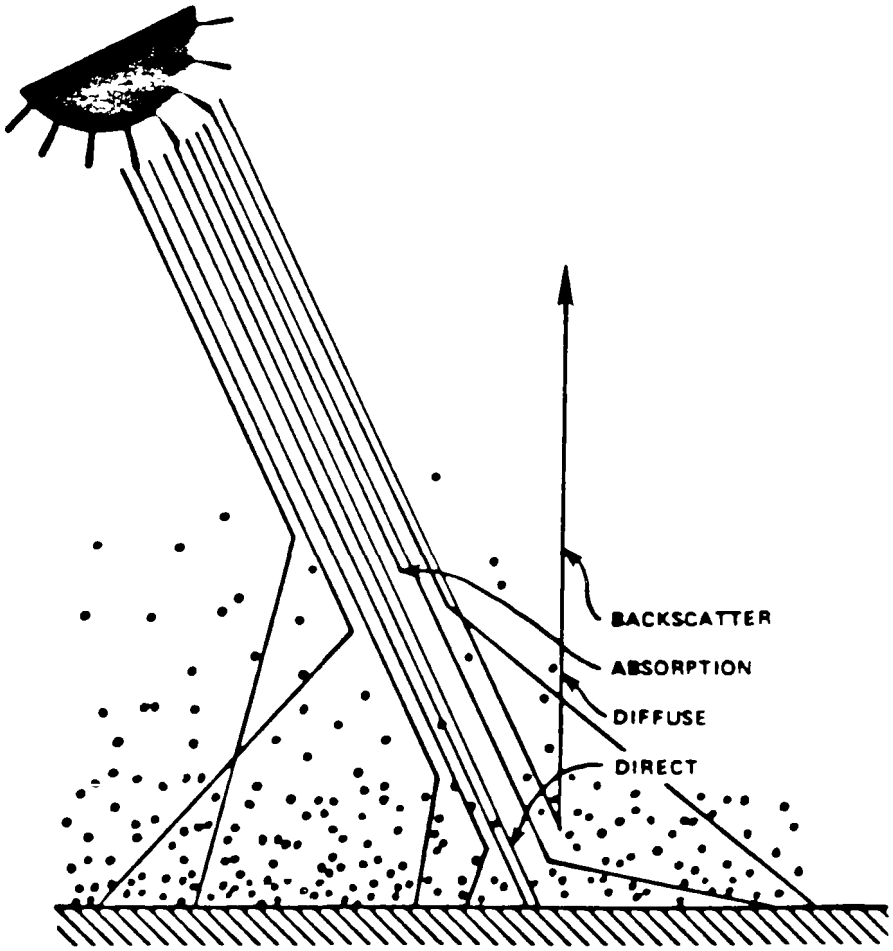

Figure 9-25. Extinction of direct solar radiation by aerosols is depicted.

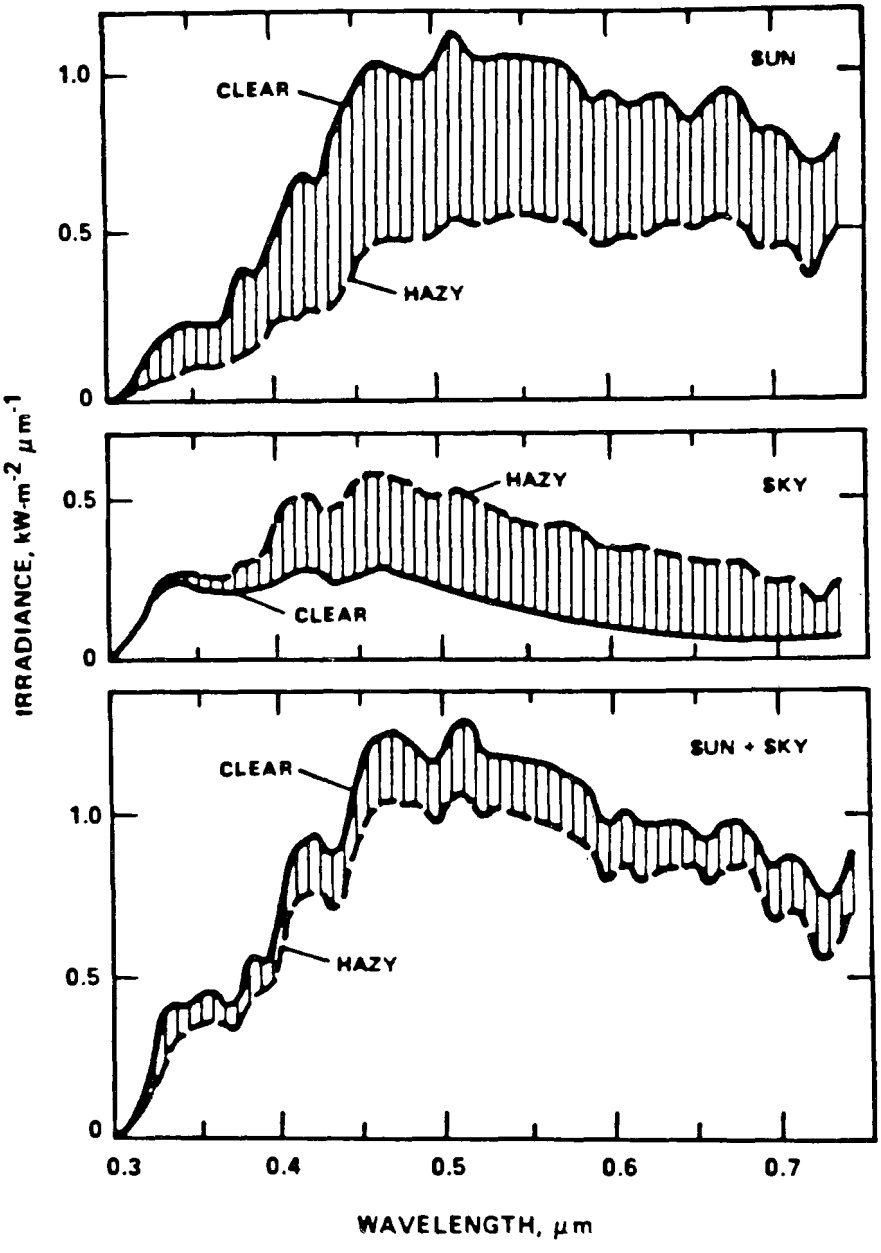

Figure 9-26. On a cloudless but hazy day in Texas, the direct solar radiation intensity was measured to be half that on a clear day, but most of the lost direct radiation has reappeared as skylight. However, there is about 20 percent of the solar radiation missing on the hazy day, some absorbed, and some backscattered to space.

Source: McCree and Keener (1974).

most of the energy has reappeared as diffuse skylight. However, there is also an overall loss of up to about 10 to 20 percent of the radiation reaching the surface.

If we take the typical backscattered fraction for haze aerosols to be 10 percent and the absorption to be also about 10 percent, as suggested by the data of Weiss (1978), then we can estimate the amount of energy lost from the surface, the amount lost to space, and the amount absorbed by the atmosphere. On a day with half of the direct beam transmitted, we conclude that 10 percent of the other half, or 5 percent, is lost to space, and the other 5 percent results in atmospheric heating. Together, these phenomena lead to a loss of 10 percent of the radiation. Although it is not possible to calculate accurately the influence this loss might have on surface temperature, rate of thawing of frozen ground, growing season, or other climatological measures, it is highly probable that this loss cools the ground and heats the hazy lower layers of the atmosphere. In turn, if this occurs, it must increase atmospheric stability, decrease convective mixing, and therefore increase the rate at which pollutants accumulate.

No detailed and routine measurements of the quality of solar radiation are available for the United States. However, the total solar energy reaching the surface is monitored routinely at many meteorological observation sites in the United States and worldwide. Unfortunately, the large variability of such data does not allow manmade aerosol effects to be distinguished from other natural causes.

A data base that gives some information on the quality of solar radiation is the U.S. turbidity network operated at about 40 stations in the country since 1961 (Flowers et al., 1969). If there are no clouds between the observer and the sun, the intensity of direct solar radiation for a given solar elevation

depends on the variable amount of dust, haze, and water vapor in the atmosphere. The extinction produced by these constituents is called "atmospheric turbidity." The seasonal pattern of atmospheric turbidity in the United States at 29 sites for 1961-66 is shown in Figure 9-27 (Flowers et al., 1969). At all sites, the highest turbidity occurs in the summertime and the lowest occurs in the winter, which is consistent with the haziness pattern obtained from visibility observations (section 9.2.3). However, the turbidity of the atmosphere in the United States has a strong spatial dependence. In the Southwestern States with an annual turbidity coefficient of about 0.06, the incoming direct solar radiation is attenuated by only 13 percent (mostly scattered) compared with Midwestern State values of about 20 percent. The highest turbidity coefficients were observed in the Eastern United States, where summer values of 0.2 and winter values of 0.1 were typical. This means that in the summertime about 35 percent of the direct solar beam is diverted to skylight, backscattered to space, or absorbed. This means that about 3.5 to 7 percent is backscattered to space and another 3.5 to 7 percent is absorbed into the atmosphere.

Since the first report of Flowers et al. (1969), the turbidity data have been reported yearly by the World Meteorological Organization (WMO, 1977). Comparison of the seasonal turbidity pattern for 1961-66 and 1972-75 is shown in Figure 9-28. Since the mid-1960's there has been a further increase in Eastern U.S. turbidity, particularly in the summer season. Currently the summer average turbidity in the region including Memphis, TN, Oak Ridge, TN, Greensboro, NC, and Baltimore, MD, is about 0.3. This corresponds to a 50 percent attenuation of the direct solar beam on an average summer day. During hazy episodes, turbidity coefficients of 0.6 to 1.0 are often reported, resulting in a condition in which 75 to 90 percent of the solar radiation is removed from the direct beam, 7.5 to 18 percent is lost to space, and 7.5 to 18 percent is lost as

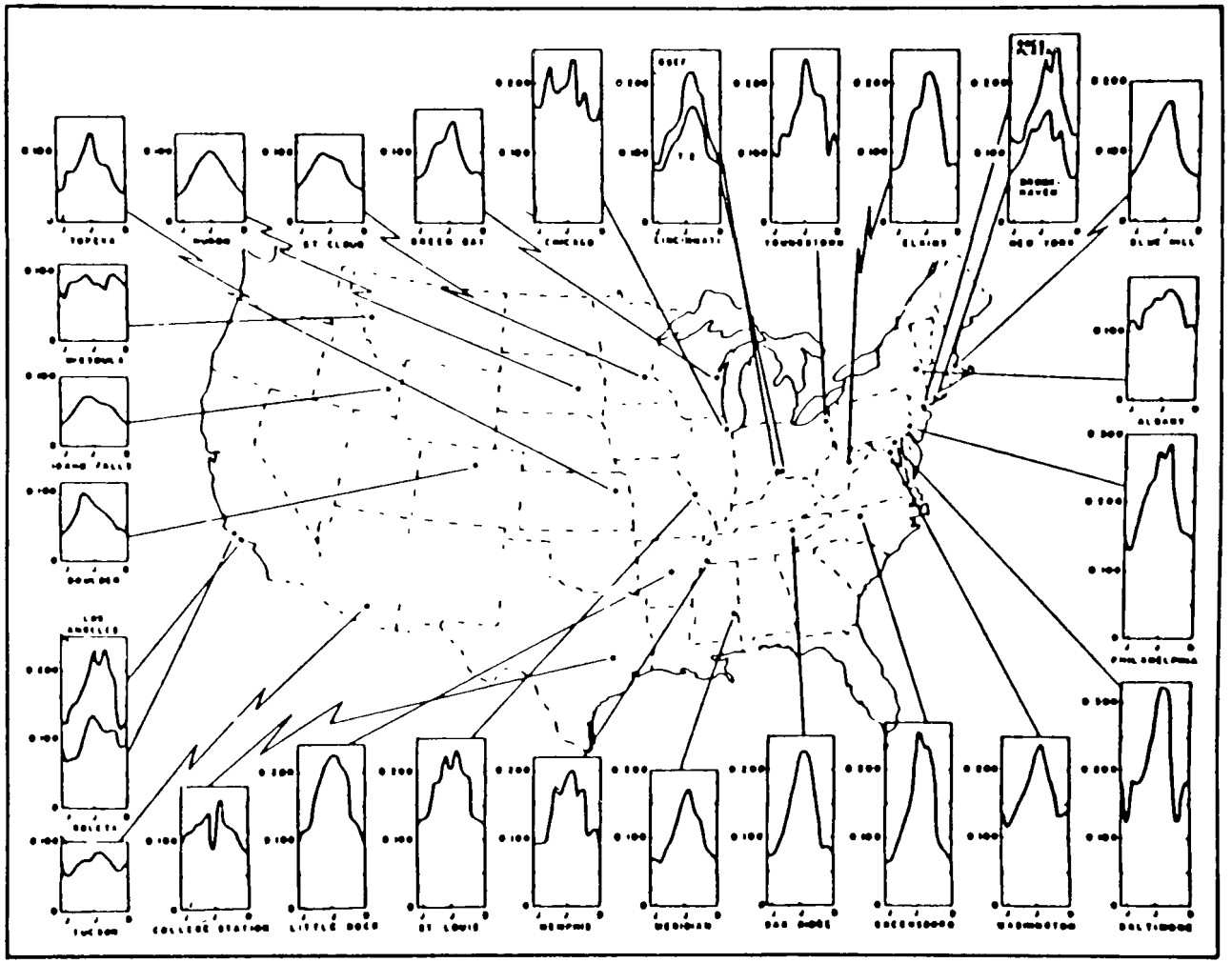

Figure 9-27. To interpret these monthly average turbidity data in terms of aerosol effects on transmission of direct sunlight, use the expression $I/I_0 = 10^{-B}$, where B is turbidity and I/I_0 is the fraction transmitted.

Source: Flowers et al. (1969).

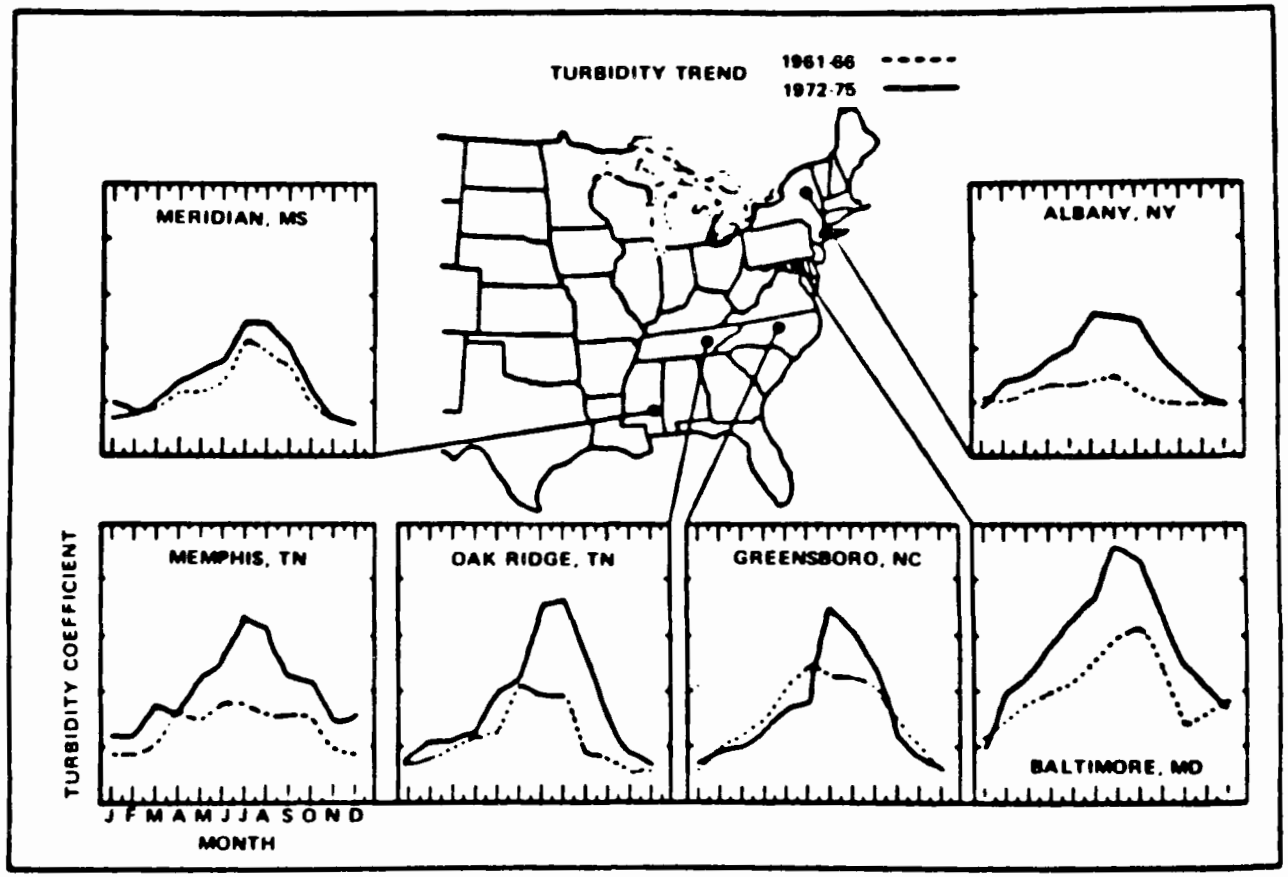

Figure 9-28. Seasonal turbidity patterns for 1961-66 and 1972-75 are shown for selected regions in the Eastern United States.

atmospheric heating. One of the consequences of such hazy atmosphere is the disappearance of shadow contrasts. It is strongly suspected but has not yet been proved that there are effects on agricultural productivity.

The spatial distribution and trends of regional-scale turbidity in the Eastern United States are consistent with the observed pattern of haziness obtained through visibility observations. Both the turbidity and visibility reduction by haze in the Eastern United States can be attributed to manmade fine particles, consisting mainly of sulfate and nitrate (section 9.2.4). Bolin and Charlson (1976) suggest that many of these radiative effects are due to sulfates and conclude that the magnitude of effects is comparable to that summarized here.

9.3.2 Total Solar Radiation: Local to Regional Scale

Changes in the total radiant energy have been observed within urban areas. Early measurements in central city locations, primarily in Europe, showed levels typically 10 to 20 percent below surrounding rural areas. Robinson (1962) discussed some observations made in London and in Vienna. In London the deficit was considerably reduced after the implementation of a clean air act. Measurements on 47 days in autumn 1973 in the Los Angeles area are summarized in Table 9-4 (Peterson and Flowers, 1977). In the St. Louis area, however, smaller urban-rural differences were observed. On 12 cloudless days in summer 1972, the average solar and UV fluxes at an urban site were only 3 and 8 percent, respectively, below those at a rural site about 50 km from the city. The difference between the St. Louis and Los Angeles and European urban areas appears to involve both decreased urban and increased rural attenuation, and it may be that neither the city of St. Louis nor its surroundings over a wide area modify solar radiation in a manner typical of other locations.

TABLE 9-4. SOME SOLAR RADIATION MEASUREMENTS IN THE LOS ANGELES AREA[a]

Measurement	Total	UV
Minimum	4	15
Average	11	29
Maximum	20	44

[a]Values for the daily average percentage decrease of total and UV solar radiation between El Monte (urban) and Mt. Disappointment (rural).

Source: Peterson and Flowers (1977).

Recently, Angell and Korshover (1975) analyzed the solar radiation duration data (hours of sunshine) for the eastern half of the United States. Data for the 1950-70 time period were obtained with on/off detectors, and these data are believed to be more reliable for long-term trend analysis than data from recorders of solar radiation intensity. Angell and Korshover noted some marked trends: in the Southeast and South Central United States, the solar radiation duration has decreased by about 4 to 6 percent; however, the North Central is increasing (Figure 9-29; Angell and Korshover, 1975). Although the authors do not attribute these trends to any specific cause, it should be noted that there has been an increase in haziness within that time period in areas with decreased solar radiation. It is conceivable, therefore, that increased haziness causes sunshine-duration detectors to delay the turn-on time in the morning and advance the turn-off time. It should also be stressed, however, that changes in the solar radiation duration may be caused by other natural or manmade phenomena.

9.3.3 Radiative Climate: Global Scale

The attenuation of solar radiation from scattering and absorption by particles in the atmosphere is probably an important factor in climatic change

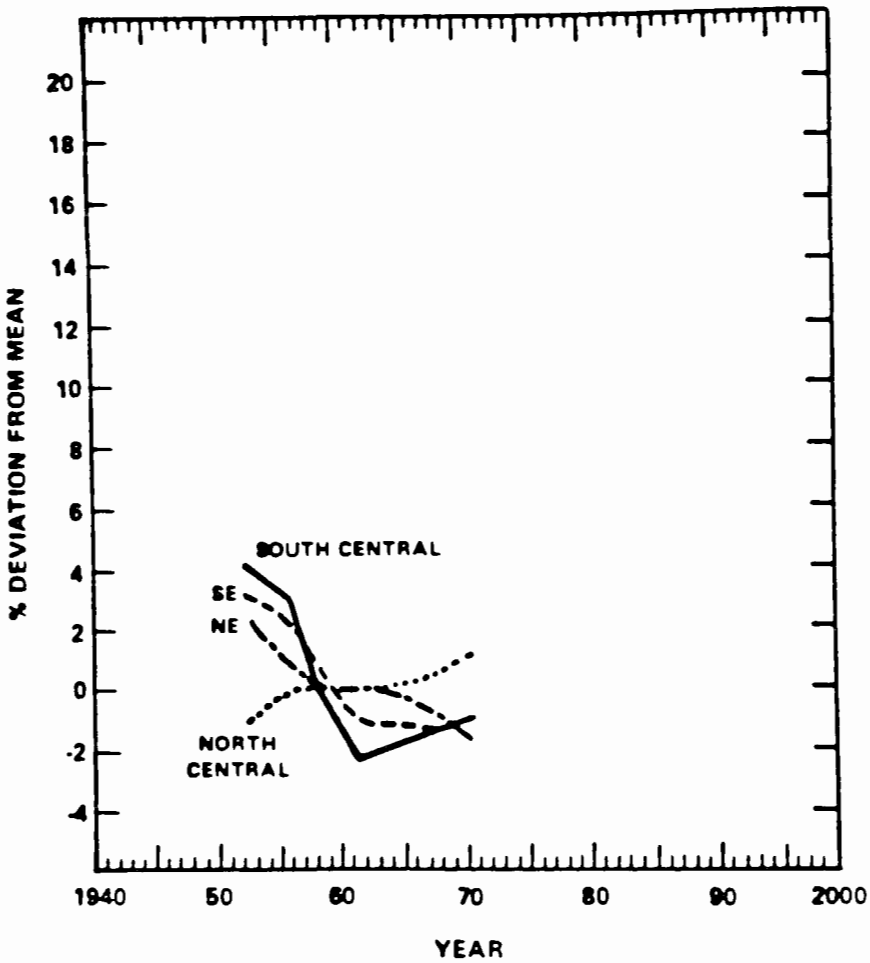

Figure 9-29. Analysis of the hours of solar radiation since the 1950's shows a decrease of summer solar radiation over the Eastern United States. There may be several causes for this trend, including an increase of cloudiness; some of the change may also be due to haze.

Source: Angell and Korshover (1975).

on all scales. On local scales associated with urban and industrial areas, any significant attenuation of radiation by air pollution can, in addition to other well-recognized factors, result in changes in local weather (e.g., Landsberg, 1970). It is possible that local- and regional-scale changes in solar radiation caused by human activity may ultimately influence the heat and water vapor contents of the atmosphere on very large scales, but solar radiation and aerosol levels measured at stations remote from pollutant sources have not as yet displayed any trend that can be related to human causes (Fischer, 1967; Ellis and Pueschel, 1971; Hodge et al., 1972).

Unfortunately, there is little agreement about whether the net effect of increased airborne particulate concentrations is the warming or cooling of the earth. Most models can predict either an increase or a decrease in the effective albedo of the earth under cloudless skies, depending on which combination of surface albedo, sun angle, particle size distribution, and particle refractive index is assumed. The effects of clouds are very important, and the contributions from infrared radiation must be considered in order to obtain a complete energy budget (Wesely and Lipschutz, 1976).

9.4 CLOUDINESS AND PRECIPITATION

The global cloud cover plays a vital role in the earth's radiative budget in reflecting energy back to space, in absorbing both solar and longwave (terrestrial) radiation, and in emitting its energy downward and outward into space. Changes in cloud cover, therefore, alter the global heat balance. Cloud- and precipitation-forming processes may be divided into two broad classes: (1) macrophysical processes, which affect the rise and descent of air currents and the amount of water vapor available for condensation; and (2) microphysical processes, which affect the nature of cloud particles formed during condensation.

The role of atmospheric aerosols, primarily those that are strongly hygroscopic, is to influence the microphysics of cloud formation.

On a global or even regional scale, the very small amounts of moisture that man adds by land practices or combustion of fossil fuels are negligible in comparison with global evaporation. On a regional scale, only one form of increasing cloudiness suggests itself: the formation of aircraft contrails (Machta and Telegadas, 1974). Aircraft contrail formation results mainly from the injection of water vapor rather than of aerosols.

In urban areas, inadvertent changes of cloudiness as well as the quantity of precipitation have been well established. Such urban impacts also include the frequencies of thunderstorms and hail as well as total amounts of rain. In a classical study, Changnon (1968) has reported a notable increase in days of precipitation, thunderstorms, and hail occurring since 1925 at La Porte, IN. Since La Porte is 30 miles east of the Chicago urban-industrial complex, he proposed that the increased precipitation results from inadvertent manmade modifications. Figure 9-30 (Changnon, 1968) shows the 5-year running totals of days with smoke and haze restricted visibility in Chicago. This measure of atmospheric pollution has a temporal distribution after 1930 rather similar to the La Porte precipitation curve. A noticeable increase in smoke-haze days began in 1935 and became more marked after 1940, when the La Porte precipitation curve began its sharp increase. The specific role of haze particles in causing the La Porte anomaly has not been established.

As part of project Metromex, studies by the Illinois State Water Survey suggest increases of about 30 percent in rain and 200 percent in thunderstorms and hail at single gauging stations downwind of St. Louis, with increases of about 10 percent over a two-county area. Here again, the physical causes of the maxima are not well understood, but they do appear to be associated with

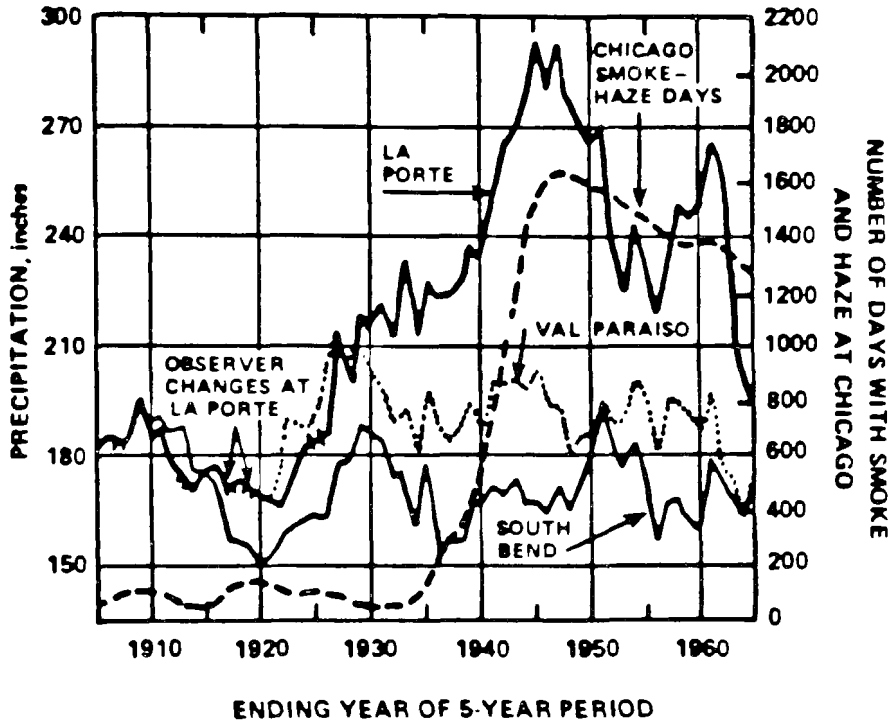

Figure 9-30. Numbers of smoke haze days are plotted per 5 years at Chicago, with values plotted at end of 5-year period.

Source: Changnon (1968).

perturbations of the planetary boundary layer and enhanced cloudiness, possibly resulting from the addition of aerosols. It is regrettable that the complex interactions of cloud- and precipitation-forming processes obscure the specific role of manmade aerosols.

The incorporation of particles into rain and fog droplets can change the "quality" of precipitation by changing its chemical composition. The most important impact on precipitation water quality is probably that of "acid rain," discussed in more detail in chapter 8.

9.5 SUMMARY

The term visibility refers to various characteristics of the optical environment such as clarity and trueness of color. Meteorologically, visibility refers to the greatest distance at which a black object can be distinguished against the horizon sky. The effects of the atmosphere on visibility can be determined from the concentrations and characteristics of atmospheric constituents, which scatter and absorb light. The scattering and absorption are used to determine the extinction coefficient. The combination of extinction and added air light (haze) washes out both bright and dark objects, decreasing the contrast of an object to the horizon.

The extinction of light in polluted air is generally dominated by particle scattering. On a regional scale, almost all of the particle scattering is contributed by fine particles in the accumulation mode. Extinction due to scattering is roughly proportional to the fine-particle mass concentration, with extinction/mass ratios in the range of 3-5 x 10^{-6} $m^{-1}/(\mu g/m^3)$.

Sulfates (sulfate and associated cations) occur primarily in the fine-particle accumulation mode. They appear to contribute disproportionately to the degradation of visibility, with an empirical extinction/mass ratio of 7±1 [10^{-6} $m^{-1}/(\mu g/m^3)$] at 70 percent relative humidity.

The impact of sulfates in reducing visual air quality in individual plumes and on the regional scale of 1000 km has been studied extensively. Considerable evidence indicates that sulfates, which make up approximately

50 percent of the fine-aerosol mass, contribute considerably more to visibility degradation than do other chemical species. Finally, the 30-year record of the spatial and temporal trends of coal combustion and visibility suggest that the increasing emissions of SO_x since the 1950s have in fact been associated with similar increases in haziness.

Several methods are used to measure extinction and its components. In the observer method, a black object is viewed against the horizon. These observations are reported commonly at weather stations. A composite value of these observations is called "prevailing visibility", which includes the greatest distance around at least 180 degrees of the horizon, not just for a single direction. This measurement procedure has certain limitations. Few sites are suitable for observations greater than 50 km. Additionally, the visual range of reflecting objects, such as snow-covered mountaintops, is influenced by the angle of the sun and sky conditions, overcast or clear.

In contrast telephotometry, the brightness of a black object is measured and expressed as a ratio to the same brightness of the nearby horizon. This method may be useful for characterizing plumes in terms of their brightness of contrast relative to sky or terrain background. At some sites, however, telephotometers cannot be used often because clouds on the horizon or above the path to the nearby black object cause errors. Also the method requires an operator.

Long-path extinction, the most direct way to measure extinction, involves measuring the decrease in intensity of a beam of light as a function of range. Unfortunately, several problems exist in calibrating a long-path transmissometer. A modification of this method has eliminated the need for absolute calibration.

The nephelometric method measures the scattering component of extinction. Many nephelometers are capable of measuring aerosol particle scattering extinction at or below 10 percent of Rayleigh scatter. This sensitivity is adequate for class I regions. The nephelometer can be used to measure the scattering coefficient at the same point where samples are taken for mass or chemical determination. Most of the data relating cause and effect (i.e., particle concentration or composition and optical effect) have been acquired with the integrating nephelometer. The instrument measures optical properties at a point, which may limit its application to cases where there is spatial uniformity of atmospheric optical properties. There may be errors introduced by differences in humidity inside the instrument relative to ambient conditions. The instrument will have two types of error if atmospheric optical properties are controlled by particles larger than 3 μm, such as in fog or dust storms.

No single method has been proven totally effective in measuring light absorption. The methods used thus far include determining the difference between extinction and scattering by combining long-path transmissometer with nephelometer, several filtering methods, and a refractive index method.

Pollutants released to the atmosphere alter the environment in ways other than visibility reduction. They may lead to slow and subtle changes in atmospheric composition and, possibly, climate. For example, a fraction of the solar radiation may be absorbed by aerosols, further reducing the amount of radiation reaching the earth's surface and, at the same time, heating the aerosol layer itself. On a hazy day, the direct solar radiation is reduced to about one-half of that on a clear day, but most of the energy has reappeared as diffuse skylight. However, there is also an overall loss of up to about 10 to 20 percent of the radiation reaching the surface.

If there are no clouds between the observer and the sun, the intensity of direct solar radiation for a given solar elevation depends on the variable amount of dust, haze, and water vapor in the atmosphere. The extinction produced by these constituents is called "atmospheric turbidity." During hazy episodes, turbidity coefficients of 0.6 to 1.0 are often reported, resulting in a condition in which 75 to 90 percent of the solar radiation is removed from the direct beam, 7.5 to 18 percent is lost to space, and 7.5 to 18 percent is lost as atmospheric heating. One of the consequences of such a hazy atmosphere is the disappearance of shadow contrast. It is strongly suspected but has not yet been proved that there are effects on agricultural productivity.

The attenuation of solar radiation from scattering and absorption by particles in the atmosphere is probably an important factor in climatic change on all scales. On local scales associated with urban and industrial areas, any significant attenuation of radiation by air pollution can, in addition to other well-recognized factors, result in changes in local weather. It is possible that local- and regional-scale changes in solar radiation caused by human activity may ultimately influence the heat and water vapor contents of the atmosphere on very large scales, but solar radiation and aerosol levels measured at stations remote from pollutant sources have not as yet displayed any trend that can be related to human causes.

Cloud- and precipitation-forming processes may be divided into two broad classes: (1) macrophysical processes, which affect the rise and descent of air currents and the amount of water vapor available for condensation; and (2) microphysical processes, which affect the nature of cloud particles formed during condensation. The role of atmospheric

aerosols, primarily those that are strongly hygroscopic, is to influence the microphysics of cloud formation. The incorporation of particles into rain and fog droplets can change the "quality" of precipitation by changing its chemical composition. The most important impact on precipitation water quality is probably that of "acidic precipitation."

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10. EFFECTS ON MATERIALS

10.1 INTRODUCTION

Sulfur oxides and particulate material damage materials. In general terms, sulfur oxides accelerate the corrosion of metals and the erosion of building stone, while airborne particles soil fibers and structures.

This chapter discusses the chemical and physical action of these air pollutants on materials and identifies other environmental factors (e.g., moisture and sunlight) that play a role in the degradation process. Laboratory and field studies are reviewed, describing the effects of single pollutants and combinations of pollutants at various concentrations. Damage functions developed from these data are provided when available in useable form. Although physical damage functions for some pollutants are fairly well developed, most are based on exposure data collected at relatively high pollutant levels. Little information exists on effects of current levels, which are generally lower.

Economic damage functions are discussed, and some equations are presented. These functions are less well established than are the physical damage functions, and since they are derived in part from data highly influenced by socioeconomic factors, they should be applied cautiously.

The chapter summarizes published analyses of the cost of materials damage, maintenance, protection, and repair associated with ambient sulfur oxides and particulate matter. However, the chapter does not attempt to integrate current air quality data, physical damage functions, and economic damage functions to arrive at a total cost associated with these pollutants

at current levels. The next draft of this chapter will address possible approaches to the problem of integrating these data sets.

10.2 SULFUR OXIDES

10.2.1 Corrosion of Exposed Metals

Sulfur oxides present in the environment accelerate the corrosion of metals. Several factors other than concentration of SO_2 are important. These will be discussed first.

10.2.1.1 Physical and Chemical Considerations--The corrosion of metals is a diffusion-controlled electrochemical process. For electrochemical action to take place, the following are necessary: (1) a potential difference between points on the metal surface; (2) a mechanism for charge transfer between the electronic conductors; and (3) a conduction path between the cathode and anode reaction centers. Measurements of the rate of SO_2-accelerated rusting of iron vary greatly from site to site, despite careful monitoring of pollutant concentrations, a fact that has often puzzled researchers. The problem has been addressed from the standpoint of several factors that might be responsible for inconsistent results. These include: (1) the deposition rate of gaseous or dissolved SO_2 and particles; (2) the variability in the electrochemical actions that cause corrosion; (3) the influence of rust on the rate of corrosion; and (4) the interaction between the effects of "wetness time" and of relative humidity (RH) on surface electrolyte concentrations.

According to Nriagu (1978), once corrosion has begun, the progress of the reaction is largely controlled by the sulfate ions formed from oxidation of the adsorbed SO_2. The actual mechanism for the oxidation of SO_2 (and its

hydrated products) at metal-water interfaces is little understood. Barton (1973) proposed the following reaction:

$$SO_2 + O_2 + 2e \rightarrow SO_4^{2-}$$

or

$$4HSO_3^- + 3O_2 + 4e \rightarrow 4SO_4^{2-} + 2H_2O$$

The electron is provided by the oxidation of the metal (M):

$$M \rightarrow M^{n+} + ne$$

Duncan and Spedding (1974), using an electrophoretic method, found that the rates of sulfate formation on iron and zinc surfaces were similar; the pseudo-first-order half-life was determined to be about 24 hr. Other workers (Karraker 1963; Yoshihara et al., 1964) reported higher oxidation rates (half-life, 10 to 100 min) in bulk solutions using Fe^{3+} catalysts as summarized in Nriagu (1978). Nriagu also noted that rust on iron and steel is first restricted to localized sites or "nests" and then spreads across the entire exposed surface. At an SO_2 concentration of about 260 $\mu g/m^3$, corrosion products were obvious on iron surfaces after 6 to 8 weeks, whereas at SO_2 concentrations of 4×10^5 $\mu g/m^3$, they could be seen after only a few hours.

Barton (1973) showed that the critical SO_2 flux for corrosion was 6 to 10 $\mu g/m^2$ per year for steel and 18 to 20 $\mu g/m^2$ per year for zinc and copper. The formation of rust drastically increases the adsorption rate for SO_2. For example, at an SO_2 concentration of >0.001 percent and relative humidity (RH) of >96 percent, virtually all of the SO_2 that comes into contact with the rusting surface is adsorbed.

According to Nriagu (1978), Barton and Bartonova (1960) postulated the following mechanism of steel corrosion:

$$Fe + H_2O \rightarrow Fe(OH^-)ads + H^+$$

$$Fe(OH^-)ads \rightarrow Fe(OH)ads + e$$

$$Fe(OH)ads + SO_4^{2-} \rightarrow FeSO_4 + OH^- + e$$

The oxidative hydrolysis of ferrous sulfate leads to the formation of ferric hydroxide and the regeneration of sulfate ions, which in turn initiate another chain reaction:

$$FeSO_4 + 2H_2O \rightarrow FeOOH + SO_4^{2-} + 3H^+ + e$$

The supply of oxygen to the cathode must be maintained; rust films may therefore differ from metal to metal, with a tightly packed film giving a low diffusion rate.

10.2.1.1.1 Relative Humidity and Corrosion Rate. According to Schwarz (1972), the corrosion rate of a metal should increase by 20 percent for each increase of 1 percent in the relative humidity (RH) above the critical RH value. It is evident that relative humidity has a considerable influence on the corrosion rate. This influence has been established in laboratory trials by Barton and Bartonova (1969) and Sydberger and Ericsson (1976). It is apparent from Figures 10-1 and 10-2 (Haynie and Upham, 1974) that the corrosion rate of steel increases with increasing relative humidity as well as with increasing SO_2 concentration.

The climate of an area is usually characterized by average relative humidity rather than relative humidity distribution. Since average relative humidity is calculated from the distribution, there should be an empirical relationship between average relative humidity and the fraction of time some

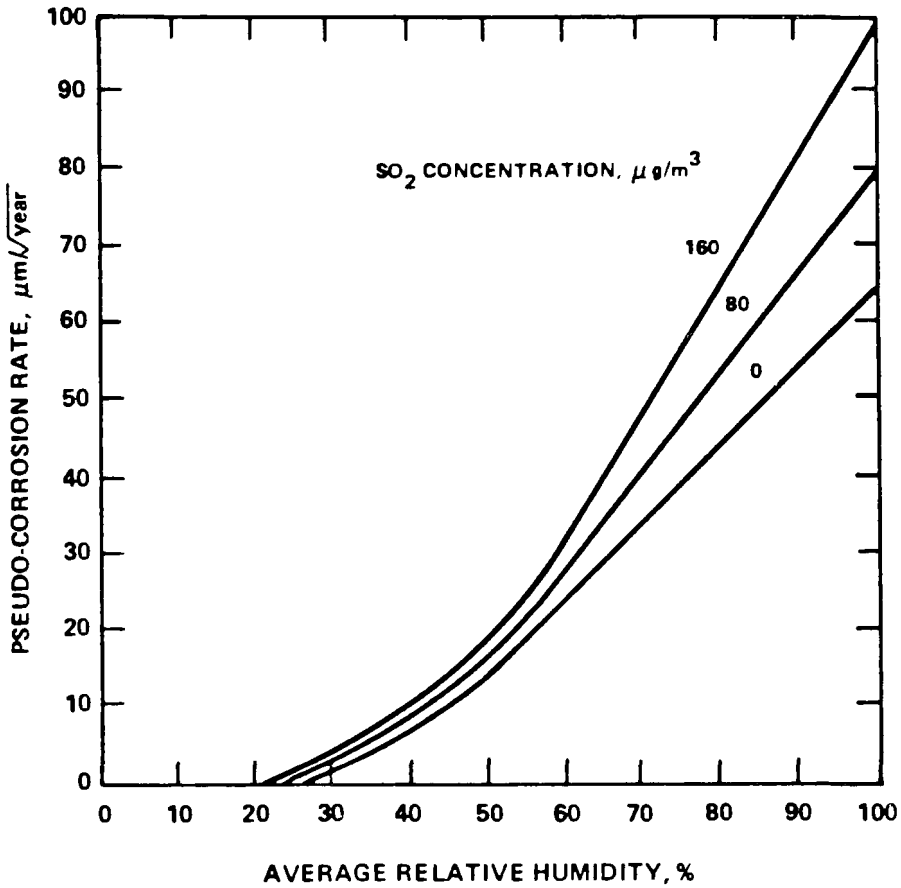

Figure 10-1. Steel corrosion behavior is shown as a function of average relative humidity at three average concentration levels of sulfur dioxide.

Source: Haynie and Upham (1974).

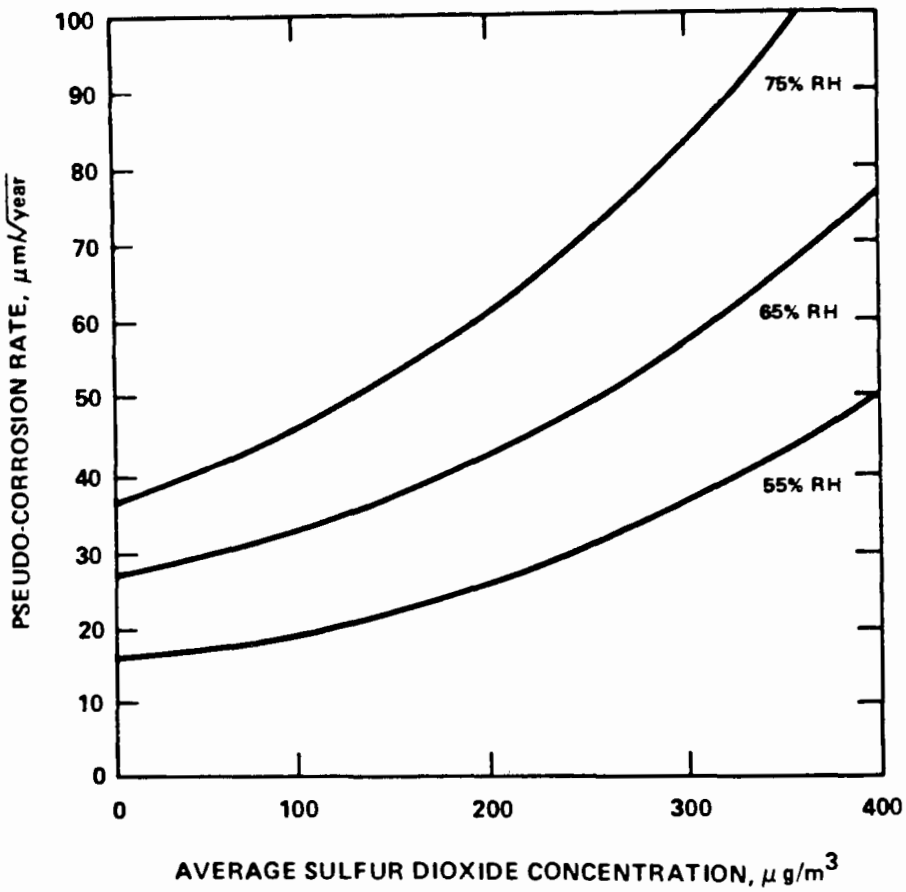

Figure 10-2. Steel corrosion behavior is shown as a function of average sulfur dioxide concentration and average relative humidity (RH).

Source: Haynie and Upham (1974).

"critical humidity value" (minimum concentration of water vapor required for corrosion to proceed) is exceeded. The fraction of time that the surface is wet must be zero when the average relative humidity is zero and unity when the average relative humidity is 100 percent. The simplest single-constant first-order curve that can be fitted to observed data and that meets these conditions is described by the equation $f = [(1 - k)RH]/(100 - kRH)$, where f is the fraction of time the relative humidity exceeds the critical value, RH is the average relative humidity, and k is an empirical constant less than unity (Haynie, 1980).

Ten quarter-year periods of relative humidity data from St. Louis International Airport were analyzed and fitted by the least-squares method to the above equation. The fraction of time the relative humidity exceeded 90 percent gave a value of 0.86 for k. This fraction and the data points are plotted in Figure 10-3 (Haynie, 1980).

When the temperature of a metal is below the ambient dewpoint, condensation of water on the metal surface will take place. The metal temperature at which condensation occurs will vary with heat transfer between ground and metal and between air and metal. Condensation will occur when the relative humidity adjacent to the surface exceeds a value in equilibrium with the vapor pressure of a saturated solution on the surface. The solution may contain corrosion products, other hygroscopic contaminants, or both. Temperature, wind, and sunshine then become factors in establishing corrosion rates, since they determine whether there will be sufficient dew condensation. Sayre (1973) established a direct relationship between the amount of dew precipitated and the corrosion rate of steel.

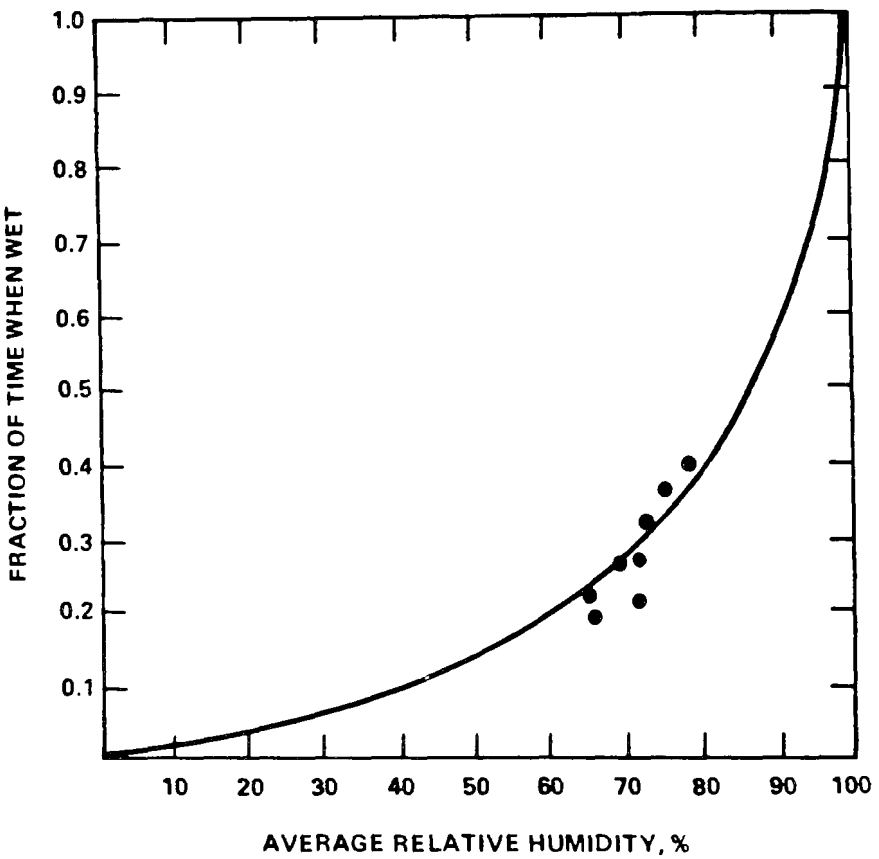

Figure 10-3. Empirical relationship between average relative humidity and fraction of time is shown for a wet zinc sheet specimen.

Source: Haynie (1980).

Haynie (1980) reported on the relationship between diffusion theory and thermodynamics for the observed effects of five variables: pollution level, relative humidity, temperature, wind velocity, and surface geometry. He observed that metals must be wet to corrode electrochemically. Surfaces are wet from condensation much more than from precipitation.

10.2.1.1.2 Influence of Rainfall on Corrosion. Steel surfaces shielded from the leaching effect of rain may corrode at a higher rate than those exposed to rain. The sulfate content of rust has been identified as a dominant factor in corrosion and is found at higher concentrations on surfaces sheltered from rain than on exposed surfaces because soluble sulfate is leached from the rust. However, sulfur deposition during rainfall must also be considered. Haagen ~~Reed and~~ and Ottaz (1975) found that the effect of rain on corrosion depends on the sulfate and sulfuric acid content of the rain.

As Kucera's (1976) review of this problem indicates, the mode of deposition complicates the analysis of acidic precipitation's effects. For example, in an area where dry deposits of hydrogen and sulfate ions exceeded deposits in wet precipitation, flat steel plates corroded more rapidly on their undersides than on their upper surfaces, suggesting that the rainfall had more of a washing effect than a corrosive action. However, in other areas where wet and dry deposition were about equal, the skyward sides of the plates corroded more quickly, indicating that the corrosive effect of the rainfall predominated. Other variables, including amount and frequency of precipitation, its pH level, humidity, and temperature, also determine the impact of acidic precipitation (Kucera, 1976).

For a more thorough discussion of the effects of acid rain on corrosion, see Chapter 8.

10.2.1.1.3 Influence of Temperature on Corrosion. From chemical reaction kinetics, one might expect corrosion rates to follow the Arrhenius law according to which the logarithm of a reaction rate is inversely proportional to the absolute temperature. However, this does not appear to be a major factor controlling corrosion rates. In most cases, as discussed later, the reaction rate is controlled by diffusion, either in the corrosion product film or in the environment. In either case, the rate of diffusion is relatively insensitive to changes in ambient temperature. A decrease in temperature raises the relative humidity while decreasing diffusivity; thus, the normal temperature range will most likely not observably affect the overall corrosion rate. Freezing should produce a step decrease in the corrosion rate because diffusion is then through a solid rather than a liquid.

Guttman (1968) and Haynie and Upham (1974), using statistical techniques of multiple linear regression and nonlinear curve fitting, could not obtain from their data a significant correlation between corrosion and temperature. However, increased temperature decreases the solubility of oxygen in the electrolyte. Moreover, temperature changes can cause condensation, and the increased quantity of condensed droplets would affect the corrosion rate. In addition, the rate of drying of a surface depends on both temperature and air movement.

The diffusion rate of oxygen in the electrolyte increases with temperature, and changes in temperature are expected to cause changes in the physical structure and in the chemical composition of the rust layer, thereby affecting its protective function and the diffusion rate of the reactants. Temperature changes may indirectly affect the pH of the electrolyte. For example, the loss of ammonia by evaporation from particulate ammonium sulfate would produce a greater acidity.

Guttman and Sereda (1968) made continuous measurements of sulfur oxides, time of wetness, and temperature in their outdoor exposure tests. The corrosion rate increased markedly with temperature, which may be attributed to a speeding up of the electrochemical process. The effects are not simply thermodynamic since there are other factors including evaporation of surface electrolyte and decrease in the solubility of oxygen and gaseous pollutants. Barton (1973) did find that the effect of increased temperature was more pronounced when the rust contained little water and sulfate.

10.2.1.1.4 Hygroscopicity of Metal Sulfates. The sulfate in rust stimulates further corrosion by a mechanism that is related to the critical relative humidity at which an electrolyte film is formed. The hygroscopicity of iron sulfates in the rust lowers the critical relative humidity for corrosion; however, sulfates are not the most deliquescent salts. For example, chloride and nitrate salts which have higher hygroscopicity than sulfates make corrosion possible at lower humidities.

Surfaces contaminated by sea salt (mostly sodium chloride) are expected to be wet when the relative humidity exceeds 75 percent. In contrast, calcium chloride keeps surfaces wet at relative humidities as low as 30 percent. A saturated solution of zinc sulfate at 20°C is in equilibrium at 90 percent relative humidity. Thus, zinc corroded by sulfur dioxide is expected to be wet when the relative humidity exceeds 90 percent (Haynie, 1980).

Some pollutants which react chemically with various materials and are consumed produce catalytic effects. The following four mechanisms act to increase corrosion rates without consuming the pollutants: (1) Hygroscopic materials increase the amount of time that a corroding surface is wet. (2) Conductivities of solutions and corrosion product films increase.

(3) Pollutants form soluble intermediate reaction products or activated complexes that destroy the protective nature of films. (4) Lowering the pH usually increases the solubility of corrosion products.

10.2.1.1.5 Electronic Conductivity of Rust. Barton (1973) postulated that sulfate ions influence the anodic dissolution of iron as a function of their concentration at the steel-rust interface. The corrosion rate of the rust layer is based in part on the high electronic conductivity of rust, which allows the reduction of oxygen to occur within the rust layer. The rate is also influenced by the porosity of rust, which permits rapid diffusion of oxygen to the cathode.

In the presence of SO_2, ferrous sulfate is formed before insoluble rust develops. The amount of SO_2 required is small; each SO_2 molecule can generate 20 to 30 molecules of rust. Once ferrous sulfate is formed, rusting can continue even though SO_2 is no longer present in gaseous form.

10.2.1.1.6 Cathodic Reduction of SO_2. Under experimental conditions, an SO_2 concentration of 10 ppm (2620 $\mu g/m^3$) has reportedly led to cathodic reduction and depolarization, yielding sulfide-containing corrosion products (Sydberger and Ericsson, 1976). However, at ambient air concentrations (0.01 to 0.2 ppm or 26 to 520 $\mu g/m^3$ in polluted areas), it would not be reasonable to expect the electrolyte to contain enough SO_2 to affect the cathodic reaction.

10.2.1.1.7 Cathodic Reduction of Rust. Evans (1972) suggests that oxidative hydrolysis of ferrous sulfate occurs slowly, and would be important only in the initial stage of corrosion. He proposes that there is a rate-controlling cathodic process. Thus, the corrosion products in the ferric state would be converted to magnetite (Fe_3O_4), by a reaction involving the reduction of ferric oxyhydroxide (FeOOH):

$$Fe^{2+} + 8FeOOH + 2e^- \rightarrow 3Fe_3O_4 + 4H_2O$$

10.2.1.1.8 Corrosion-Protective Properties of Sulfate in Rust. The rust layer on steel is somewhat protective against further corrosion, though far less so than the corrosion layer on zinc and copper. A limiting factor in rust's protection of steel is the content of soluble sulfate in rust.

Rust samples investigated by Chandler and Kilcullen (1968) and by Stanners (1970) contained 2 to 2.5 percent soluble sulfate and 3 to 6 percent total sulfate. The outer rust layer contained a small amount (0.04 to 0.2 percent) of soluble sulfate, compared with 2 percent in the inner rust layer. The concentration of insoluble sulfate was fairly uniform throughout the rust layers.

The emphasis on the composition of the rust layer has led to studies of the corrosion-protective properties of rust as a function of exposure history (Nriagu, 1978; Sydberger, 1976). Steel samples initially exposed to low concentrations of sulfur oxides and then moved to sites of higher sulfur oxide concentrations corroded at a slower rate than did samples continuously exposed to the higher concentrations. Exposure tests started in summer showed slower corrosion rates during the first years of exposure than did those started in winter.

The long-term corrosion rate of steel appears to depend on changes in the composition and structure of the rust layer. During the initiation period, which varies in length with the SO_2 concentration and other accelerating factors, the rate of corrosion increases with time (Barton, 1973). Because it is porous and nonadherent, the rust initially formed offers no protection; in fact, it may accelerate corrosion by retaining hygroscopic sulfates and chlorides, thus producing a microenvironment with a high moisture content (most often reported in terms of percent relative humidity). After the initiation

stage, the corrosion rate decreases as the protective properties of the rust layer improve. Satake and Moroishi (1974) relate this slowing down to a decrease in the porosity of the rust layer. During a third and final stage, a stationary rate of corrosion is attained and the amount of sulfate rust is proportional to atmospheric sulfur oxide concentrations. Where there is no appreciable deposition of sulfur or chloride compounds, the corrosion of steel is low, even with high atmospheric humidity and temperature (Haynie and Upham, 1974). The quantitative determination of corrosion rates becomes difficult if it is not known how long the metal has a surface layer of electrolyte. Variations in the "wet states" will occur with relative humidity, temperature, rain, dew, fog, and evaporation caused by wind. The surface electrolyte layer may form on a metal surface as a result of rain, dew, or adsorption of water from the atmosphere. Capillary condensation in rust can be related to the minimum atmospheric moisture content which allows corrosion to occur (i.e., critical relative humidity). Centers of capillary condensation of moisture on metals can occur in cracks, on dust particles on the metal surface, and in the pores of the rust (Tomashov 1966).

The water content of rust formed by laboratory exposure of steel samples to various SO_2 concentrations was examined by Barton and Bartonova (1969). They concluded that water content of rust increased with SO_2 in the atmosphere. The hygroscopic nature of soluble salts in rust is believed to be the prime factor affecting water sorption by the rust layer.

10.2.1.2 <u>Effects of Sulfur Oxide Concentrations on the Corrosion of Exposed Metals</u>--Most of the laboratory studies reviewed in this section have measured corrosion rates related to exposure to sulfur dioxide alone or in combination with other compounds. In field exposure studies, where sulfur oxides almost

invariably occur in combination with other airborne pollutants, an attempt is made, on the one hand, to assign separate values to sulfur oxides and, on the other, to describe pollutant interactive effects on corrosion. The section unavoidably overlaps somewhat with a later section on particles, since sulfur oxides exist in particulate phase. Here, the emphasis is on the direct role of sulfur oxides in the corrosion process (e.g., the oxidation of SO_2 with moisture on a metal surface). In a later section, sulfur oxide particles are discussed mainly in terms of their indirect role (e.g., their ability to increase wetness time of a metal surface).

10.2.1.2.1 Ferrous Metals. Ferrous metal products and structures are exposed widely to ambient pollutant levels. Rusting of these metals is the best documented form of metallic corrosion affected by sulfur oxides. This subsection reviews studies of rusting rates of ferrous metals, including iron, steel, and steel alloys.

Addition of small amounts of certain elements, especially copper, improves the corrosion resistance of mild steel. The American Society for Testing and Materials (ASTM) has established this fact in an extensive series of exposure tests (Guttman and Sereda, 1968). Larrabee (1959) showed that carbon steel, copper steel, and a Cr/Si/Cu/P low-alloy steel used in an industrial environment for 10 years were more resistant to corrosion than carbon steel. Stainless steels contain more than 12 percent chromium and are widely used in outdoor exposures; they are specified for use in many industrial processes in which corrosive liquids rapidly attack ordinary steels.

The most important additive in low-alloy steels is copper. Larrabee and Coburn (1961) established that the addition of 0.03 percent copper to steel reduces corrosion losses in an industrial area by up to 70 percent. Low-alloy

steels usually contain 0.2 to 0.5 percent copper. Other investigators, including Schwenk and Ternes (1968) and Brauns and Kalla (1965), have also shown that adding copper to steel at these levels will decrease metal loss in industrial atmospheres.

Phosphorus is also effective in raising the corrosion resistance of steel. Larrabee (1959) found less corrosion in copper alloy steels containing 0.05 to 0.1 percent added phosphorus.

The high corrosion resistance of stainless steels incorporating chromium, molybdenum, and nickel, is attributed to the protective properties of the oxide film formed on these alloys; however, in heavily polluted atmospheres, this film is not completely protective. Particles in settled dust, including sulfates and chlorides, can promote rupture of the oxide film and cause pitting corrosion, which may be influenced by the surface finish (see section 10.3.1). Smoothly polished or electropolished surfaces are less likely to retain solid deposits originating from airborne particles (Larrabee, 1959).

Stainless-steel alloys contain chromium, molybdenum, and sometimes nickel. The lowest alloyed types have little corrosion resistance; in particular, #13 Cr steel suffers pitting attack in industrial atmospheres. Evgang and Rockel (1975) report that the austenitic steels of 18 percent Cr and 8 percent Ni are reasonably resistant in urban atmospheres but have shown slight rusting in industrial areas. The rusting is decreased when the steel surface is cleaned of atmospheric deposits.

10.2.1.2.2 Laboratory and Field Studies Emphasizing Ferrous Metals. It is useful to consider laboratory and field studies of corrosion effects separately because the attribution of cause to effect is much clearer in laboratory experiments; field studies are often beset with many "confounding variables."

The following are included as examples of confounding variables associated with field studies; organized as temporal and spatial.

- o temporal fluctuations in temperature, wind moisture content, insolation, rainfall and chemical characteristics (e.g., acidic rain) and atmospheric pollutant concentrations
- o spatial differences such as aspect, altitude, electromagnetic fields and indigenous microorganisms

10.2.1.2.2.1 Laboratory Studies. Spence and Haynie (1974) described the design of a laboratory experiment to identify the effects of environmental pollutants on various materials including ferrous metals. The environmental system consisted of five exposure chambers to control temperature and humidity and chill racks to simulate the formation of dew. Gaseous pollutants included those usually monitored in field exposures: sulfur dioxide, nitrogen dioxide, and ozone. Experiments were statistically designed for analysis of variance, and a system was selected to study the interactive effects of pollutants and other variables. The effect of particles was not included in the design. The chambers were equipped with a xenon arc light to simulate sunlight. The system was designed to maintain air contact with the various materials at preselected temperatures, relative humidities, flow rates, and pollutant concentrations. A dew-light cycle was used; it produced faster deterioration than did conditions of constant humidity and temperature.

Haynie et al. (1976) exposed weathering steel in the chamber study described above and measured concentrations of sulfur dioxide, nitrogen dioxide, and ozone in various combinations and at two levels of pollutant concentration. The corrosion rate was measured by loss in weight of the weathering steel (a Cor Ten A product). Six panels were exposed under 16 polluted-air and 4 clean-air conditions, and measurements were taken at 250, 500, and 1000 hr of exposure. The weight losses were converted to equivalent thickness loss

values. As expected, corrosion was most severe at high SO_2 concentrations and high humidity. The results of earlier field exposures (see following section) had shown that the presence of high oxidant concentrations decreased the corrosion rate. The chamber exposures showed that ozone neither inhibited nor accelerated corrosion. The authors concluded that some other oxidant or unmeasured factor that was covariant with ozone caused the inhibition effect. However, if the data from the sites with high concentrations of oxidant in the field exposure experiments were excluded, a damage function from the laboratory study was an excellent predictor of the field results.

Sydberger and Ericsson (1976) studied the corrosion of mild steel at 1, 10, and 100 ppm (2620, 26,200, 262,000 $\mu g/m^3$) SO_2 across the range of critical humidities (80 to 96 percent RH). The flow rate of the SO_2 atmosphere was varied, and some samples were sprayed with water to simulate rain or condensation. The chemical composition of the corrosion products was studied by X-ray diffraction, infrared spectrometry, and electron spectroscopy for chemical analyses (ESCA) techniques. The flow rates of the SO_2 atmospheres markedly influenced the corrosion rates. It appears that corrosion rates are related not only to the SO_2 concentration in the atmosphere, but also to the supply of SO_2 per unit surface area and time. Spraying the samples with distilled water at intervals substantially increased corrosion.

Sydberger and Ericsson's (1976) analysis of the corrosion product (rust layer) was based on the concepts of Schwarz (1972) and Barton (1973) that sulfate is the primary corrosion stimulant in rust formation. Anodic activity is maintained by the concentration of ferrous sulfate in the electrolyte. An SO_2 supply of 4 $\mu g/cm^2/hr$ at the lowest humidity initiated corrosion at a low rate. A rise above 50 percent RH increased corrosion markedly. Of particular

interest was the finding that a variation of the flow rate at 1 ppm (2620 $\mu g/m^3$) SO_2 with 96 percent RH gave significant differences in corrosion rates. This study of the effect of rust on corrosion showed that even at high humidity and high sulfate content, the corrosion rate decreased to a low level when the SO_2 concentration was low.

The reaction between SO_2 and wet metal surfaces was examined by Vannenberg and Sydberger (1970). This laboratory study involved the exposure of copper, aluminum, zinc, iron, 18/8 stainless steel, and rusted iron to SO_2 and oxygen at high humidity. Under reflux conditions, the products of corrosion were leached out into the reflux water where pH and conductivity were measured as a function of time. The experiments with iron, stainless steel, and rust demonstrate that iron oxides strongly catalyze the formation of sulfuric acid from SO_2. With the samples of copper and aluminum, the increase in conductivity was slight; it appears that these metals do not provide good surfaces for the oxidation of SO_2. Thus, copper and aluminum show better corrosion resistance than do iron and zinc.

10.2.1.2.2.2 Field Studies. Sydberger, in his review of studies on corrosion of steel by sulfur pollution, noted that Schikorr found a good correlation between the corrosion rate and the amount of sulfur compounds deposited on steel, zinc, and nickel. There was a clear relationship between corrosion and SO_2 adsorption on iron samples exposed in the urban atmosphere of Stuttgart. Several studies have established that adsorption on a rusty steel surface did not depend on relative humidity or temperature. Schikorr reported SO_2 adsorption by the Liesegang-bell method (Sydberger, 1976).

For outdoor exposures, the primary rate-controlling factor in the delivery of pollutants to a surface is eddy diffusion. This value is not constant and

is a function of the horizontal wind velocity gradient away from the surface. The transport of a pollutant to a surface is usually expressed as a "deposition velocity" (u), defined as the flux to the surface divided by the ambient pollution level at some specific measuring height. Reported deposition velocities for gaseous pollutants have usually been within an order of magnitude of 1 cm/sec. These values are consistent with calculated estimates based on an analogy with momentum flux and measured wind velocity profiles.

The amount of SO_2 reaching a steel surface depends on wind direction, wind velocity, and the orientation of the surface to the emission source. The concept that SO_2 deposition varies with flow direction and velocity suggests that data on concentration alone cannot be used to determine the supply of SO_2 to metal surfaces, therefore surface adsorption methods like the Liesegang-bell and the lead candle method may provide valuable information in relating supply of sulfur oxides to metal surfaces (Sydberger, 1976). Upham's (1967) work indicated, however, that corrosion of mild steel at seven Chicago sites increased with time and with increasing mean SO_2 concentration (Figure 10-4).

Haynie and Upham (1971) continuously monitored urban pollutants including SO_2, nitrogen dioxide, and ozone (oxidants) to determine whether previously unconsidered variables might affect steel corrosion. Their 5-year program, begun in 1963, involved sites in Chicago, Cincinnati, New Orleans, Philadelphia, San Francisco, Washington, Detroit, and Los Angeles. They studied three types of steel expected to show different levels of resistance to atmospheric corrosion: (1) a plain carbon steel containing some copper (0.1 percent copper); (2) a copper-bearing steel (0.22 percent copper); and (3) a low-alloy weathering steel (0.4 percent copper with 0.058 percent phosphorus). The exposure periods were 4, 8, 16, and 32 months. The same steels were exposed at rural

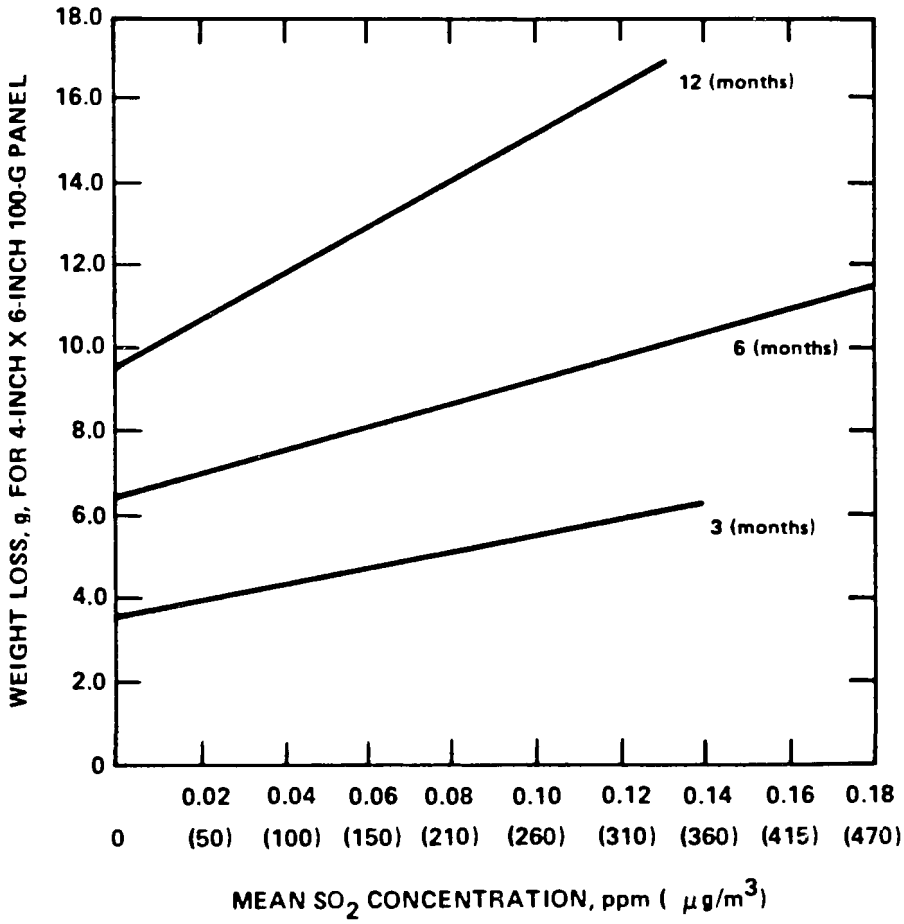

Figure 10-4. Relationship between corrosion of mild steel and corresponding mean SO_2 concentration is shown for seven Chicago sites.

Source: Upham (1967).

sites as a control. The rural sites proved to have higher than expected corrosion rates, presumably caused by the transport of SO_2 from the cities. Pollution levels were not measured at these sites. Multiple regression analysis was able to establish significant correlations between average SO_2 concentrations and corrosion of all three steels.

A first consideration was climatic conditions. For metallic corrosion to occur, a certain level of wetness on the metal surface is required to provide an electrolyte film in which electrochemical action can take place. The average humidities recorded by Haynie and Upham were thought to be high enough to produce this critical wetness threshold. Temperature was a statistically insignificant variable, because the range of average temperatures was less than 15 percent (Haynie and Upham, 1971).

Inspection of the monitored SO_2 and oxidant concentrations revealed wide variations from site to site. Multiple-regression analysis showed that high concentrations of oxidants correlated with lowered metallic corrosion rates.

Mansfeld (1980) made observations at nine test sites in and around St. Louis for 30 months beginning in October, 1974, as part of the Environmental Protection Agency's Regional Air Pollution Study to determine the effect of airborne pollutants on galvanized steel, weathering steel, stressed aluminum, marble, and house paint--essentially the same materials examined in the chamber study reported by Haynie et al. (1976). During 1975 and 1976, atmospheric corrosion monitors (ACM) of the type described by Mansfeld and Kenkel (1976) were installed at four sites to measure time of wetness. Each ACM consists of a copper-zinc or copper-steel couple that registers current flow when an electrolytic path forms between the two plates as a result of deposition of water from the air, dew, or rain on corrosion products. The ACM measures the

time that the panel is wet enough for the electrochemical mechanism of corrosion to occur. Parameters measured in Mansfeld's study included the following: wind speed, wind direction, temperature, ozone concentration, total hydrocarbon concentration, total sulfur and NO_x concentration, hydrogen sulfide concentration, sulfur dioxide concentration, relative humidity, sulfate concentration, nitrate concentration, total suspended particle concentration, and time of wetness. Mansfeld determined weight losses for galvanized steel, weathering steel, house paint, and marble; he removed aluminum tension samples after failure. Concentrations of SO_2 measured by Mansfeld (1980) were generally an order of magnitude lower than the 130 ppb concentrations reported by Upham (1967) at urban sites in St. Louis.

Mansfeld's data show that damage to a particular material does not necessarily occur at the same corrosion rate at each site. Preliminary statistical analysis of the results failed to show significant correlation between corrosivity and pollutant concentration. There was substantial error in the measurement of relative humidity, an extremely important corrosion variable. This makes data interpretation difficult; more sophisticated statistical techniques are now being applied to the data.

In another study (1974), Haynie and Upham observed enameling steel containing 0.019 percent carbon and 0.028 percent copper at 57 sites in the National Air Sampling Network (NASN). They measured corrosion by weight loss and quantitatively determined other pollutants, including gaseous sulfur dioxide, total suspended particles, and the amount of sulfate and nitrate in the particles. Sulfur dioxide levels ranged from 9 to 374 $\mu g/m^3$, total suspended particles from 11 to 182 $\mu g/m^3$, and relative humidity from 29 to 76 percent. The average temperature remained within a fairly narrow range and was considered

constant. The temperature, the quantity of total particles, and the presence of nitrate in the particles did not significantly affect the corrosion rate of steel. The concentration of sulfur dioxide was significant only when sulfate was not included in the regression analysis. At each site, sulfate content of the particles and sulfur dioxide concentration were closely related; sulfate content was used in the analysis of the data. On the basis of this study, Haynie and Upham derived the following empirical expression to obtain the best relationship between corrosion of enameling steel and atmospheric SO_2 content:

$COR = a_0 t^{\frac{1}{2}} e^{(a_2 sul - a_2/RH)}$ where COR = depth of corrosion (μm)

sul = average level of sulfate in particles ($\mu g/m^3$)

RH = average relative humidity (percent)

t = time a_0, a_1, a_2, are coefficients of determination.

Sulfate was considered a more accurate proxy for SO_2 because of the strong covariance between sulfate and SO_2. Average relative humidity factor is a substitute variable for the fraction of time the steel is wet.

Considerable effort has gone into isolating environmental variables that would predict long-term corrosion rates. Empirical expressions for corrosion of various steels exposed to the atmosphere (see Table 10-1) have been developed by Oma et al. (1965), Chandler and Kilcullen (1968), Guttman and Sereda (1968), and Haynie and Upham (1974). These equations may be used to relate reduction in SO_2 and sulfates to reduction in corrosion of metals, serving as a basis for a benefit appraisal. The effects of various particles containing SO_2 and sulfate on the corrosion of iron are illustrated in Figure 10-5 (from Rosenfeld, 1973).

Matsushima et al. (1974), in studies of low-alloy weathering steels, considered the impact of the washing action of rain, the ease with which water

TABLE 10-1. SOME EMPIRICAL EXPRESSIONS FOR CORROSION OF EXPOSED FERROALLOYS

Exposure Material	Site	Duration	Empirical Equation	Parameter Units	Source	Note/Comments
Steel A	Sheffield England	1 year	$y = 0.51 + 0.01x$	y = corrosion rate in mils/year x = SO_2 in $\mu g/m^3$	Chandler and Kilcullen (1968)	Authors stated that SO_2 and smoke has a major influence on the corrosion rate of steel and accounted for about 50% of the variations found at the different sites. Other factors, such as time of wetness, were found equally important in determining the corrosion rate of steel. 95% confidence limit $\pm$ 0.75 mils for any point on regression.
Steel B	Sheffield England	1 year	$y = 0.82 + 0.006x$	y = corrosion rate in mils/year x = SO_2 in $\mu g/m^3$	Chandler and Kilcullen (1968)	95% confidence limit $\pm$ 0.5 mils for any point in regression.
Enameling steel	NASN sites	1-2 years	$cor = a_0\sqrt{t}\ [e^{(a_1 sul - a_2/RH)}]$	cor = depth of corrosion, μm sul = average level of sulfate in suspended particulate, $\mu g/m^3$ RH = average relative humidity, percent t = time in years *a_0 - 183.5 *a_1 = 0.06421 *a_2 = 163.21	Haynie & Upman (1974)	std. dev. 85.0; 95% conf. limits 13.4 lower, 353 upper std. dev. 0.00451; 95% conf. limits 0.0552 lower, 0.0732 upper std. dev. 32.8; 95% conf. limits 97.6

TABLE 10-1. (Continued)

Exposure Material	Site	Duration	Empirical Equation	Parameter Units	Source	Note/Comments
Enameling steel	NASN sites	1-2 years	$cor = 325 \sqrt{t}\ [0.00275SO_2-(163.2/RH)]$	parameter units same as for previous equation	Haynie and Upham (1974)	Sul and SO_2 relationship defined as $sul = 8.9 \mp 0.0429\ SO_2$ $\pm 2S = 8.2$
Steel	Ottawa	1-12 mos.	$y = -0.572 + 1.69B + 0.215\ C - 0.268B^2 + 0.174AB$ y = corrosion loss of steel in g/panel A = (time of wetness, days -14.3)/5.0 B =temperature, ^oF -5.25)/15.0 C = (SO_2, ppm -0.0202)/ 0.024		Guttman and and Sereda (1968)	Authors noted that this equation and others derived from the same base equation do "not enable one to identify the atmospheric factor which exerts the most critical effect on corrosion or to observe how the others modify this effect".

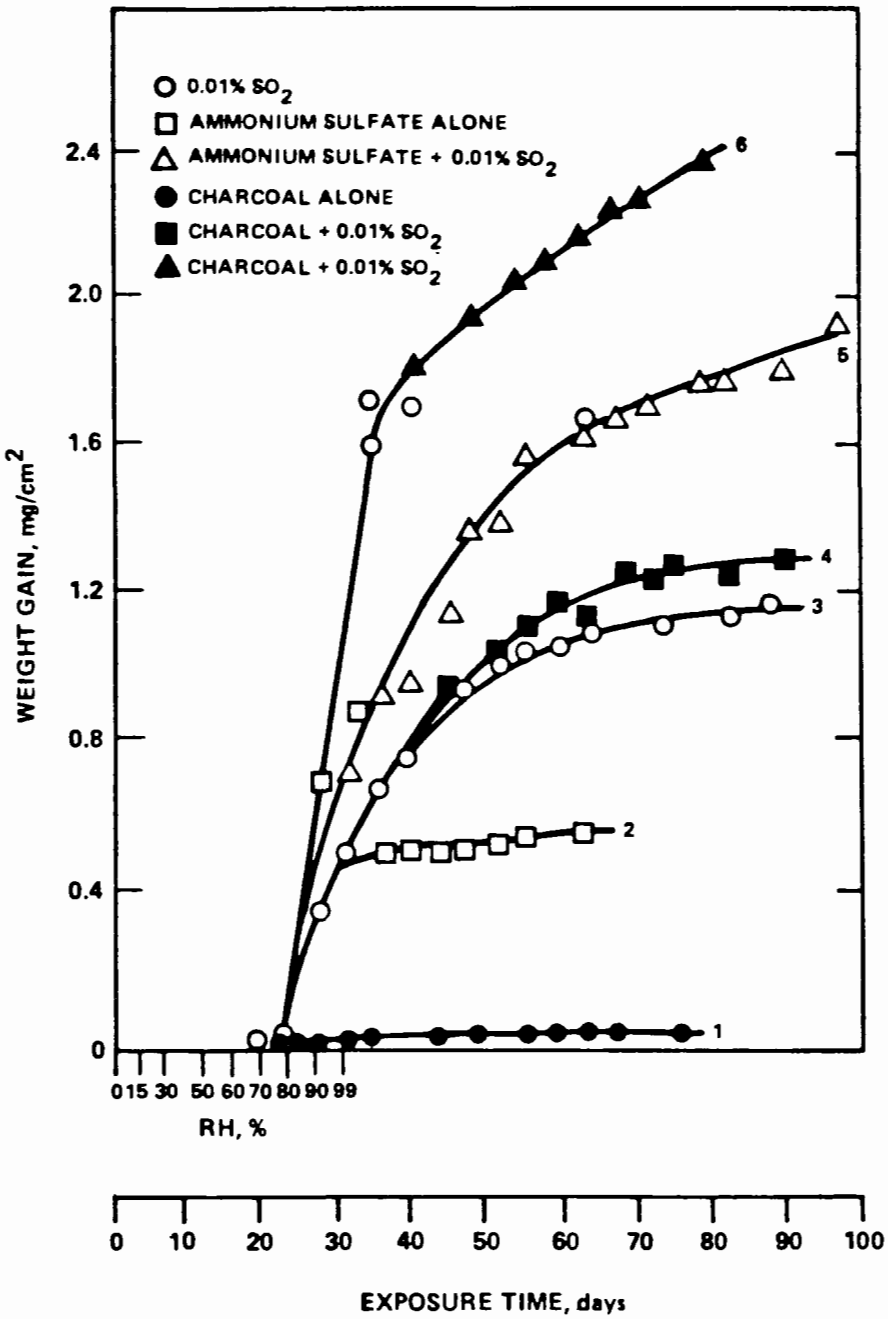

Figure 10-5. Effects of particles on the rate of iron corrosion are shown for: 1, charcoal alone; 2, ammonium sulfate alone; 3, 0.01 percent SO_2; 4, charcoal + 0.01 percent SO_2; 5, ammonium sulfate + 0.01 percent SO_2; 6, charcoal + 0.01 percent SO_2.

Source: Adapted from Rosenfeld (1973).

would drain off the surface, and the drying effect of sunlight to determine the effect of these variables on the retention of particles that influence the electrolytic corrosion mechanism and the time of wetness. The authors hypothesized that the geometry of unpainted weathering steels may not favor the development of a protective oxide film of rust. The model structure used in the exposure trials contained horizontal and inclined roofs, vertical wall panels, and window frames. Two sites were chosen: an industrial location and a residential site in the Kawasaki area, which has a cold, dry winter and a hot, humid summer.

The results show that the successful use of weathering steel is related not only to the severity of pollution but also to the specific interplay between shelter and the uniform washing action of rain. Thus, for areas in which the structural factors are unfavorable, the optimum rust film is slow to form and may deteriorate. Rust films develop and are then destroyed, and the surface never develops a protective film. Generally, boldly exposed surfaces such as horizontal or inclined roofs show the least corrosion.

10.2.1.2.3 Nonferrous Metals. Sydberger and Vannenberg (1972) examined the influence of relative humidity and rust on the adsorption of sulfur dioxide on metal surfaces, using radioactive sulfur. The concentration of SO_2 was 0.1 ppm (262 $\mu g/m^3$), and relative humidity was varied between 50 and 98 percent. Polished and preexposed samples of iron, zinc, copper, and aluminum were compared for their adsorption properties. Iron, zinc, and copper were preexposed to SO_2 concentrations (0.01 percent or 2.6×10^5 $\mu g/m^3$) at 98 percent RH and 22°C for 3 hr. The aluminum samples were preexposed for 30 hr. The principal corrosion product identified by X-ray diffractometry was hydrated metal sulfate. Exposures were made in an atmosphere containing 1.0×10^{-5}

percent (262 μg/m^3) SO_2 at relative humidities ranging from 50 to 98 percent. Adsorbed SO_2 was measured at 30-min intervals with a Geiger counter.

The corrosion rate at 90 percent RH was initially high for zinc and copper but quite low for aluminum. Adsorption of SO_2 on preexposed iron samples was high. At 80 percent RH, almost all of the SO_2 was adsorbed. The high adsorption rate is perhaps explained by the rapid oxidation of adsorbed sulfur dioxide caused by the catalytic effect of the rust. The initial rate of adsorption on polished iron below 80 percent RH is related to the absence of corrosion; however, at increased humidity, corrosion is initiated and the adsorption rate increases.

Of particular significance is the observation that adsorption takes place at humidities below the critical humidity (Sydberger and Vannenberg, 1972). This finding suggests that SO_2 will be adsorbed on a rusty iron surface during periods of low humidity and will affect the corrosion rate as humidity rises. The critical humidities for nonferrous metallic surfaces, as summarized from Rosenfeld (1978) and NAS (1977), appear on Table 10-2. The corrosion products of copper and aluminum have an extremely low adsorption capacity below 90 percent RH, confirming the lower sensitivity of these metals to corrosion by SO_2 (see Figure 10-6, from Sydberger and Vannenberg, 1972).

TABLE 10-2. CRITICAL HUMIDITIES FOR VARIOUS METALS

Metal	Critical humidity, % RH
Aluminum	75-80
Brass	60-65
Copper	65-70
Nickel	65-70
Zinc	70-75

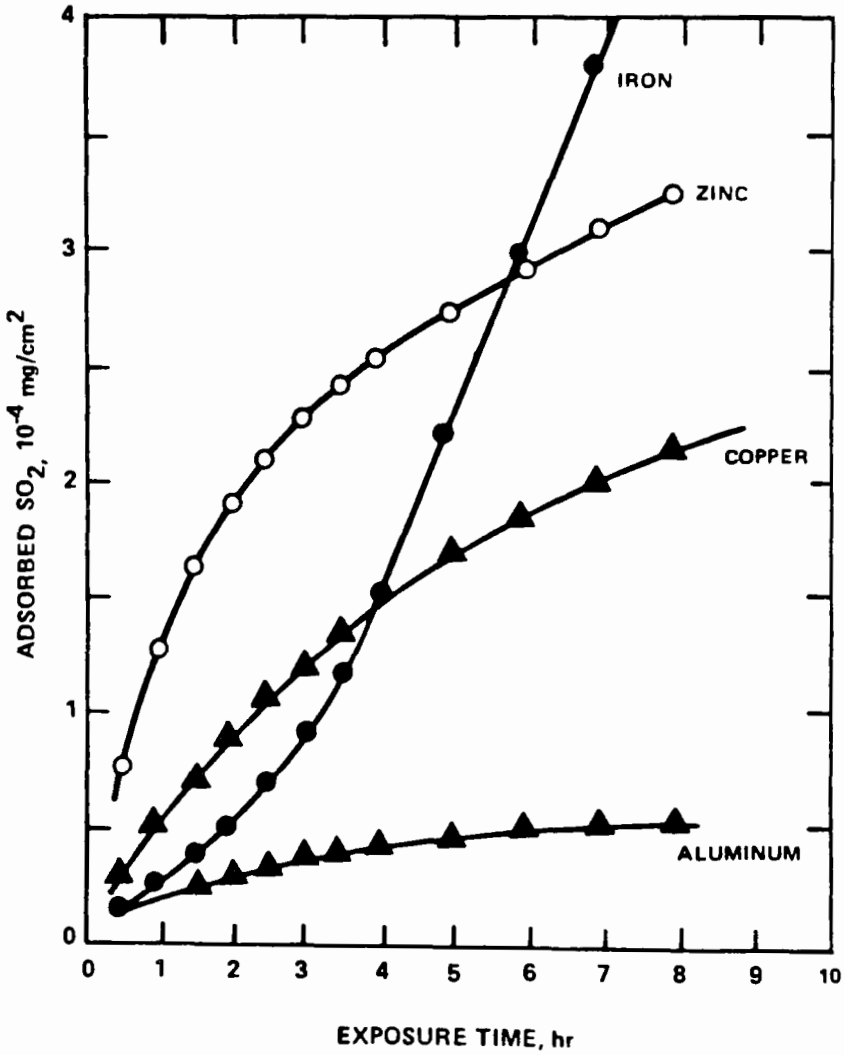

Figure 10-6. Adsorption of sulfur dioxide on polished metal surfaces is shown at 90 percent relative humidity.

Source: Adapted from Sydberger and Vannenberg (1972).

Aluminum is generally considered to be corrosion resistant. It forms a protective film of aluminum oxide which is not dissolved at low concentrations of acid sulfate particles. When the film becomes contaminated with dirt and soot particles, there is a change in surface appearance characterized by mottling and pitting. Simpson and Horrobin (1970) reported that aluminum undergoing long exposure in industrial areas displayed white areas of crystalline corrosion products. Aluminum surfaces exposed for periods of more than 5 years to a sulfate concentration of 0.14 ppm (550 $\mu g/m^3$) had pits as deep as 14 mils (0.36 mm).

Fink et al. (1971) summarized measured corrosion rates (mils per year) and depth of pitting (mils) for rural, mild industrial (30 $\mu g/m^3$ or 0.01 ppm SO_2), normal industrial (370 $\mu g/m^3$ or 0.14 ppm SO_2 and 80% RH), and severe industrial areas. Their overall conclusion was that although some loss of thickness occurred in the first 2 years, structures composed of aluminum and its alloys are resistant to air pollutants.

In another study, Haynie (1976) found that stressed aluminum specimens exposed to SO_2 at concentrations of 79 and 1310 $\mu g/m^3$ (0.5 ppm) lost approximately 8.6 and 27.6 percent of their bending strength, respectively. He also noted that 7005-T53 high-strength aluminum alloy tubing, which contains very little copper, is susceptible to stress-corrosion cracking in industrial environments.

Abe et al. (1971) exposed copper and copper alloys for 2 years in marine, rural, highly industrial, and urban areas in which there was great variation in pollutant and salt content. Analyses of the metallic surface deposits showed the presence of basic sulfate, sulfide, and chloride of copper. The

green patina on copper was analyzed and determined to be basic copper sulfate in urban areas and basic copper chloride in seacoast areas. These surfaces were protective against further corrosion.

The formation of these basic copper salts, according to Simpson and Horrobin (1970), can take up to 5 years and will vary with the concentration of sulfate or chloride particles, the humidity, and the temperature. They reported the corrosion rate of copper to be 0.9 to 2.2 μm/year in industrial atmospheres, compared with 0.1 to 0.6 μm/year in rural areas.

The high corrosion resistance of nickel and copper compared with unalloyed steel is attributed by Sydberger (1976) to the ability of these metals to form a layer of insoluble basic sulfate that protects the metal surface. Such layer formation does not occur on steel because of the action of sulfuric acid from the oxidation of SO_2 in an oxidative hydrolysis of ferrous sulfate.

10.2.2 Protective Coatings

Some materials are coated for protection against the effects of exposure. The coatings provide either sacrificial protection or barrier protection. In galvanization, zinc is applied to ferrous metal for sacrificial protection. Thus, while the galvanized surface may suffer corrosion damage, it helps to prevent rusting of steel products such as gutters, cables, wire fencing, and building accessorites. Barrier protection is provided by varnishes, lacquers, and paints by sealing the underlying surface material against intrusion by moisture.

10.2.2.1 Zinc-Coated Materials--Zinc is used to protect steel because this coating is fairly resistant to atmospheric corrosion. Zinc is anodic with respect to steel; when zinc and steel are in contact with an electrolyte, the electrolytic cell provides current to protect the steel from corrosion with some oxidation of the zinc.

Zinc is generally exposed as a protective coating in the form of galvanized steel products such as gutters, cables, wire fencing, and building accessories. It is used to protect steel since a zinc coating is fairly resistant to atmospheric corrosion. Zinc is anodic with respect to steel; when zinc and steel are in contact with an electrolyte, the electrolytic cell provides current to protect the steel from corrosion with some oxidation of the zinc.

Guttman (1968) carried out a long-term exposure of zinc panels with measurement of the atmospheric factors. He found that zinc is corroded by SO_2 and that time of wetness and concentration of SO_2 are the major factors that determine the rate of corrosion.

Kucera (1976) noted strong correlations between the corrosion rate and (1) the adsorption of SO_2 on zinc surfaces and (2) the concentrations of SO_2.

Fleetwood (1975) conducted 5-year exposure studies of zinc and iron in a number of locations ranging from dry tropical to industrial. He estimated the service life of galvanized steel to be 15 to 20 years in an industrial area containing pollutants, and 300 years in a dry tropical unpolluted area.

Haynie and Upham (1970) exposed zinc panels in eight cities, continuously monitoring SO_2 concentration and collecting meteorological data, including temperature and relative humidity, from the nearest weather stations. They developed the following empirical equation, which correlates corrosion rate with average sulfur dioxide concentration and relative humidity: $Y = 0.001028 (RH - 48.8) SO_2$, where Y = zinc corrosion rate (μm/yr), RH = average annual relative humidity, and SO_2 = average SO_2 concentration ($\mu g/m^3$). The regression intercept indicated that no corrosion would occur below an average relative humidity of 48.8 percent. This expression gave a reasonably good linear fit with the experimental corrosion results obtained by Haynie and Upham for SO_2

concentration and relative humidity. Based on the St. Louis study results (Haynie, 1980), the corrosion of small steel specimens of zinc or galvanizing steel follows the relationship:

$$C_z = 2.32\ t_w + 0.134\ v^{0.781} \cdot SO_2 \cdot t_w,$$

t_w = time-of-wetness in years,

v = wind velocity in m/s, and

SO_2 = $\mu g/m^3$ SO_2

A damage coefficient (for purposes of the chapter, damage = any measurable adverse effect) for a pollutant can be calculated from the stoichiometry of a reaction and the deposition velocity. For the reaction between SO_2 and zinc to form zinc sulfate, the coefficient is 0.045, when the zinc corrosion rate is expressed in micrometers per year, SO_2 in micrograms per cubic meter, and the deposition velocity (u) in centimeters per second. For a small zinc or galvanized steel sheet specimen, the damage coefficient for SO_2 is calculated to be $0.0123\ cv^{0.78}$. At a wind velocity of 4 m/sec, the value is 0.0363 ($\mu m/yr$)/($\mu g/m^3$). For the same conditions, a similar calculation for marble yields a coefficient of 0.136 ($\mu m/yr$)/($\mu g/m^3$).

Haynie (1980) restudied the results of six exposure investigations to relate the corrosion of zinc and galvanized steel to the concentration of sulfur dioxide. Each investigation was different and the data were evaluated differently; thus, no direct comparison of the results as they were published was possible. Haynie reevaluated the data from each study, using the same technique in order to make comparisons.

The damage coefficients obtained from all of these studies are compared in Table 10-3. The SO_2 coefficient for the chamber study is low, whereas the analogous coefficients for the CAMP (Haynie and Upham, 1970) and ISP (Cavender

et al., 1971) studies are high and agree with each other. The remaining three SO_2 coefficients are in good agreement. The average of the time-of-wetness coefficients are within a range of ± 0.75 from a mean of 1.73 μm/yr.

The specified thickness of galvanized coating varies with intended use. Furthermore, the thickness of a particular coating varies considerably from one point to another. Bird's measurements revealed that 5 percent of coating thickness measurements varied from the mean by more than 46 percent (Bird, 1977).

TABLE 10-3. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE SITES

Study	Time-of-wetness coefficient, μm/yr	SO_2 coefficient, (μm/yr)/(μg/m^3)	Number of data sets
CAMP (Haynie and Upham, 1970)	1.15 ± 0.60	0.081 ± 0.005	37
ISP (Cavender et al., 1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman, 1968	1.79	0.024	>400
Guttman and Sereda, 1968	2.47 ± 0.86	0.027 ± 0.008	136
Chamber study (Haynie et al., 1976)	1.53 ± 0.39	0.018 ± 0.002	96
St. Louis (Mansfeld, 1980)	2.36 ± 0.13	0.022 ± 0.004	153

Haynie confirmed this variability with 475 thickness measurements on a single galvanized steel sheet. The life of a coating is generally proportional to its thickness; thus, rusting of the substrate steel will occur first at the thinnest spots and last at the thickest spots.

The American Society for Testing and Materials (ASTM) as reported in Haynie (1980) has observed rusting at thin spots on galvanized steel wire, fencing, and sheet exposed to various types of atmospheres over many years. Some of their exposures were started in 1916 and were continued until the test could reveal no additional information. In the case of sheet, the product was completely rusted and showed perforations. In general, the amount of corrosion at each site varied linearly with time. Corrosion rates at each site were calculated on the basis of time to first rust and time to complete rust for various zinc thicknesses, assuming ± 40 percent thickness variability.

Originally, State College, Pa., was selected by ASTM as a control site representing a "clean" rural environment; however, the corrosion is higher there than at five other rural locations including the rural-marine environment of Santa Cruz, Calif., where high relative humidities are expected to accelerate corrosion. It is possible that the State College environment is influenced by pollution from Altoona, which is 40 miles to the southwest (the prevailing upwind direction). ASTM made no pollution measurements but recognized the effects of "industrial" and "severe industrial" environments.

Zinc corroded nearly twice as fast on wire and fencing as it did on sheet, a finding that is consistent with the theoretically predicted effects of surface configuration on SO_2 deposition velocity. One would expect a greater deposition velocity onto fencing than onto sheet material. ASTM noted that fencing corrodes less near the ground than it does near the top because

wind velocity increases with height, with a resultant increase in deposition velocity.

The average corrosion rates shown in Table 10-4 correspond to actual corrosion rates that are two to four times greater when the substrate is wet. Theoretical calculations indicate that the average SO_2 levels at the Pittsburgh site over the long period of exposure were between 350 and 700 $\mu g/m^3$. The average at the Altoona site could have been as high as 1000 $\mu g/m^3$.

From the relationships between theoretical and experimental studies, Haynie (1980) concluded the following:

1. Both short-term laboratory evidence and long-term exposure results for galvanized steel are consistent with theoretical considerations.
2. Damage functions for some materials can be calculated from theoretical relationships that consider factors controlling time of wetness and pollutant fluxes.
3. Wind speed and material geometry should be considered in evaluating atmospheric corrosion effects.

Harker et al. (1980) examined the variables controlling the corrosion of zinc by SO_2 and sulfuric acid. They used an aerosol flow reactor. Under steady-state conditions, they made the following measurements:

Environmental Measurements

- Percent RH and temperature (at two points)
- Average flow velocity (Pitot tube)
- Flow velocity profile (recorded when a steady state had been established),

Aerosol Measurements

- Aerosol size distribution and number concentration determined at intervals during test by TSI 3050 analyzer
- Two total-mass filter samples collected
- Total-deposition sample collected on aluminum foil throughout each experiment
- TEM deposition grid samples collected continuously
- X-ray photoelectron spectroscopy samples (both zinc plate and aluminum foil) collected continuously during experiment

TABLE 10-4. CORROSION RATES OF ZINC ON GALVANIZED STEEL PRODUCTS EXPOSED TO VARIOUS ENVIRONMENTS PRIOR TO 1954

Site	Mean corrosion rate and estimated standard deviation, μm/year	
	Sheet	Wire and fencing
Altoona, PA	7.57 ± 0.54	
Pittsburgh, PA	5.63 ± 0.34	10.86 ± 1.02
Sandy Hook, NJ	2.74 ± 0.30	4.37 ± 0.45
Bridgeport, CT		4.25 ± 0.44
Lafayette, IN		2.94 ± 0.34
Ithaca, NY		2.68 ± 0.42
State College, PA	1.27 ± 0.29	2.48 ± 0.24
Ames, IA		1.68 ± 0.19
College Station, TN		1.22 ± 0.43
Santa Cruz, CA		0.83 ± 0.26
Manhattan, KS		0.79 ± 0.27
Davis, CA		0.76 ± 0.42

Source: Haynie (1980)

Corrosion rate measurements were recorded continuously by an ACM detector, which had been pretreated with either 0.1 N sulfuric acid or ammonium sulfate. Experimental conditions were selected from the following ranges:

Temperature, °C	12-20
Relative humidity, %	65-100
Mean flow velocity, m/sec	0.5-8
Sulfur dioxide concentration, ppb (volume)	46-216
Sulfate aerosol mass concentration, mg/m^3	1.2
Aerosol size distribution, μm diameter	0.1-1.0

The factors controlling the rate of corrosion in Harker's study were relative humidity, pollutant flux, and chemical form of the pollutant. Corrosion occurred only at relative humidities high enough (more than 60 percent) to wet the surface; temperature did not appear to be a controlling factor within the range 12-20°C. The rate of corrosion for SO_2 was about twice that for sulfuric acid at an equivalent flux.

The investigators noted deposition velocities of 0.07 cm/sec for 0.1-1.0 μm sulfate aerosols and 0.93 cm/sec for SO_2 at a velocity of 35 cm/sec. These factors indicate that the effects of SO_2 will dominate the effects of H_2SO_4 in most urban areas.

10.2.2.2 Paint Technology and Mechanisms of Damage--The specific action of SO_2 and particles in paint deterioration has received comparatively little attention from the paint industry. There are at present no ASTM proce dures for evaluating the effect of SO_2, nitrogen dioxide, and/or ozone on paints. Degradation by ultraviolet light has received major emphasis; outdoor test stations have been located in Florida and in Arizona, where SO_2 levels are low.

The erosion of paint is measured by loss of thickness of the paint layer, which can result from the chemical action of SO_2 and the action of light and ozone to cause degradation of the polymer. Film erosion rates are used by paint manufacturers to determine the fail point for their formulations. Film

formers have been developed that are resistant to acids, e.g., epoxies, urethanes, vinyls, and chlorinated rubbers. Protective coatings for metals are applied over primers that contain anticorrosive metallic compounds. Alkyd is often used as the top coat. Oil-base and vinyl-acrylic latex paints contain groups that may be more susceptible to sulfur acids.

In the formulation of paints, the ratio of pigments to film formers is of importance in the overall properties of gloss, hardness, and permeability to water. If the amount of film former is too low, soiling is increased and the paint may lose the film flexibility needed for durability and become brittle.

Condensation of water on the surface to which the paint layer adheres causes a separation (peeling) of the paint film from the surface. The permeability of paints to water has been reported by Hay and Schurr (1971). Pores occur in many kinds of film as a result of shrinkage of the resin on setting, solvent or water evaporation, and leaching out of soluble chemicals in the film. High-permeability films are desirable for surfaces that must allow water to pass through, such as wooden exterior walls behind improperly ventilated kitchens. Low-permeability coatings are needed to protect surfaces that corrode when repeatedly kept moist. The low permeability of chlorinated rubber is advantageous for use on concrete, an application it shares with styrene-acrylic.

Hay and Schurr (1971) found that the use of primer and top coat having the same low pigment volume concentration is effective in preventing rust. When the relative amount of pigment and extender in the primer is increased, its ability to diffuse water also increases. When the top coat retards the diffusion of water out from the primer, the water in the primer is trapped and tends to cause corrosion, mildew, peeling, and blistering.

Paint films permeable to water are susceptible to penetration by sulfur dioxide and sulfate aerosols. The absorption of SO_2 was observed by Holbrow (1962), who found sulfites and sulfates in paint, and by Walsh et al. (1977), who used radioactive SO_2 to determine rates and saturation values for SO_2 absorption. Paint absorbed SO_2 more readily than did wool carpeting or wallpaper.

Exposure to sulfur dioxide under laboratory conditions has been shown to affect certain wet paint films. Holbrow (1962) found that the drying time of linseed, tung, and certain castor oil paint films increased by 50 to 100 percent on exposure to 2620 to 5240 $\mu g/m^3$ (1 to 2 ppm) SO_2. The touch-dry and hard-dry times of alkyl and oleoresinous paints with titanium dioxide pigments were also reported to increase substantially; however, the exposure time of the wet films was not reported. Analysis of the dried films indicated that SO_2 had chemically reacted with the drying oils, altering the oxidation-polymerization process. It was therefore concluded that concentrations of SO_2 encountered in fogs or near industrial sites can increase the drying and hardening times of certain kinds of paints.

No studies have been reported on the effects of SO_2 on the drying of latex paints, which account for more than 50 percent of exterior household use. At the time of application, SO_2 may interfere with the evaporation of water and the coalescence of the polymer-pigment particles. Water in the coating reacts with SO_2 to form sulfurous acid, which could cause instability of the protective colloid around latex particles, resulting in flocculation. Incomplete film formation is thus possible, leading to loss of protective and esthetic value.

Holbrow (1962) also studied the effects of sulfur dioxide on dried paint film. In these experiments, paint films were allowed to dry, refrigerated, and exposed for 15 min to an atmosphere containing 1.2 percent sulfur dioxide.

The paint films with condensed moisture were finally placed in an accelerated-weathering chamber. For all paints except a pentaerythritol alkyd paint, the gloss decreased significantly after 1 day in the accelerated-weathering chamber. Without the accelerated weathering, the actions of sulfur dioxide and moisture on the paint films produced only a slight reduction in gloss. Examination of the films under the light microscope revealed very fine wrinkles. Holbrow concluded that the sulfur dioxide had sensitized the film, permitting water to be absorbed during the weathering cycle.

Bluing of Brunswick green paints has been observed during the early life of the film. Holbrow (1962) reproduced this effect in the laboratory by exposing the film to sulfur dioxide and moisture and then to warmth and moisture. The bluing was probably caused by conversion of the lead chromate pigment of the Brunswick green paints to lead sulfate. Exposure of the film to sulfur dioxide and moisture only was not sufficient to produce the bluing. Holbrow concluded that sulfur dioxide could be retained in paint films for a period of weeks; however, damage (color change) would occur only when the film was exposed to warmth and moisture.

Svoboda et al. (1973) compared pigmented and unpigmented paint film for SO_2 permeability and found that the rate of penetration of SO_2 into a paint film was related to the pigment content. Zinc oxide and titanium dioxide pigments caused a 50 to 70 percent decrease in the rate of penetration of SO_2 into the paint film.

Spence et al. (1975) carried out a chamber study of the effects of gaseous pollutants on four classes of paints formulated for exterior exposure: oil-base house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic

coil coating. The house paints were applied to aluminum panels by spraying. The vinyl- and acrylic-painted panels were cut from coil-painted commercial stock. The oil-base paint film was 58 μm thick; the acrylic latex, 45 μm; the vinyl coil coating, 27 μm; and the acrylic coil coating, 20 μm. The exposure chambers controlled temperature, humidity, SO_2, nitrogen dioxide, and ozone. Each exposure chamber had a xenon arc lamp to provide ultraviolet radiation. A dew/light cycle was included; light exposure time was followed by a dark period wherein coolant circulated through racks holding the specimens, thereby forming dew on the panels. Each dew/light cycle lasted 40 min and consisted of 20 min of darkness with formation of dew, followed by 20 min under the xenon arc. The total exposure time was 1000 hr. Damage was measured after 200-hr, 500-hr, and 1000-hr intervals by loss of weight and by loss of film thickness. In evaluating the data, loss of weight was converted to equivalent loss of film thickness.

Visual examination of the panels coated with oil-base house paint revealed that all exposure conditions caused considerable damage. The erosion rate varied from 4.2 to 48.6 μm/year, with an average of 18.2 μm/year. The investigators concluded that SO_2 and relative humidity markedly affected the rate of erosion of oil-base house paint. The presence of nitrogen dioxide increased the weight of the paint film. A multiple linear regression on SO_2 concentration and relative humidity yielded the following relation:

$$E = 14.3 + 0.0151\ SO_2 + 0.388\ RH,$$

where E = erosion rate in μm/year, SO_2 = concentration of SO_2 in $\mu g/m^3$, and RH = relative humidity in percent. The authors reported the 95 percent tolerance limits on 99 percent of the calculated rates to be ± 44 μm/year.

The formation of blisters on acrylic latex house paint was noted at the high SO_2 levels. The blisters resulted from a rather unexpected severe pitting and buildup of aluminum corrosion products on the substrate. The paint acted as a membrane retaining moisture under the surface and excluding oxygen which would passivate the aluminum. The vinyl coating and the acrylic coating are resistant to SO_2 and are used in protective coatings for metals. The visual appearance of the vinyl coil coating showed no damage. The average erosion rate was low, 3.29 μm/year. The average erosion rate for a clean air exposure was 1.29 μm/year. Acrylic coil coating showed an average erosion rate of 0.57 μm/year.

A study of the effects of air pollutants on paint was conducted by Campbell et al. (1974). The paints studied included oil and acrylic latex house paints, a coil coating finish, automotive refinish and an alkyd industrial maintenance coating. These coatings were exposed to clean air, SO_2 at 262 and 2620 $\mu g/m^3$ and ozone at 196 and 1960 $\mu g/m^3$ (i.e., equivalent to 0.1 and 1.0 ppm of each pollutant). Other controlled study variables included light, temperature, and relative humidity. In addition, one-half of the coatings were shaded during the laboratory exposures.

The laboratory exposure chamber operated on a 2-hour light-dew cycle (i.e., 1 hour of xenon light at 70 percent RH and 66°C followed by 1 hour of darkness at 100 percent RH and 49°C). Coating erosion rates were calculated after exposure periods of 400, 700, and 1000 hours. Estimated erosion rates and statistical characterizations of the data are summarized in Table 10-5.

As shown in the table, erosion rates at O_3 or SO_2 concentrations of 0.1 ppm were not significantly associated with clean air exposures. At 1 ppm pollutant concentrations erosion rates were significantly increased with oil

TABLE 10-5. PAINT EROSION RATES AND T-TEST PROBABILITY DATA

TABLE 10-5a. PAINT EROSION RATES AND T-TEST PROBABILITY DATA FOR CONTROLLED ENVIRONMENTAL LABORATORY EXPOSURES (67)

Type of paint	Mean erosion rate (mil loss X 10^{-5}/hour with 95% confidence limits) for unshaded panels and probability that differences exit		
	Clean air control	SO_2 (1.0 ppm)	O_3 (1.0 ppm)
House paint			
oil	20.1 ± 7.2	141.0 ± 19.0 99%	44.7 ± 10.5 99%
latex	3.5 ± 1.5	11.1 ± 1.0 99%	8.5 ± 5.9 93%
Coil coating	11.9 ± 2.3	34.1 ± 4.7 99 %	14.9 ± 2.5 94 %
Automotive refinish	1.8 ± 0.8	3.1 ± 2.6 75%	5.1 ± 1.3 99%
Industrial maintenance	18.6 ± 5.1	22.4 ± 7.0 66%	28.1 ± 14.0 85%

TABLE 10-5b. PAINT EROSION RATES AND T-TEST PROBABILITY DATA FOR FIELD EXPOSURES (67)

Type of paint	Mean erosion rate (mil loss X 10^{-3}/month with 95% confidence limits for panels facing south and % probability that differences exist			
	Rural (clean air)	Suburban	Urban (SO_2 dominant)	Urban (oxidant dominant)
House paint				
oil	4.3 ± 7.5	14.8 ± 4.9 99.3%	14.2 ± 4.9 98.1%	21.0 ± 6.2 99.2%
latex	1.8 ± 0.5	3.0 ± 0.7 99.2%	3.8 ± 0.3 97.8%	6.5 ± 5.6 94.3%
Coil coating	2.1 ± 0.8	10.0 ± 1.9 99.9%	9.5 ± 0.8 99.9%	8.8 ± 1.7 99.9%
Automotive refinish	0.9 ± 1.1	2.3 ± 0.7 97.6%	1.6 ± 0.4 86.2%	1.7 ± 0.4 91.6%
Industrial maintenance	3.6 ± 1.6	8.2 ± 4.2 97.3%	6.6 ± 3.9 91.2%	7.8 ± 2.4 99.7%

based house paint experiencing the largest erosion rate increases, latex and coil coatings moderate increases, and the industrial maintenance coating and automotive refinish the smallest increases (TRC 1976; Yocom and Upham 1977; and Campbell et al., 1974). Coatings that contained extender pigments, particularly calcium carbonate, show the greatest erosion rates from the SO_2 exposures. Results of field exposures also support these conclusions (Campbell et al., 1974).

From the above discussion, the following observations can be made regarding mechanisms of damage to painted surfaces:

1. The major cause of deterioration of paints is sunlight, with some contribution from ozone.
2. SO_2 and particles accelerate deterioration of paints, particularly at high humidity.
3. Laboratory exposures of paints to light, SO_2, and humidity can identify effects of resistant and nonresistant paint formulations, but the particles and the degree of oxidation of SO_2 to sulfuric acid remain undefined.
4. The effect of SO_2 in the mechanism by which light degrades the polymeric paint film is not known.
5. Exterior house paints based on alkyds and latexes of vinyl acetate-acrylic are esters and therefore subject to acid hydrolysis by SO_2 and its derived sulfates. Pigment extenders, including calcium carbonate, also make these paints susceptible to attack by acids.
6. The ease of application and the need for water permeability are the bases for the continued use of alkyd and latex exterior house paints. These paints are as a class vulnerable to SO_2 and particles.

7. Although laboratory and service tests show a more severe change at higher SO_2 concentrations, the action of SO_2 is primarily catalytic; thus, SO_2 is not consumed by chemical action but remains in the paint layer.

8. The anticorrosive primers and paints recommended for use on steel and zinc withstand long exposures.

10.2.3 Fabrics

Fibers that suffer destructive action upon exposure to acids derived from SO_2 include (1) cellulosic fibers such as cotton and its close relative viscose rayon, a regenerated cellulose, and cellulose acetate; and (2) polyamide fibers such as nylon 6 and 66. Polyester, acrylic, and polypropylene fibers are not damaged directly by SO_2. ~~Sulfate particles, which are mostly ammonium sulfate, damage these fibers by acid hydrolysis~~.

The effect of sulfuric acid on industrial fabrics, particularly those exposed outdoors, is significant. Of the total quantity of fibers produced, it is estimated that 15 to 20 percent are employed by industry in a wide range of applications that has been reviewed by Gay and Terekevis (1970).

Brysson et al. (1967) exposed cotton fabrics at 12 different environmental sites in St. Louis, MO. and Chicago, IL. for a period of up to one year (1963-64). The seven sites in the St. Louis metropolitan area represented industrial, urban, suburban, and rural-suburban environments. Four of the Chicago sites represented downtown, industrial, commercial, and rural environments An additional site 20 miles southwest of Chicago at Argonne National Laboratory was also used.

Air pollution in the St. Louis area was assessed using periodic 24-hour high volume air sampler runs measuring suspended particulate matter and sulfation.

Sulfation values were determined by the lead peroxide candle method. Monthly dustfall measurements were also used. Air pollution was determined at the Chicago sites by two means; a high volume air sampler measured 24-hour total particulate matter 3 days per week and SO_2 was monitored by bubble type absorbers for 24 hours twice a week.

Two fabric types were exposed in this study, scoured cotton, print cloth and army duck. Study results indicate that there is a significant relationship between air pollution and strength degradation and degree of fabric soiling. High pollutant levels (mean sulfation 5 mg SO_3/100 $cm^2$1day and/or SO_2 concentrations of 0.2 ppm or 520 $\mu g/m^3$) can reduce the effective life to one-sixth when compared with low pollution sites (0.5 mg SO_3/100 $cm^2$1day and/or 0.02 ppm or 60 $\mu g/m^3$ SO_2 concentrations). The relationship between suspended particulate matter and fabric strength degradation was not as good as that for SO_2. No correlation between dustfall and strength degradation/effective life was demonstrated by the study (Brysson et al. 1967).

In a review of the Brysson et al. (1967) study, Upham and Salvin (1975) report a correlation coefficient of 0.95 for retention of breaking strength versus sulfation was obtained for cotton duck cloth. The correlation coefficient for the thinner cotton print was 0.96. Of all the pollutants measured, SO_2 was most responsible for causing fabric damage (Upham and Salvin, 1975).

10.2.4 Building Materials

The deterioration of inorganic building materials occurs initially through surface decay. Moisture and salts are the most important factors in building material damage. The mechanism of damage from air pollution involves the formation of salts from reactions in the material. Subsequently, these surface salts dissolve in moist air and are washed away by rainfall. The components

of inorganic building materials can react with sulfur dioxide, sufates, and other particulate matter. The role and levels of these pollutants associated with the deterioration is assessed in the following sections (Winkler, 1975; Arnold et al. 1977).

10.2.4.1 Stone--Certain types of building stone adsorb sulfur dioxide and undergo chemical changes that weaken the material and lead to erosion. Particles soil the stone surface and act as nuclei for absorption of sulfate aerosols, which react chemically and produce efflorescence and spalling.

Calcium carbonate, a constituent of various stones including marble, sandstone, and limestone, reacts to form calcium sulfate and carbon dioxide. Magnesium carbonate reacts with SO_2 to form magnesium sulfate. The end products are the relatively water-soluble calcium sulfate, magnesium sulfate, and calcium bicarbonate.

Sengupta and DeGast (1972) noted that SO_2 adsorption also causes physical changes in stone involving porosity and water retention. Removal of calcium carbonate changes the physical nature of the stone surface. The hard, nonporous layer that forms as a result of alternate freezing and thawing may blister, exfoliate, and separate from the surface. If the stone contains some substances that are unaffected by SO_2, the surface deteriorates unevenly. The conversion of calcium carbonate into calcium sulfate, which crystallizes to a product of much greater volume, results in a type of efflorescence termed crystallization spalling.

Acidic precipitation also contributes to the weathering process of building stone in at least two ways, according to Gauri (1979). For example, marble that is directly exposed to rainfall undergoes nearly continuous erosion as the acid dissolves the calcium carbonate, allowing calcite granules to break

away and wash off. Also, the sulfuric acid in acidic precipitation reacts with the calcium carbonate and forms calcium sulfate, a corrosive salt in itself. If, however, the marble is under a roof and not directly exposed to rain, the calcium sulfate will form a hard crust on the surface, which is often black because of soot in the atmosphere. The formation of a crusty surface affords no real protection to the marble, however. Instead, the crust merely allows sulfate salts and acidic moisture to penetrate even further into the stone and continue the weathering action even longer than they would if they were exposed to the open air. As a result, the crust and surface layer of the stone eventually exfoliate.

10.2.4.2 Cement and Concrete--Cement is an alkaline material that reacts with SO_2 and suffers erosion and spalling effects; it can be protected by paint. Concrete is also subject to damage by sodium sulfate. Sulfate-resistant cement is prepared by reducing the "calcium aluminate" content.

The chemical action of SO_2 or sulfates on cement and concrete is of a dual nature. Calcium hydroxide in cement and concrete can be converted to calcium sulfate, which reacts to form calcium sulfate aluminum hydrate (ettringite), with a substantial increase in volume. Many dams and culverts are in continuous contact with sulfate salts, derived from natural soil components. Cement for dams and culverts requires special formulation for sulfate resistance when exposed to sulfate concentrations > 200 ppm in water (Nriagu, 1978).

Portland cement, the major active constituent of concrete, is manufactured by the high-temperature reaction of a mixture of limestone, alumina, silicates, and iron salts found in clay. Litvin (1968) examined concrete samples containing Portland cement and marble aggregate with sand at an industrial site in Buffington, Indiana. Some changes were noted in the marble aggregate, but a more observable

change was found in the cement portion. Sealants were evaluated as protective coatings; their use was accompanied in some cases by surface efflorescence.

10.2.5 Electrical Equipment and Components

Robbins (1970) and ITT Electro-Physics Labs (1971) studied the damaging effects of SO_2 and particles on electronic components and estimated the cost of this damage. The report by ITT Electro-Physics Labs considered damage to 11 categories of electronic components for which a literature survey indicated that sulfur dioxide pollution would be mainly responsible. However, information gained directly from manufacturers indicated that particles were the major factor in degradation and failure of electronic components and equipment. The following five types of damage from particles were reported:

- Interference with the photoresist process to fabricate integrated circuits.
- Release in a vacuum of gases adsorbed on particles.
- Spot formation on TV screens and cathode ray tubes.
- Creation of microscopic leakage paths in semiconductors and integrated circuits.
- Creation of gross leakage paths in all electronic equipment.

Reduction of SO_2 and particulate concentrations would have little effect on costs for the prevention of corrosion; low concentrations of pollutants would still require essentially the same protective measures. Corrosion-resistant metals are used even in environments where air pollution is minimal, since their cost is far outweighed by the expense of equipment failure. But at current precious metal prices, alternatives may be sought.

10.2.6 Paper

Modern papers are manufactured from wood pulp, which is cellulose. On exposure to acids, paper is hydrolyzed and loses strength.

Spedding et al. (1971), in work with radioactive labeling techniques, determined that SO_2 is readily absorbed by paper and oxidized to sulfuric acid by the metallic impurities in the paper. The reaction may also involve the lignins in the paper, resulting in the formation of lignosulfonic acids. Walsh et al. (1977) showed that SO_2 is rapidly absorbed by uncoated wallpaper and less rapidly absorbed by vinyl-coated paper.

Sulfuric acid can accumulate in paper at concentrations of up to 5 percent by weight, according to Ede (1979). Although most paper is used in objects with a short service life, the preservation of documents has been of concern in museums and archives. Coating paper with polymers impervious to gases is an established process. It is, however, aimed more at preventing wear and soil than at preventing SO_2 damage.

The preservation of books in libraries is of major concern. The extent of the problem is emphasized by the estimate that 50 percent of the books printed between 1900 and 1940 are in need of conservation. The New York Public Library, conserves books by microfilming, lamination, and electrostatic reproduction. The library spent $900,000 between 1952 and 1967 to microfilm books which had deteriorated because of air pollution (Waddell, 1974).

10.2.7 Leather

Leather has a high capacity for absorbing SO_2. Spedding et al. (1971) reported that the rate of SO_2 diffusion to the leather surface is the controlling factor in SO_2 uptake. The formation, in the presence of water, of sulfuric acid is followed by hydrolysis of the protein (collagen) of which leather is principally composed.

The destruction of leather by absorption of SO_2 has long been known and was described in detail by Prenderleith (1946). The buildup of sulfuric acid

in aged leathers correlates with deterioration, which can be reduced by inactivating the sulfate ion and by pH buffering. Deterioration of leather is important in bookbinding and in leather upholstery; the use of artificial leathers has reduced damage costs.

10.2.8 Elastomers and Plastics

10.2.8.1. Elastomers--The deterioration of natural rubber and synthetic elastomers under weathering conditions has been studied extensively. Heat, light, oxygen, certain metallic ions, and particularly ozone cause deterioration, but there is no mention in the literature of SO_2 damage to rubber. In fact, rubber is used as an acid-resistant coating. The problem of determining ambient air pollution effects on rubber is complicated by the presence of ozone, which attacks the double bonds in both natural rubber and the synthetics butadiene-styrene and butadiene-acrylonitrile.

Haynie et al. (1976) conducted a chamber study on rubber to determine the effects of ozone, SO_2, and nitrogen dioxide under controlled conditions of temperature, humidity, and light. Exposures were made at concentrations of 0.1 and 1.0 ppm for each pollutant (in $\mu g/m^3$; 262 and 2620 for SO_2, 196 and 1960 for O_3 and 188 and 1880 for NO_2). As expected, ozone was responsible for accelerated cracking of the rubber. Sulfur dioxide did not have any effect.

10.2.8.2 Plastics--Verdu (1974) presented a theoretical study of the effect of air pollutants on the weathering of plastics. He attributed a direct deteriorating effect on plastics to ozone and suggested that air pollutants such as sulfur dioxide may form active compounds through photochemical reactions leading to oxidation chain reactions. In light-exposure trials, SO_2 increased the rate of polymer degradation of polystyrene.

10.2.9 Works of Art

The deteriorating effects of SO_2 and particles are well known to museum conservators whose function is to preserve and restore works of art. The rate of pollutant-related deterioration has increased markedly in the last 50 years. The damage is striking in Europe, where ancient buildings, paintings, frescoes, bronze sculptures, stained glass windows, and marble statuary have suffered deterioration. Damage occurring in Venice, Florence, Rome, Athens, London, and Cologne has been attributed to the effect of SO_2 from industrial areas in these cities (Yocom and Upham, 1977). The United States is also concerned about the deterioration of public buildings and monuments. The National Bureau of Standards was asked by the National Park Service to investigate methods for preservation of stone after erosion was noted in the facade of the Lincoln Memorial in Washington, DC (Sleater, 1977).

The damage to the Acropolis caused by SO_2 and SO_3 has resulted in a massive interdisciplinary effort by the Greek government to protect the ancient buildings from further deterioration (Yocum, 1979). The dome of the cathedral in Cologne,located in a highly polluted urban area, has suffered serious erosion of its sandstone due to the reaction of sulfur acids with calcium carbonate to form calcium sulfate, which is leached out by rain (Luckat, 1976).

Newton (1974) has investigated the cause of deterioration of medieval stained glass windows. He found that the main cause of decay is the leaching of potassium ions from the silicate glass by condensed water. Another cause is SO_2, which produces opaque white crusts containing $CaSO_4 \cdot H_2O$ and syngenate ($Ca \cdot CaSO_4 \cdot K_2SO_4 \cdot H_2O$). The poor durability of medieval glass is due to its high content of alkaline earths such as lime and magnesia.

Riedeier (1974) conducted a study of the corrosion of bronze sculpture by air pollutants. Sulfates were found in the corroded surfaces.

Sayre (1973) examined several cases of damage to Northern Italian frescoes (paintings on lime plaster). The damage has become most evident in the 20th century. The paintings show high levels of efflorescent material determined to be calcium sulfate. Treatment with barium salts produces stable barium sulfate which contains absorbed SO_2. To protect the cleaned surfaces, waxes were recommended.

Sleater (1977) investigated damage to stone from the action of SO_2, salt, sodium sulfate, and light. Conservation materials including epoxy resins, fluorosilicates, and silicone resins were evaluated. The conservation methods recommended to the National Park Service varied with the exposure conditions.

10.3 PARTICULATE MATTER

A report by the National Academy of Sciences (1977) on airborne particles notes that deposition of dust and soot on building materials not only significantly reduces the esthetic appeal of structures, but also, either alone or in concert with other environmental factors, results in direct chemical attack. It is difficult to determine the specific types of particles and chemical constituents that have damaged or soiled a particular structure.

10.3.1 Corrosion and Erosion

Early studies indicated that suspended particulate matter played a signifi cant role in metal corrosion. Sanyal and Singhania, writing in 1956, termed the influence of suspended particulate matter "profound." They ascribed the corrosive effects of particles to (1) electrolytic, hygroscopic, and/or acidic properties and (2) their ability to sorb corrosive gases, i.e., sulfur dioxide. It has been pointed out that it is quite difficult to predict corrosion rates

separately for sulfur dioxide and particulate matter since they frequently coexist at high levels (Chandler and Kilcullen, 1968). Other field studies have established no conclusive correlation between total suspended particulate matter and corrosion (Mansfeld, 1980; Haynie and Upham, 1974; and Upham, 1967), though further analysis of recent data is still under way.

Barton (1973) reported that dustfalls contribute to the initial stages of corrosion but that their influence becomes less important as a layer of rust forms. There are two classes of particulate matter that appear to be definitely associated with corrosion: hygroscopic salts (including those of natural origin such as sodium chloride, see previous subsection 10.2.1.1.4) and acid smut.

A review of atmospheric factors affecting metal corrosion provided evidence for a relationship between salinity and corrosion (Guttman and Sereda, 1968). Corrosion of metals can be accelerated by deposition of particles due to their hygroscopic nature. The hygroscopic influence on metal corrosion rates has been previously discussed in section 10.2.1.1.4. Particles can also disrupt the protective oxide films formed on metal surfaces such as aluminum and stainless steel resulting in pitting (NAS, 1977).

Acid smut is highly corrosive, sticky material formed in and emitted mainly from furnaces burning liquid fuels containing sulfur, notably in power plants (Ireland et al., 1968). This material would not usually be considered suspended particulate matter, as it occurs as large particles or even large masses which fall out close to the source.

Japanese investigators analyzed a large (>10 drums [sic]) sample of acid smut and found the sulfuric acid content to be 30 percent (Oyama et al., 1974). Damage to painted surfaces, automotive finishes; and even agricultural

crops can be substantive. As noted in a review of residual oil firing problems, "public reaction can be quite severe" (Exley, 1970). A report on the status of "public nuisances" in the electric power industry of Japan reported progress in determining the cause of acid smut and in developing preventive techniques (Overseas Public Nuisance Study Mission, 1965).

Tests of quartz particles on steel indicated that particles >5 μm cause progressively more erosion damage until saturation is reached. Regardless of particle attack angle erosion varied with a simple power of velocity--2.0 for small particles and 2.3 for particles $\gtrsim$ 100 μg (NAS, 1977).

10.3.2 Soiling and Discoloration

Soiling is the accumulation of particulate matter on the surface of a material. It produces a change in reflection from opaque materials and reduces light transmission through transparent materials (Beloin and Haynie, 1975; NAS, 1977).

Soiling due to airborne particles from manmade sources results in increased cleaning costs for building and other materials and reduction in the useful life of fabrics.

10.3.2.1 Building Materials--Under high wind conditions, large particles entrained in the windstream actually result in a slow erosion of surfaces similiar to sandblasting. Particles also fill surface pores of many sandstones causing them to become uniformly darkened. Particles can contribute to chemical decay of marble, limestone and dolomite stone work and concrete structures because they carry acids and soluable salts (NAS, 1977). Dose-response relationships were developed for suspended particulate matter and various building materials by Beloin and Haynie (1975). These relationships were based on exposure studies carried out at sites where suspended particulate levels

ranged from an annual geometric mean of 60 $\mu g/m^3$ to 250 $\mu g/m^3$. The authors suggest that the relationships shown in Table 10-6 can be used in the calculation of soiling costs due to suspended particulate matter (Beloin and Haynie, 1975).

10.3.2.2 Fabrics--Although particulate matter obviously soils fabrics, researchers have noted that it is only damaging when the particles are highly abrasive and the fabrics are frequently flexed. Curtains, hanging in open windows, serving as filters in polluted areas provide a good example. Weakened as a result of such exposure, curtains often split in parallel lines along the folds. The more tightly woven the cloth, the more resistant it is to soiling this physical damage (NAS, 1977).

Because of soiling, fabrics must be washed more often. Washing reduces fabric strength, leading to loss of appearance and concomitantly results in shortened life expectancy. However, other factors, sunlight, water vapor, SO_x, NO_x and ozone concentrations are believed to more significantly effect service life of fabrics. Insolation decoloration is considered to be the most important service life reduction factor (NAS, 1977). Effects of elevated sulfur oxide concentrations has been previously discussed.

10.3.2.3 Household and Industrial Paints--Exterior paints can be soiled by liquids and by solid particles composed of soot, tarry acids, and various other constituents. Water-soluble chlorides and sulfates of iron, copper, calcium, and zinc are commonly found in rainwater and in particulate samples from urban areas. Holbrow (1962) examined the effects of small quantities of these four salts during laboratory studies of the weathering of paint panels. The presence of 0.1 ppm of iron in the test water produced yellow staining, whereas 0.5 ppm of copper produced severe brown staining of the paint panels.

TABLE 10-6. SOILING OF BUILDING MATERIALS AS A FUNCTION OF SUSPENDED PARTICULATE DOSE.

Material	Independent Variable	N	A	B	S_A^2	S_B^2	S_E^2	R^2	Remarks
Oil base paint	$\sqrt{SP(\mu g/m^3) \times t(months)}$	400	89.43	-0.2768	0.0641	0.000069	7.6510	0.745	Excludes all data beyond 12 months
Flat base paint	Ditto	400	86.13	-0.2618	0.0571	0.000061	6.8265	0.738	Ditto
Sheltered acrylic emulsion paint	"	400	91.54	-0.593	0.1156	0.000123	13.8143	0.880	Ditto
Acrylic emulsion paint	"	720	90.79	-0.4131	0.0497	0.000026	8.3791	0.902	
Shingles	$\frac{SP(\mu g/m^3) \times t(years)}{10}$	48	41.69	-0.331	0.1895	0.000312	3.8685	0.884	Excludes two 24 month Tarrant readings
Shingles	$\sqrt{SP(\mu g/m^3) \times t(months)}$	48	43.50	-0.199	0.5771	0.000258	7.6992	0.769	Ditto
Concrete	Ditto	160	41.75	-0.0458	0.1338	0.000080	7.5011	0.143	
Coated limestone	"	80	44.57	+0.0779	0.2464	0.000164	6.9046	0.347	
Uncoated limestone	"	80	46.99	-0.0503	0.1500	0.000089	4.2035	0.266	
Coated red brick	"	80	12.95	-0.0296	0.0223	0.000013	0.6255	0.459	
Uncoated red brick	"	80	14.88	-0.0374	0.0331	0.000020	0.9274	0.477	
Coated yellow brick	"	80	45.05	-0.1133	0.5337	0.000317	14.9533	0.342	
Uncoated yellow brick	"	80	43.21	-0.1133	0.2740	0.000168	7.6773	0.503	
Glass	"	45	0.2806	+0.0314	0.008077	0.000007	0.6851	0.340	Haze readings including 3 periods for right panes prior to 12 months

N, Number of data sets (dependent upon the number of controlled variables in the factorial experiment).

A, Intercept of linear regression.

B, Slope of linear regression.

S_A^2, Estimated variance of intercept.

S_B^2, Estimated variance of slope.

S_E^2, Residual variance (error).

R^2, Correlation index (fraction of variability accounted for by regression).

Source: Beloin and Haynie, 1975.

The conditions to which the paint panels were exposed and the types of paints tested were not given. Holbrow stated, however, that the effects may be expected during actual exterior exposure of paint films.

Finishes on automobiles parked near industrial sites have often been severely damaged. Staining and even pitting of auto finishes have been traced to iron particles from nearby industrial operations (Fochtman and Langer, 1957). Cars parked near brick buildings being demolished have been damaged by alkali mortar dust during humid weather. Repainting of damaged auto finishes was required because of color changes that were not reversible by washing or polishing. The auto finishes damaged in these instances were probably of the lacquer type.

Parker (1955) reported that large numbers of black specks collected on freshly painted buildings in industrial areas. The exterior surfaces of these buildings became distinctly soiled and required cleaning or repainting in 2 or 3 years, depending on the particulate concentration in the air. When particulate matter became embedded in the paint film, the coating was physically and esthetically damaged. Embedding of particles also provides nucleation sites at which other pollutants can concentrate. For example, particles on a painted surface can act as nuclei for absorption of aerosols containing dissolved sulfates. Cowling and Roberts (1954) suggest that particles promote the chemical deterioration of paint by acting as wicks to transfer the SO_2 corrosive solution to the underlying surface.

10.4 ECONOMIC DAMAGE OF AIR POLLUTION TO MATERIALS--SULFUR OXIDES AND PARTICULATE MATTER

Economic estimates of the costs attributable to some of the damaging effects of sulfur oxides and particulate matter on materials are available from the literature. Some of these estimates were derived directly from

consumer or business surveys. Others were derived from estimates of maintenance and replacement costs based upon available damage functions and ambient air data. Extrapolation of these study results for application to the present situation is not easily done, and in some cases cannot be done with accuracy, since both fluctuations in the value of the dollar in the intervening years and changes in air quality must be considered in any such adjustment of past reported dollar cost of materials damage. Therefore, in the present document, all dollar costs assigned to materials damage and soiling are given as reported. Damage functions have been provided where available; ambient air qualtiy trends are discussed in Chapter 5; no attempt has been made to perform integration of the two data sets.

Salmon (1970) cites economic damage from sulfur oxides to the following materials, listed in decreasing order of the extent of damage: metals, cotton, finishes and other coatings, building stone, paints, paper, leather. Paint, zinc, and cement/concrete account for 70 percent ($2.647 billion) of the estimated annual economic loss of all major materials ($3.8 billion). Carbon steel, which has virtually no resistance to SO_2 and sulfate, accounts for $54 million of the total loss. According to this estimate, the annual economic loss of paint and zinc ($1.873 billion) far exceeds the corrosion costs of the metal (carbon steel) that these coatings protect.

10.4.1 Corrosion of Metals

Realistic estimation of the economic damage to metals attributable to sulfur oxides and particles must take into account several factors, including the costs of specific protective treatment. For metals, these costs include those for the use of anticorrosive primers, the practice of sandblasting before painting, and the use of paints that are resistant to acid hydrolysis.

A recent study published by the U. S. Department of Commerce (Bennett et al., 1978) estimated that metallic corrosion cost $70 billion in the United States in 1975. This study used a modified version of the Battelle Columbus Laboratories National Input/Output Model, and the results were subjected to an uncertainty analysis by the National Bureau of Standards. The model, which incorporated a broad range of cost items (e.g., materials, labor, energy, and technical capabilities), indicated a total annual corrosion cost of $82 billion. About 40 percent of this cost, or $33 billion, was considered avoidable. Avoidable costs were defined as those which could be reduced by the most economic application of available corrosion technology. Adjusted for possible errors, such as in the treatment of useful lives of automobiles, a total annual cost of $70 billion was considered reasonable. Uncertainty in the total corrosion cost figure was estimated at ±30 percent. Analysis suggested that avoidable costs of metallic corrosion represent about 15 percent of the total, but could range from 10 to 45 percent.

Roebuck and McCage (1974) estimated that $15 billion in corrosion losses occur annually in the United States, largely from the corrosion of steel. The National Commission on Materials Policy estimated that $5 billion could be saved annually by using known procedures to decrease corrosion of industrial steel, such as sandblasting the surface before painting and applying two coats of paint, which would protect the metal for many years with little maintenance.

Fink et al. (1971) estimated that corrosion caused by air pollution of external metal structures costs $1.45 billion annually, as shown in Table 10-7.

Another method for estimating the economic damage from corrosion is to determine the annual cost of industrial paints used for anticorrosion systems.

TABLE 10-7. SUMMATION OF ANNUAL EXTRA LOSSES DUE TO CORROSION DAMAGE BY AIR POLLUTION TO EXTERNAL METAL STRUCTURES FOR 1970

Steel system or structure	Basis for calculation	Annual loss in $1000
Steel storage tanks	Maintenance	$ 46,310
Highway and rail bridges	Maintenance	30,400
Power transformers	Maintenance	7,450
Street lighting fixtures	Maintenance	11,910
Outdoor metal work	Maintenance	914,015
Pole-line hardware	Replacement	161,000
Chain-link fencing	Maintenance and replacement	165,800
Galvanized wire and rope	Replacement	111,800
Transmission towers	Maintenance	1,480
		$1,450,165

Source: Fink et al. (1971). Haynie (1974) estimated that 90 percent of the cost to prevent corrosion damage cost was attributable to galvanizing expenses.

This cost is estimated by totaling the costs of surface preparation, paint, and labor. Coatings applied at this combined cost would protect metal structures against corrosion for about 10 years, whereas "ordinary" coatings of paint would provide protection for only 2 years.

Painting of structural steel in bridges was investigated by Moore and O'Leary; the practice involves sandblasting the steel to produce a rust-free surface and to remove mill scale. Without such surface preparation, water is immediately absorbed and sets up a corrosion system, rusting occurs, and the paint surface deteriorates in 2 to 3 years. The metal surface is protected by a primer that inhibits rust formation, and the primer coat is covered with two coats of SO_2-resistant paint, such as vinyl resin, which is substantially more expensive than household paint. Banov (1973) estimated the cost of sandblasting at 25¢/ft^2 and the total labor cost at four to five times the cost of the paint. The cost of painting structural steel to give a service time of 10 years or more in urban areas can be as high as \$1 to \$1.25/ft^2. Michelson and Tourin (1967) estimated the extra cost of paint application on external steel structures at \$250 million.

Damage from particles occur during the manufacture of electrical components. To prevent such problems, parts must be fabricated in "clean rooms" with filtered air. If equipment malfunctions in the plant or in service, additional maintenance costs are incurred for cleaning, repair, or replacement of defective equipment. ITT (1971) estimated \$15.5 million per year in added costs for clean rooms and maintenance.

Robbins (1970) conducted a survey of the effects of SO_2 and particles on electrical contacts such as in switches, relays, connectors, and computers. The presence of corrosion films or layers of particulate dust can cause failures

in these low-power circuits, according to Baker (1975). Corrosion failure of electrical contacts is costly because of additional maintenance of equipment and in time lost for equipment shutdowns. To reduce corrosion, contacts are electroplated with corrosion-resistant metals such as gold, platinum, palladium, and silver. Less expensive metals are susceptible to corrosion failure, mostly from the action of SO_2 and H_2S. Robbins estimated that 15 percent of the gold and platinum used in the United States for electrical contacts in 1970 was for the specific purpose of combating SO_2 corrosion, with the remainder going for protection against other environmental pollutants. The use of palladium in electrical components has presented a problem in that it acts on compounds derived from plastics to catalyze the formation of an organic polymer film which acts as an insulator.

In areas where electrical instrumentation and computers are used, air is dehumidified and purified to help protect against corrosion. Robbins (1970) suggested that the use of activated carbon filters and high-efficiency fine particle filters represents a cost attributable to SO_2 and particulate contaminants, as itemized in Table 10-8.

TABLE 10.8. COSTS ATTRIBUTABLE TO SO_2 AND PARTICULATE CONTAMINANTS IN THE ELECTRONIC COMPONENTS INDUSTRY

	Millions of dollars
	1970
Use of precious metals	20
Protective measures--filters and air conditioning	25
Loss due to failures	10
Research	5
Total	60

10.4.2 Exterior Household Paints

Spence and Haynie (1972) presented a survey and economic assessment of the deterioration of exterior paints ("trade paints") caused by air pollution. Included in this category were both oil-base paints and latex paints containing polyvinyl acetate-acrylic as the binder. The total annual economic damage to exterior household paints was estimated at $540 million (1972 prices), including paint loss and a labor factor of three times the cost of the paint.

Salmon (1970) estimated that the annual cost of soiling of household paint would be $35 billion if surfaces were maintained as clean as they are in a clean environment. The annual cost of deterioration damage to paints was estimated to be $1.2 billion. A 1974 study by Midwest Research Institute recalculated the annual cost of damage to be $22 billion for soiling and $753 million for deterioration. These figures appear to be based on Salmon's hypothetical situation evaluation, which has been criticized as unrealistic. With a total cost of $2.5 billion for annual production of household paints, the damage far exceeds the production cost, even with a labor factor of 6 to 8.

Michelson and Tourin (1967) investigated the frequency of house repainting as a function of suspended particulate concentration. Questionnaires were sent to residents of three suburbs of Washington, DC (Suitland, Rockville, and Fairfax) and two cities in the upper Ohio Valley (Steubenville and Uniontown). Data were compiled from the questionnaires to show maintenance intervals for exterior repainting in each of the five communities, but paint types were not reported. In Steubenville, where the mean annual particulate concentration was 235 $\mu g/m^3$, repainting occurred about every year. In Fairfax, where the mean annual particulate concentration was 60 $\mu g/m^3$, repainting occurred every 4 years. Thus, maintenance frequency increased as particulate concentration

increased, as shown in Figure 10-7 (Michelson and Tourin, 1967). A plateau at the low and high extremes of particulate concentration should be expected. The results of this investigation suggest that a significant relationship exists between frequency of repainting and particulate concentration. However, it would appear that additional maintenance data are needed, particularly for cities with mean annual particulate concentrations greater than 150 $\mu g/m^3$, to establish a more definite correlation. Any correlation of frequency of repainting with concentration of particulate matter must take into account the fact that SO_2 is usually present in high concentration where particle counts are high.

Booz Allen and Hamilton (1970), in a study conducted for EPA, reported on painting maintenance frequencies in several zones of the Philadelphia metropolitan area (see Table 10-11) with different population characteristics, climates, and types of industry. Socioeconomic factors were delineated by pollution zone; however, paint types were not reported. The percentage of households with incomes of less than $6000 increased with pollution level, a finding that partially explains why there was no statistically significant correlation between painting frequency and particulate level.

10.4.3 Fibers

Cotton and nylon are subject to damage by acids derived from SO_2. This damage is of major importance to the military and to other users of industrial fabrics. High pollutant levels (mean sulfation 5 mg SO_3/100 cm^2/day and/or SO_2 concentrations of 0.2 ppm or 520 $\mu g/m^3$) can reduce the effective life to one-sixth when compared to low pollution sites (0.5 mg SO_3/100 cm^2/day and/or 0.02 ppm or 60 $\mu g/m^3$ SO_2 concentrations) (Brysson et al. 1967).

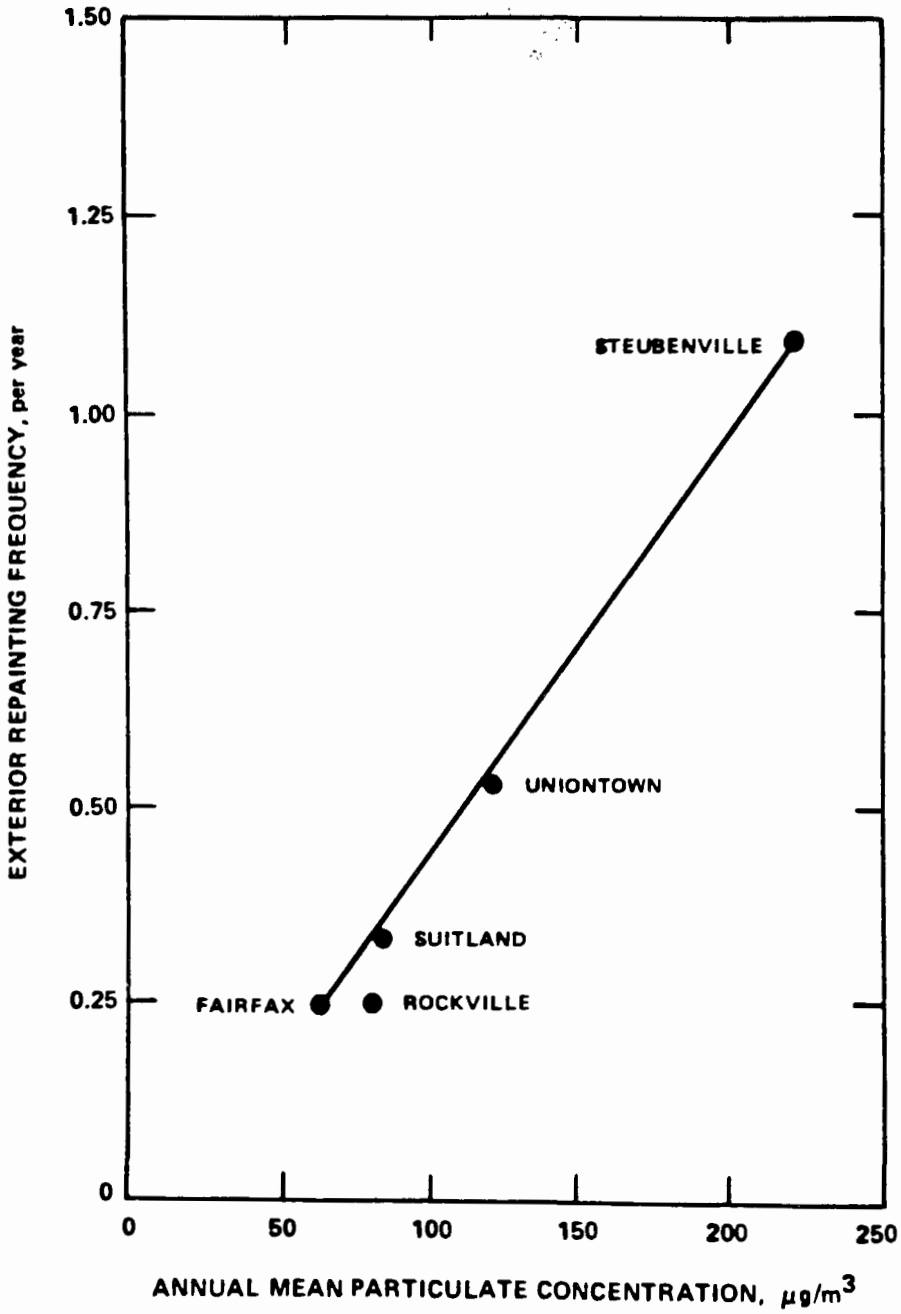

Figure 10-7. There is a clear relationship between maintenance frequency for exterior repainting and particulate concentration.

Source: Michelson and Tourin (1967).

The magnitude of the cost of SO_2 damage to fibers can be developed by comparing the total quantity of fibers used in industry to the amount with outdoor exposure where SO_2 damage to cotton has been demonstrated. Of the 1.257 trillion pounds of fiber used for industrial purposes in 1965, the Textile Organization reported that 583 million pounds were cotton and that 300 million pounds had the outdoor uses shown in Table 10-9.

TABLE 10-9. AMOUNTS OF COTTON FIBER USED FOR VARIOUS OUTDOOR PURPOSES

Use	Amount, 10^6 lb
Automotive upholstery and seat covers	56
Fire hose	20
Cordage	56
Tarpaulins, tents, awnings, etc.	70
Bags and bagging	63
Miscellaneous (agricultural cloth, flags)	35
Total	300

In a report of a telephone survey of consumer awareness of damage to textiles due to air pollution, Upham and Salvin (1975) noted that Philadelphia respondents did not perceive soiling of fabrics as a damage effect. There was a reluctance to communicate this type of information, which is somewhat personal.

10.4.4 Masonry, Cement, and Building Stone

Damage by SO_2 to masonry, concrete, and building stone containing calcium compounds has been well established. In concrete, sulfur dioxide reacts with alkaline conglomerates, resulting in spalling and efflorescence. Protection against SO_2 and acidic rain requires treatment of the porous structure with

special sealers and paints in order to preserve the appearance and prevent crumbling of the stone. No monetary cost has been assigned to the erosion of building stone.

10.4.5 Soiling

Studies on soiling have been limited to household cleaning costs. In a study by Booz Allen and Hamilton (1970), $5 billion for annual household cleaning costs was attributed to particulate pollution. This amount did not include laundering, dry cleaning, and personal care items (i.e., face and hair).

Watson and Jaksch (1978) estimated physical soiling and frequency-of-cleaning functions for each of the five indoor and three outdoor cleaning and maintenance tasks shown in Table 10-10, using the study of Beloin and Haynie (1975) to establish the relationship between level of particulate matter and soiling rate and the work of Esmen (1973) to estimate various levels of particulate soiling for rural, suburban, and industrial locations. They determined frequency-of-cleaning functions from the Booz Allen and Hamilton study (1970), which surveyed 1090 households in the Philadelphia SMSA during 1969. Table 10-11 gives average pollution and total cleaning and painting expenditures for this area, and Table 10-12 shows the consumers' gain in Philadelphia from reducing airborne particle pollution.

From a range of 27 cleaning and maintenance operations, Watson and Jaksch (1978) designated 11 as sensitive to airborne particle levels. Table 10-13 indicates which operations were emphasized as requiring special attention; each of these is a low-cost, done-at-home cleaning procedure. Watson and Jaksch concluded that the frequency of the low-cost cleaning operations depended on the level of airborne particles but that the frequency of professional house painting was unaffected by variation in airborne particle levels.

A survey of commercial buildings occupied by stores was not useful, since stores are cleaned on a contract basis and the work is done regardless of the amount of soil that has collected.

The Booz Allen and Hamilton (1970) report has been criticized on the basis that its analysis of the data did not include other sources of damage

TABLE 10-10. CLEANING AND MAINTENANCE TASKS[a]

Indoor	Outdoor
Painting walls and ceilings	Painting walls
Wallpapering	Painting trim
Washing walls	Washing windows
Washing windows	
Cleaning venetian blinds	

Watson and Jaksch (1978)

TABLE 10-11a. POLLUTION AND CLEANING AND PAINTING EXPENDITURES FOR PHILADELPHIA PERCENT OF HOUSEHOLDS IN ZONE PERFORMING TASKS[a]

Pollution zone	Average particulate level, $\mu g/m^3$	Percent of households in zone j out of all households[a]	Indoor tasks				
			Painting walls and ceilings	Wall-papering	Washing windows	Washing walls	Cleaning venetian blinds
1	61	47.3	76.6	36.9	97.2	42.7	34.0
2	87	23.0	72.0	45.4	97.9	41.3	48.2
3	112	19.1	67.9	43.1	97.0	45.8	62.5
4	133	10.6	59.0	52.6	98.0	37.1	59.4

			Outdoor Tasks		
			Painting walls	Painting trim	Washing windows
1	61	47.3	38.6	66.5	89.5
2	87	23.0	28.5	68.9	89.5
3	112	10.1	11.4	54.5	86.3
4	133	10.6	10.4	55.0	89.3

[a]Source: Watson and Jaksch (1978)

TABLE 10-11b. POLLUTION LEVELS AND CLEANING AND PAINTING EXPENDITURES FOR PHILADELPHIA ANNUAL EXPENDITURE OR E_{ij}, MILLIONS OF 1970 DOLLARS[a]

Pollution zone	Average particulate level $\mu g/m^3$	Indoor tasks: Painting walls and ceilings	Wall-papering	Washing walls	Washing windows	Cleaning venetian blinds
1	61	28.2	23.4	9	8.6	3.2
2	87	12.9	14.0	4.4	4.0	2.2
3	112	10.1	11.1	3.6	3.7	2.4
4	133	4.8	7.5	2	1.7	1.2
Total expenditure or TE_i[b]		56	56	19	18	9

		Outdoor tasks: Painting walls	Painting trim	Washing windows
1	61	20.2	24.8	8.6
2	87	7.2	12.4	4.2
3	112	2.4	8.2	3.3
4	133	1.2	4.6	1.9
Total expenditure or TE_i[b]		31	50	18

[a]Annual expenditure or E_{ij} is defined $PH_j \cdot PHT_{ij}/\Sigma PH_j \cdot PHT_{ij} \cdot TE_i$, where PH_j is percent of households in zone j out of all households, PHT_{ij} is percent of households in zone j performing task i, and TE_i is total expenditure for task i.
[b]Source is Booz Allen and Hamilton (1970) for five of the tasks. Costs for the remaining three were derived as follows: wallpapering costs are assumed to equal inside painting costs, venetian blind cleaning costs are assumed to equal one-half of window cleaning costs, and costs of cleaning windows are assumed to equal costs of cleaning windows inside.
Source: Watson and Jaksch (1978)

TABLE 10-12. REPORTED GAIN TO CONSUMERS FROM REDUCING PARTICULATE MATTER (1970 dollars)

Area	Total gain, $ million[a]		Gain per household, $	
	Primary standard	Secondary standard	Primary standard	Secondary standard
Philadelphia				
$a_i = 0.35$	14.4	27.5	10	19
$a_i = 1.0$	42.5	82.6	29	26
$a_i = 2.0$	93.2	195.2	63	132
123 SMSA's including Philadelphia[b]				
$a_i = 0.35$	537	919	14	24
$a_i = 1.0$	1613	2830	43	75
$a_i = 2.0$	3816	7268	101	192

[a]For the primary standard, gain is from reducing particulate matter from measured levels in 1970 down to 75 $\mu g/m^3$. Similarly, for the secondary standard, gain is from reducing particulate matter from measured levels in 1970 down to 60 $\mu g/m^3$. The gain in going from the primary to the secondary standard is the difference between the primary and secondary gains.

[b]Estimates for other SMSA's are made by assuming: (1) total expenditure for each task in any other SMSA equals expenditure per household for each task in the Philadelphia region times the number of households in any other SMSA (the numbers of households by SMSA are taken from County and City Book; (2) the fractional distribution of total expenditure across pollution zone (i.e., E_{ij}/TE_i) is the same as that indicated for Philadelphia; and (3) the distribution of particulate matter in any other SMSA relative to its mean particulate level is the same as in the Philadelphia region: $AP_{jk} = (AP_{jPhila}/mean_{Phila})\ mean_k$, where AP_{jk} is the average particulate reading in the jth zone and kth SMSA, and $mean_k$ is the annual geometric mean for suspended particulates in the kth SMSA.

Source: Watson and Jaksch (1978).

TABLE 10-13. RELATIONSHIP OF CLEANING AND MAINTENANCE TO AIR PARTICULATE LEVELS

Maintenance operation	Relationship	
	Sensitive	Insensitive
Inside		
Clean and oil air conditioners		x
Clean furnace		x
Clean venetian blinds and shades	x	
Dry clean carpeting		x
Dry clean draperies		x
Paint walls and ceilings		x
Replace air conditioner filter	x	
Replace furnace filter		x
Shampoo carpeting		x
Shampoo furniture		x
Wallpaper walls		x
Wash floor surfaces	x	
Wash walls		x
Wash windows (inside)	x	
Wax floor surfaces	x	
Outside		
Clean and repair awnings		x
Clean and repair screens	x	
Clean and repair storm windows	x	
Clean gutters	x	
Clean outdoor furniture	x	
Maintain driveways and walks		x
Maintain shrubs, flowers, etc.		x
Paint outside trim		x
Paint outside walls		x
Wash automobiles		x
Wash windows	x	
Wax automobiles		x

Source: Watson and Jaksch (1978).

that might be responsible for extra maintenance such as painting. There is doubt as to which operations in Table 10-13 are really sensitive to air particulate levels. Also, the labor of the homemaker was not added to the cost of the cleaning materials, and the number of urban homes surveyed was small.

Much effort has been expended on attempts to quantify the cost of soiling attributable to SO_2 and particulates. The Beaver Report (1954) suggested an annual total for damage by all forms of air pollution in Great Britain of 152 million pounds sterling in direct costs, of which 25 million was for laundry, 30 million for more frequent painting and decorating, and 20 million for cleaning and depreciation of buildings other than houses; thus, about half the total cost of pollution was attributed to soiling.

Michelson and Tourin (1967) compared the costs of air pollution in the highly polluted area of Steubenville, Ohio, with those in the relatively clean Uniontown, PA, area. The per capita costs for inside and outside maintenance of houses (painting and cleaning), laundry, dry cleaning, and personal care (hair and facial) were $84 higher in Steubenville than in Uniontown. Cost figures were based on data obtained from questionnaires, but the results have been questioned on the grounds that socioeconomic factors influenced responses and that there were insufficient statistically reliable data.

Narayan and Lancaster (1973) conducted a questionnaire survey in a rural area and a polluted area in New South Wales, Australia, to determine the difference in cost of household upkeep. The cost of maintaining a house in the polluted Mayfield area was about $90 per year higher than in the relatively unpolluted Rotar area. This cost differential was attributed to the higher levels of air pollution and airborne particulate matter in Mayfield; however, the accuracy of the cost data was considered questionable, since the attitude of the respondents could have introduced a biased point of view.

Waddell (1974) in his review of the economic damage of air pollution noted that the Michelson and Tourin (1967) and Booz Allen and Hamilton (1970) studies considered principally the costs of household cleaning and maintenance. He questioned the validity of extrapolating the Michelson and Tourin value of $84 per capita because of insufficient information and socioeconomic problems in obtaining defensible data. He further pointed out that the Booz Allen and Hamilton report contradicts the intuitively recognized fact that there are significant soiling costs associated with airborne particles. In particular, he stated that soiling costs should include laundering, dry cleaning, hair and facial care, washing of automobiles, and costs of cleaning commercial establishments and public structures. Waddell (1974) concluded that there are insufficient data to assess these soiling costs though they "undoubtedly run into the millions of dollars annually".

Waddell (1974) also reviewed the concept of property value as an estimator, noting the assumption that the inconvenience of living in a polluted area with soiling and odors leads to lower property values. He cited Jacksch and Stoevener's (1970) study in Toledo, Oregon, using dustfall measurements as the variable. Their hypothesis was that air pollution costs, though recognized, were not quantitatively known, but that this cost was reflected in the value of property. They found that reduction in property values from increasing air pollution was greater in the higher priced, newer sections of town than in low-cost housing. Table 10-14 summarizes the various property value studies that include the effects of both SO_2 and particles on the market value.

The economic effects of soiling were examined by Liu and Yu (1976) in a Midwest Research Institute project undertaken for the EPA's Corvallis Environmental Research Laboratory. The objectives were to generate physical and

TABLE 10-14. SUMMARY OF PROPERTY VALUE STUDIES

Study	City	Pollution measure	Pollution coefficient	R_2	Marginal capitalized damage
Ridker-Henning	St. Louis	Sulfation[a]			100[b]
Zerbe	Toronto	Sulfation[a]	-0.12	0.94	97[b]
	Hamilton	Sulfation[a]	-0.08	0.92	
Anderson-Crocker	St. Louis	Sulfation Suspended particles	-0.10 -0.12*	0.76	
	Kansas City	Sulfation Suspended particles	-0.08 -0.09*	0.82	300-700[c]
	Washington, DC	Sulfation Suspended particles	-0.07 -0.06**	0.70	
Crocker	Chicago	Sulfur dioxide Suspended particles	0.06** -0.40	0.77	470[d]
Peckham	Philadelphia	Sulfation Suspended particles	-0.10 -0.12	0.76	600-750[c]
Spore	Pittsburgh	Sulfation Dustfall	-0.03* -0.12	0.81	150-200[e]

[a]Single pollution variable probably measures effect of both sulfation and suspended particles.
[b]Mean change in MPV per change of 0.1 mg SO_3/100 cm^2/day.
[c]Mean change in MPV per change of 0.1 mg SO_3/100 cm^2/day plus 10 μg/m^3/day change in suspended particles.
[d]Mean change in MPV per change of 0.001 ppm/72 hr of SO_2 plus 10 μg/m^3/day change in suspended particles.
[e]Mean change in MPV per change of 0.005 ppm/day of SO_2 plus a 5 tons/mi^2/month change in dustfall.
*Not significantly different from zero at the 0.01 level.
**Not significantly different from zero at the 0.05 level.
Source: Waddell (1974)

economic damage functions, by receptor, for SO_2 and suspended particles and to establish some cost/benefit relationships. The study included the effects of air pollution damage on health, household soiling, materials, and vegetation.

Liu and Yu used the data of Booz Allen and Hamilton (1970) on soiling and maintenance operations (Table 10-10) to identify and quantify soiling damage. They surveyed costs for each of nine professional cleaning companies in Kansas City, and developed a methodology that could be used on a nationwide basis for estimating damage attributable to soiling by SO_2 and particles. They calculated the gross cost of cleaning and the net (extra) cost from increases in suspended particles using a formula they derived. For these calculations, a suspended particulate level of 45 $\mu g/m^3$ was chosen as the level necessitating extra cleaning.

Liu and Yu (1976) derived net and gross household cleaning costs for 65 large cities with populations greater than 500,000 and for 83 medium-size cities of 200,000 to 500,000. For the nine cleaning operations, the extra costs for Chicago, New York, and Los Angeles in 1970 were $516 million, $418 million, and $388 million, respectively. The costs for cleaning venetian blinds at a unit market value of $3.50 and washing outside windows at $1.50 gave total extra costs of $1.956 billion and $926 million, respectively, for 40 metropolitan areas. Per capita costs for household maintenance activities ranged from $5 per person in San Antonio, Texas, to $104 per person in Cleveland, Ohio. These per capita costs were estimated to be in the range of $200 by Michelson and Tourin (1967), who added other soilage categories such as laundering and personal care into their figures. The total net soilage cost for the urban areas was $5.033 billion, and the gross soilage damage was $17.367 billion.

The magnitude of economic damage attributed to soiling appears large. Some European countries assess damage costs due to pollution as a percentage of their gross national product. The following equations have been used in their studies:

$$NSCO_i = b_i\ (TSP-45) \cdot UC \cdot U \cdot HU, \text{ and}$$

$$GSCO_i = a_i + b_i(TSP-45) \cdot UC \cdot U \cdot HU,$$

where $NSCO_i$ is the net (extra) soiling cost, $GSCO_i$ is the gross soiling cost, a_i and b_i are related to the estimated coefficients for each cleaning task, UC is the unit market value, U is the number of objects cleaned per house, HU is the number of people per household, and TSP is the concentration of total suspended particles. Liu and Yu (1976).

10.4.6 Damage Functions

A reasonable estimate of the economic damage to materials from sulfur oxides and particulate matter depends on the validity of the physical damage functions, the distribution of pollutant levels and receptors, and the dollar value associated with the damaged material.

Gillette (1975) reported significant reductions in economic damage to materials from sulfur oxides attributable to improvements in existing air quality levels throughout the United States. Comparing annual SO_2 concentrations from more than 200 monitoring sites with the estimated inventory of materials exposed in the proximity of these sites, he decreased his nationwide estimate of material damage from more than $900 million in 1968 to less than $100 million in 1972. These estimates, which are probably conservative, were derived by carefully distinguishing between physical and economic losses and by attributing current estimates of losses to current exposure levels.

The distinction between physical and economic damage to materials was based upon the concept of normal or economic use life of materials. Whereas physical deterioration to materials may occur at relatively low exposure levels, economic losses will occur only if the material requires early replacement or increased maintenance before its normal or economic use life is spent. Given the prevailing ambient concentrations observed, most materials were not adversely affected economically except for metallic products which were subjected to corrosion or paint damage. While material losses were much greater during the early 1960's the losses in more recent years are substantially less and reflect the considerable progress that has occurred in improving air quality. (Gillette, 1975).

Beloin and Haynie (1975) proposed dose-response relationships between concentration of airborne particulate matter and soiling of building material. They noted that soiling is a continuous function of time and particulate concentration; that is, particulate matter at any concentration will eventually cause soiling.

Damage functions have been derived that indicate that reductions in SO_2 and in particulate matter will decrease economic damage. In developing these functions, a particulate matter concentration of 45 $\mu g/m^3$ was selected as the concentration below which soiling costs would not be perceived as extra costs from increased cleaning activities. For corrosion of metals, deterioration of paint films, weakening of cotton fibers, and changes in masonry surfaces, the catalytic action of sulfates makes it difficult to correlate SO_2 concentrations with pollution damage; however, field trials under monitored conditions and laboratory studies have shown that damage is less where SO_2 concentrations are lower.

The economic damage from SO_2 and particulate matter has been recognized by industry. The market response is empirical proof that pollution damage must be counteracted by protective measures, such as controls or use of alternative materials. In most cases, the cost of replacing a product that has suffered premature damage is far greater than the cost of protective measures or of alternative materials not damaged by SO_2 and particulate matter.

Physical damage functions that have been reported for various metals and paints are summarized in Table 10-15. Economic damage functions are presented in Table 10-16.

10.5 SUMMARY

A principal deleterious effect of sulfur oxide pollution is the corrosion of metals. SO_2-accelerated rusting is an electrochemical process that results in the formation of metal sulfates. Soluble sulfates in rust can stimulate further corrosion because of their hygroscopicity and electrical conductivity; however, insoluble sulfates in the rust layer provide corrosion protective properties, particularly for steel.

Moisture is a key factor in the corrosion process. Corrosion rates of metals increase rapidly with relative humidity. On the other hand, steel surfaces shielded from rain may corrode at a higher rate than those exposed to rain, which washes soluble sulfate from rust. The influence of temperature on SO_2-assisted corrosion of metals is complex and has not been clearly defined.

Alloying steel with small amounts of copper, chromium, and phosphorus improves corrosion resistance. The high corrosion resistance of stainless steels incorporating chromium, molybdenum, and nickel is attributed to the protective properties of the oxide film formed on these alloys. In heavily

TABLE 10-15. PHYSICAL DAMAGE FUNCTIONS FOR MATERIALS

Material	Dose-Response relationships	R^2
Metals		
Steel		
Carbon steel	$Y = 9.013 \left[e^{0.00161\ SO_2}\right]\left[(4.768t)^{0.7512 - 0.00582\ OX}\right]$	0.91
Copper-bearing steel	$Y = 8.341 \left[e^{0.00171\ SO_2}\right]\left[(4.351t)^{0.8151 - 0.00642\ OX}\right]$	0.91
Weathering steel A	$Y = 8.876 \left[e^{0.0045\ SO_2}\right]\left[(3.389t)^{0.6695 - 0.00544\ OX}\right]$	0.91
Weathering steel B	$corr = 5.64\ SO_2 + e^{(55.44 - 31{,}150/RT)}\ t_w$	0.91
Enameling steel A	$corr = 183.5\ \sqrt{t}\left[e^{(0.06421\ sul - 163.21/RH)}\right]$	
Enameling steel B	$corr = 325\ \sqrt{t}\left[e^{(0.00275\ SO_2 - 163.2/RH)}\right]$	
Galvanized steel	$corr = 0.0187\ SO_2 + e^{(41.85 - 23{,}240/RT)}\ t_w$	0.91
Zinc	$Y^* = 0.001028\ (RH - 48.8)\ SO_2$	0.92
Paints		
Oil-base house paint	Erosion rate = $14.323 + 0.01506\ SO_2 + 0.3884\ RH$	0.61

corr = corrosion, μm Y = corrosion, μm Y* = corrosion rate, μm/yr SO_2 in μg/m^3 OX = μg/m^3 Sul = μg/m^3 sulfate
R gas constant (1.98 cal/gm mol/°K) RH in % T = OK t = time of exposure t_w = years

TABLE 10-16. ECONOMIC DAMAGE FUNCTIONS ON MATERIALS[a]

$$SDCZ = -23{,}328.4 + 43.1\ ME + 943.3\ SO_2 + 148.1\ TSP - 235.0\ SUN$$
$$(19{,}929)\quad (3.4)^*\quad (171.6)^*\quad (356.0)^*\quad (1{,}820.4)$$

$$+ 2{,}679.3\ RHM + 21.9\ YP \qquad R^2 = 0.64$$
$$(1{,}750.2)\quad (18.9)$$

$$DDCZ = 7{,}562.2 + 1.4\ ME + 30.5\ SO_2 + 47.9\ TSP - 76.2\ SUN$$
$$(6{,}460.4)\quad (0.1)^*\quad (5.5)^*\quad (11.5)^*\quad (59.0)$$

$$+ 86.8\ RHM + 712.6\ YP \qquad R^2 = 0.63$$
$$(56.7)\quad (615.5)$$

$$SDCP = -141{,}199.7 + 577.2\ HU + 15.2\ YP + 911.3\ RHM + 69.1\ SO_2$$
$$(259{,}861.3)\quad (3.4)^*\quad (2.6)^*\quad (235.3)^*\quad (23.2)^*$$

$$+ 305.3\ SUN \qquad R^2 = 0.995$$
$$(245.9)$$

$$DDCP = -4{,}820.1 + 19.7\ HU + 0.5\ YP + 31.1\ RHM + 2.3\ SO_2 + 10.4\ SUN$$
$$(887.2)^*\quad (0.1)^*\quad (0.08)^*\quad (8.0)^*\quad (0.8)^*\quad (8.4)$$

$$R^2 = 0.995$$

[a]The values below the coefficients are standard errors, with * to indicate that the coefficients are significant at the 1 percent level. All coefficients and standard errors are reduced by a factor of 10^3.

SDCZ = soiling damage, cost of zinc
DDCZ = deteriorating damage, cost of zinc
SDCP = soiling damage, cost of paint
DDCP = deteriorating damage, cost of paint
ME = no. of manufacturing establishments in metropolitan area
SO_2 = sulfur dioxide, in $\mu g/m^3$
TSP = total suspended particulate in mg/m^3
SUN = possible annual sunshine days
RHM = relative humidity
YP = per capita income
HU = number of households in metropolitan area

polluted atmospheres, sulfate particles in settled dust can rupture this surface film, causing pitting.

Many laboratory and field studies have investigated the corrosive effects of sulfur dioxide and sulfates on ferrous metals. Haynie's chamber studies confirmed that corrosion is most severe under conditions of high SO_2 concentration and high humidity. Sydberger's laboratory experiments showed that corrosion rates are related to the supply of SO_2 per unit surface area and that a rise in humidity above 50 percent increases corrosion rates markedly. Even at high humidity and high sulfate content, the corrosion rate decreased to a low level when the SO_2 concentration was low. Sydberger and Vannenberg established that at relative humidities ranging from 50 to 98 percent, the principal corrosion product of iron, zinc, copper, and aluminum exposed to SO_2 was hydrated metal sulfate. Some adsorption of SO_2 took place below the critical humidities (60-80 percent) for all the metals investigated. In general, copper and aluminum showed better corrosion resistance in the laboratory than did iron and zinc.

Sydberger reported good correlation between corrosion rates and the amount of sulfur compounds on steel, zinc, and nickel during field exposures. The correlation between ambient SO_2 and the amount of SO_2 deposited on metal surfaces was dependent on both wind direction and velocity. Studies have shown that eddy diffusion is another factor in SO_2 deposition. Haynie and Upham found that the relationship between SO_2 concentrations and corrosion rates of steel is complicated by climatic variables and special conditions at particular sites. Temperature appeared to have little effect. Mansfeld's

exposure studies with copper-zinc and copper-steel galvanic couples confirmed the high variability of metallic corrosion rates from site to site and established time of wetness as a critical parameter of corrosion.

Haynie and Upham derived a physical damage function relating depth of steel corrosion to particulate sulfate level as a proxy for SO_2 and average relative humidity as a proxy for time of wetness. Oma et al., Chandler and Kilcullen, and Guttman and Sereda have also developed empirical expressions to predict long-term corrosion rates of various steels exposed to the atmosphere. These equations may be used to relate reduction in SO_2 and sulfate levels to reduction in corrosion of metals, serving as the basis for a cost-benefit appraisal. Matsushima et al. demonstrated that the corrosion of weathering steel is related not only to the severity of pollution but also to the interplay of shelter and the washing action of rain.

Nickel and copper are more corrosion resistant than unalloyed steel. Sydberger attributed this resistance to the ability of these nonferrous metals to form layers of insoluble basic sulfates that protect their surfaces. Steel is galvanized (coated with zinc) for corrosion resistance in applications such as gutters, cables, wire fencing, and building accessories. The key factors that determine the extent to which zinc is corroded by SO_2 are time of wetness and SO_2 concentration. Fleetwood estimated the expected service life of galvanized steel at 15-20 years in a polluted industrial area and 300 years in a dry, tropical, unpolluted area.

ASTM reported that zinc corroded nearly twice as fast on wire and fencing than on sheets. Corrosion of the fencing was least severe near the ground. Haynie (1980), in discussing these results, noted that these findings are consistent with the predicted effects of surface configuration on SO_2

deposition. Harker et al. examined the variables controlling the corrosion of zinc by sulfuric acid and SO_2. They determined that relative humidity, pollutant flux, and chemical form of the pollutant were most important. In these studies, corrosion occurred only at relative humidities high enough (>60%) to wet the surface. They concluded that SO_2 corrosion dominates over H_2SO_4 aerosol corrosion in most urban areas.

Aluminum is generally considered resistant to corrosion because it forms a protective oxide film that is not dissolved at low concentrations of acid sulfates or other aerosol particles. Copper corrodes slowly upon exposure to SO_2, forming basic sulfates and sulfides in industrial areas, as well as chlorides in seacoast locations. The resulting patina protects against further corrosive action.

Many nonmetallic materials are also damaged by sulfur oxides and/or soiled by particles. These materials include paints and other protective coatings, fabrics, building materials, electrical components, paper, leather, plastics, and works of art. The chemical action of SO_2 erodes paint layers, and light and ozone cause degradation of the polymer. Oil-base and vinyl acrylic latex paints contain chemical groups that may be especially susceptible to sulfuric acid. Paint films permeable to water may be penetrated by sulfur dioxide and aerosols containing sulfuric acid, as observed by Holbrow. Holbrow noted that drying times of certain paint films exposed to 2620 to 5240 $\mu g/m^3$ (1 to 2 ppm) SO_2 increased by 50 to 100 percent because of a chemical alteration of the polymerization process. Holbrow also found that SO_2 could sensitize dried paint film, permitting water to be absorbed during the weathering cycle, especially at high humidity. Svoboda reported that SO_2 penetrated paint binder films pigmented with zinc oxide and titanium dioxide 50 to 70 percent faster than it did unpigmented films.

Cotton, rayon, and nylon fabrics are damaged by acids derived from SO_2. Polyester, acrylic, and polypropylene fibers are damaged by ammonium sulfate particles by acid hydrolysis. SO_2-related damage to clothing is negligible because the acids are neutralized during alkaline laundering. On the other hand, deterioration of household furnishings such as curtains, draperies, upholstery, and carpeting may be considerable. Sulfuric acid damages outdoor industrial fabrics such as ropes, tarpaulins, awnings, banners, flags, tents, and parachutes.

Certain types of building stone adsorb SO_2 and undergo chemical changes which weaken the material and lead to erosion. The end products are the relatively water-soluble calcium sulfate, magnesium sulfate, and calcium dicarbonate. Sangupta and DeGast observed that SO_2 adsorption on stone leads to blistering, exfoliation, efflorescence, and spalling. Concrete, which is an alkaline material, reacts with SO_2 and suffers erosion and spalling if not protected by paint. Concrete is also subject to chemical damage by sodium sulfate. Sulfate-resistant cement for use in dams and culverts is prepared by reducing the proportion of calcium aluminate used in the mixture.

Sulfur dioxide and particles have deleterious effects on electrical contacts in switches, relays, connectors, and computers. To reduce corrosion, contacts are electroplated with corrosion-resistant metals such as gold, platinum, palladium, and silver.

Sulfur dioxide is readily absorbed by paper and oxidized to sulfuric acid by metallic impurities; the paper then hydrolyzes and loses strength. Leather also has a high capacity for absorption of SO_2. The material is weakened by hydrolysis of the proteins that make up the collagens in leather. Verdu attributed the weathering of plastics in part to the joint action of SO_2 and

light. He found that sulfur dioxide increased the rate of polymer degradation of polystyrene in light-exposure trials.

The damaging effects of SO_2 and particles are well known to museum conservators whose function is to preserve and restore works of art. Action of SO_2 has been implicated in the deterioration of the Acropolis in Greece and the dome of a large cathedral in Cologne, Germany. Sulfate damage has been found in medieval stained glass windows, bronze sculptures, marble and stone statues, and Northern Italian fresco paintings on lime plaster.

Airborne particles aid corrosion by producing acid electrolytes; by functioning as nuclei to promote the condensation of water containing SO_2 or sulfates; and by forming a solid structure to retain active pollutants such as chlorides, organic matter, and sulfates. Deposition of dust and soot on building materials reduces the esthetic appeal of structures and can also result in erosion and direct chemical attack. Periodic sandblasting is required to renew the appearance. Cotton, rayon, and polyester fabrics soiled by airborne particles require more frequent cleaning, which leads to increased costs and reduces the useful life of fabrics.

Exterior paints are soiled by particles of soot, tarry acids, and various other constituents such as sulfates of iron, copper, calcium, and zinc. Staining and pitting of auto finishes has been traced to iron particles from nearby industrial operations and to alkali mortar dust from buildings being demolished. Parker reported that numerous black specks collected on freshly painted buildings in industrial areas, distinctly soiling the exterior surfaces and necessitating repainting in 2 or 3 years. Cowling and Roberts have suggested that particles promote the chemical deterioration of paint by acting as wicks to transfer SO_2 to the underlying surface.

Salmon cites economic damage from sulfur oxides to the following materials, listed in decreasing order of the extent of damage: metals, cotton, finishes and other coatings, building stone, paints, paper, leather. Paint, zinc, and cement/concrete account for 70 percent ($2.647 billion) of the estimated annual economic loss of all major materials ($3.8 billion). Carbon steel, which has virtually no resistance to SO_2 and sulfate, accounts for $54 million of the total loss. According to this estimate, the annual economic loss of paint and zinc ($1.873 billion) far exceeds the corrosion costs of the metal (carbon steel) that these coatings protect.

Estimates of the annual cost of corrosion of metals (mainly steel) in the United States range from $1.5 billion to $85 billion. Robbins estimated in 1970 that $20 million is spent annually for precious metals to combat direct SO_2 corrosion of electrical contacts and $40 million for indirect costs associated with equipment failure and air cleaning. Costs of pollution-caused soiling and deterioration damage to exterior household paints have been estimated at $540 million to $36.2 billion (the latter figure has been criticized as unrealistic).

A 1970 Booz Allen and Hamilton study attributed $5 billion for annual household cleaning costs to particulate pollution, exclusive of laundering, dry-cleaning, personal care items, and labor of the homemaker. Watson and Jaksch, using data from the Booz Allen and Hamilton study, concluded that the frequency of low-cost cleaning and maintenance operations depends on the level of airborne particles and that the frequency of professional house painting is unaffected by variations in air particle levels. Michelson and Tourin determined that the annual per capita costs for painting and cleaning of houses, laundering, dry-cleaning, and personal care (hair and facial) were $84 higher (1967 dollars)

in the highly polluted area of Steubenville, Ohio, than in the relatively clean city of Uniontown, PA. Their cost figures, based on data from questionnaires, have been questioned; critics suggest that socioeconomic factors influenced responses and that there were insufficient statistically reliable data. In a similar survey conducted in 1973, Narayan and Lancaster concluded that the cost of maintaining a house in the polluted Mayfield area of New South Wales, Australia, was about $90 per year higher than in the relatively unpolluted Rotar area. This cost differential was attributed to differences in airborne particulate matter in the two areas. Waddell reviewed the concept of property value to estimate economic damage, noting that a polluted area with soiling and odors may have lower property values. He cited the finding of Jacksch and Stoevener that reduction in property values due to increasing air pollutants was greater in the higher priced, newer sections of a city than in areas of low-cost housing.

Liu and Yu examined the economic effects of soiling in an effort to generate physical and economic damage functions and to establish some cost/benefit relationships. The study included the effects of air pollution damage on health, household soiling, materials, and vegetation. In 1970, extra costs for nine selected cleaning operations in Chicago, New York, and Los Angeles were $516 million, $418 million, and $388 million, respectively. The cleaning costs for venetian blinds and outside windows were $1.956 billion and $926 million, respectively, for 40 metropolitan areas. Annual per capita costs for household maintenance activities ranged from $5 in San Antonio to $104 in Cleveland. In urban areas, costs of soiling related to air pollution was $5.033 billion, or 29 percent of the total soiling costs of $17.367 billion.

Many physical and economic damage functions have been developed to estimate materials damage from sulfur oxides and particulate matter. Their accuracy is hampered by problems in identifying dose-response relationships for specific damage from specific pollutants because of many variables influencing exposure in the environment.

Damage functions indicate that reductions in SO_2 and particulate matter will decrease economic damage. Because of the catalytic action of sulfates, it is difficult to correlate SO_2 concentrations to deterioration of metal, paint, cotton fiber, and masonry. Nevertheless, field trials under closely monitored conditions and laboratory studies have shown that damage to these materials is less severe where SO_2 concentrations are lower. In most cases, the cost of replacing a product that has suffered premature damage is far greater than the cost of using protective measures or alternative materials resistant to damage from SO_2 and the particulate matter.

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GLOSSARY

$AaDO_2$: Alveolar-arterial difference or gradient of the partial pressure of oxygen. An overall measure of the efficiency of the lung as a gas exchanger. In healthy subjects, the gradient is 5 to 15 mm Hg (torr).

A/PR/8 virus: A type of virus capable of causing influenza in laboratory animals; also, A/PR/8/34.

Abscission: The process whereby leaves, leaflets, fruits, or other plant parts become detached from the plant.

Absorption coefficient: A quantity which characterizes the attenuation with distance of a beam of electromagnetic radiation (like light) in a substance

Absorption spectrum: The spectrum that results after any radiation has passed through an absorbing substance.

Abstraction: Removal of some constituent of a substance or molecule.

Acetaldehyde: CH_3CHO; an intermediate in yeast fermentation of carbohydrate and in alcohol metabolism; also called acetic aldehyde, ethaldehyde, ethanal.

Acetate rayon: A staple or filament fiber made by extrusion of cellulose acetate. It is saponified by dilute alkali whereas viscose rayon remains unchanged.

Acetylcholine: A naturally-occurring substance in the body which can cause constriction of the bronchi in the lungs.

Acid: A substance that can donate hydrogen ions.

Acid dyes: A large group of synthetic coal tar-derived dyes which produce bright shades in a wide color range. Low cost and ease of application are features which make them the most widely used dyes for wool. Also used on nylon. The term acid dye is derived from their precipitation in an acid bath.

Acid mucopolysaccharide: A class of compounds composed of protein and polysaccharide. Mucopolysaccharides comprise much of the substance of connective tissue.

Acid phosphatase: An enzyme (EC 3.1.3.2) which catalyzes the disassociation of phosphate (PO_4) from a wide range of monoesters of orthophosphoric acid. Acid phosphatase is active in an acidic pH range.

Acid rain: Rain having a pH less than 5.6, the minimum expected from atmospheric CO_2.

Acrolein: CH_2=CHCHO; a volatile, flammable, oily liquid, giving off irritant vapor. Strong irritant of skin and mucuous membranes. Also called acrylic aldehyde, 2-propenal.

Acrylics (plastics): Plastics which are made from acrylic acid and are light in weight, have great breakage resistance, and a lack of odor and taste. Not resistant to scratching, burns, hot water, alcohol or cleaning fluids. Examples include Lucite and Plexiglass. Acrylics are thermoplastics and are softened by heat and hardened into definite shapes by cooling.

Acrylic fiber: The generic name of man-made fibers derived from acrylic resins (minimum of 85 percent acrylonitrite units).

Actinic: A term applied to wavelengths of light too small to affect one's sense of sight, such as ultraviolet.

Actinomycetes: Members of the genus Actinomyces; nonmotile, nonspore-forming, anaerobic bacteria, including both soil-dwelling saprophytes and disease-producing parasites.

Activation energy: The energy required to bring about a chemical reaction.

Acute respiratory disease: Respiratory infection, usually with rapid onset and of short duration.

Acute toxicity: Any poisonous effect produced by a single short-term exposure, that results in severe biological harm or death.

Acyl: Any organic radical or group that remains intact when an organic acid forms an ester.

Adenoma: An ordinarily benign neoplasm (tumor) of epithelial tissue; usually well circumscribed, tending to compress adjacent tissue rather than infiltrating or invading.

Adenosine monophosphate (AMP): A nucleotide found amoung the hydrolysis products of all nucleic acids; also called adenylic acid.

Adenosine triphosphatase (ATPase): An enzyme (EC 3.6.1.3) in muscle and elsewhere that catalyzes the release of the high-energy, terminal phosphate group of adenosine triphosphate.

Adrenalectomy: Removal of an adrenal gland. This gland is located near or upon the kidney and is the site of origin of a number of hormones.

Adsorption: Adhesion of a thin layer of molecules to a liquid or solid surface.

Advection: Horizontal flow of air at the surface or aloft; one of the means by which heat is transferred from one region of the earth to another.

Aerodynamic diameter: Expression of aerodynamic behavior of an irregularly shaped particle in terms of the diameter of a sphere of unit density having identical aerodynamic behavior to the particle in question.

Aerosol: Solid particles or liquid droplets which are dispersed or suspended in a gas.

Agglutination: The process by which suspended bacteria, cells or similar particles adhere and form into clumps.

Airborne pathogen: A disease-causing microorganism which travels in the air or on particles in the air.

Air pollutant: A substance present in the ambient atmosphere, resulting from the activity of man or from natural processes, which may cause damage to human health or welfare, the natural environment, or materials or objects.

Airway conductance: Inverse of airway resistance.

Airway resistance (R_{aw}): The pressure difference between the alveoli and the mouth required to produce an air flow of 1 liter per second.

Alanine aminotransferase: An enzyme (EC 2.6.1.2) transferring amino groups from L-alanine to 2-ketoglutarate. Also known as alanine transaminase.

Albumin: A type of simple, water-soluble protein widely distributed throughout animal tissues and fluids, particularly serum.

Aldehyde: An organic compound characterized by the group $-\overset{\overset{\displaystyle O}{\|}}{C}-H$.

Aldolase: An enzyme (EC 4.1.2.7) involved in metabolism of fructose which catalyzes the formation of two 3-carbon intermediates in the major pathway of carbohydrate metabolism.

Algal bloom: Sudden spurt in growth of algae which can affect water quality adversely.

Alkali: A salt of sodium or potassium capable of neutralizing acids.

Alkaline phosphatase: A phosphatase (EC 3.1.3.1) with an optimum pH of 8.6, present ubiquitously.

Allergen: A material that, as a result of coming into contact with appropriate tissues of an animal body, induces a state of sensitivity resulting in various reactions; generally associated with idiosyncratic hypersensitivities.

Alpha-hydroxybutyrate dehydrogenase: An enzyme (EC 1.1.1.30), present mainly in mitochondria, which catalyzes the conversion of hydroxybutyrate to acetoacetate in intermediate biochemical pathways.

Alpha rhythm: A rhythmic pulsation obtained in brain waves exhibited in the sleeping state of an individual.

Alveolar capillary membrane: Finest portion of alveolar capillaries, where gas transfer to and from blood takes place.

Alveolar macrophages (AM): Large, mononuclear, phagocytic cells found on the alveolar surface, responsible for the sterility of the lung.

Alveolar oxygen partial pressure (PAO_2): Partial pressure of oxygen in the air contained in the air sacs of the lungs.

Alveolar septa: The tissue between two adjacent pulmonary alveoli, consisting of a close-meshed capillary network covered on both surfaces by thin alveolar epithelial cells.

Alveolus: An air cell; a terminal, sac-like dilation in the lung. Gas exchange (O_2/CO_2) occurs here.

Ambient: The atmosphere to which the general population may be exposed. Construed here <u>not</u> to include atmospheric conditions indoors, or in the workplace.

Amine: A substance that may be derived from ammonia (NH_3) by the replacement of one, two or three of the hydrogen (H) atoms by hydrocarbons or other radicals (primary, secondary or tertiary amines, respectively).

Amino acids: Molecules consisting of a carboxyl group, a basic amino group, and a residue group attached to a central carbon atom. Serve as the building blocks of proteins.

p-Aminohippuric acid (PAH): A compound used to determine renal plasma flow.

Aminotriazole: A systemic herbicide, $C_2H_4N_4$, used in areas other than croplands, that also possesses some antithyroid activity; also called amitrole.

Ammonification: Decomposition with production of ammonia or ammonium compounds, esp. by the action of bacteria on nitrogenous organic matter.

Ammonium: Anion (NH_4^+) or radical (NH_4) derived from ammonia by combination with hydrogen. Present in rainwater, soils and many commercial fertilizers.

Amnestic: Pertains to immunologic memory: upon receiving a second dose of antigen, the host "remembers" the first dose and responds faster to the challenge.

Anaerobic: Living, active or occurring in the absence of free oxygen.

Anaerobic bacteria: A type of microscopic organism which can live in an environment not containing free oxygen.

Anaphylactic dyspneic attack: Difficulty in breathing associated with a systemic allergic response.

Anaphylaxis: A term commonly used to denote the immediate, transient kind of immunological (allergic) reaction characterized by contraction of smooth muscle and dilation of capillaries due to release of pharmacologically active substances.

Angiosperm: A plant having seeds enclosed in an ovary; a flowering plant.

Angina pectoris: Severe constricting pain in the chest which may be caused by depletion of oxygen delivery to the heart muscle; usually caused by coronary disease.

Angstrom Å: A unit (10^{-8} cm) used in the measurement of the wavelength of light.

Anhydride: A compound resulting from removal of water from two molecules of a carboxylic (-COOH) acid. Also, may refer to those substances (anhydrous) which do not contain water in chemical combination.

Anion: A negatively charged atom or radical.

Anorexia: Diminished appetite; aversion to food.

Anoxic: Without or deprived of oxygen.

Anthraquinone: A yellow crystalline ketone, $C_{14}H_8O_2$, derived from anthracene and used in the manufacture of dyes.

Anthropogenic: Of, relating to or influenced by man. An anthropogenic source of pollution is one caused by man's actions.

Antibody: Any body or substance evoked by the stimulus of an antigen and which reacts specifically with antigen in some demonstrable way.

Antigen: A material such as a foreign protein that, as a result of coming in contact with appropriate tissues of an animal, after a latent period, induces a state of sensitivity and/or the production of antibody.

Antistatic agent: A chemical compound applied to fabrics to reduce or eliminate accumulation of static electricity.

Arachidonic acid: Long-chain fatty-acid which serves as a precursor of prostaglandins.

Area source: In air pollution, any small individual fuel combustion or other pollutant source; also, all such sources grouped over a specific area.

Aromatic: Belonging to that series of carbon-hydrogen compounds in which the carbon atoms form closed rings containing unsaturated bonds (as in benzene).

Arterial partial pressure of oxygen (PaO_2): Portion of total pressure of dissolved gases in arterial blood as measured directly from arterial blood.

Arterialized partial pressure of oxygen: The portion of total pressure of dissolved gases in arterial blood attributed to oxygen, as measured from non-arterial (e.g., ear-prick) blood.

Arteriosclerosis: Commonly called hardening of the arteries. A condition that exists when the walls of the blood vessels thicken and become infiltrated with excessive amounts of minerals and fatty materials.

Artifact: A spurious measurement produced by the sampling or analysis process.

Ascorbic acid: Vitamin C, a strong reducing agent with antioxidant properties.

Aspartate transaminase: Also known as aspartate aminotransferase (EC 2.6.1.1). An enzyme catalyzing the transfer of an amine group from glutamic acid to oxaloacetic, forming aspartic acid in the process. Serum level of the enzyme is increased in myocardial infarction and in diseases involving destruction of liver cells.

Asphyxia: Impaired exchange of oxygen and carbon dioxide, excess of carbon dioxide and/or lack of oxygen, usually caused by ventilatory problems.

Asthma: A term currently used in the context of bronchial asthma in which there is widespread narrowing of the airways of the lung. It may be aggravated by inhalation of pollutants and lead to "wheezing" and shortness of breath.

Asymptomatic: Presenting no subjective evidence of disease.

Atmosphere: The body of air surrounding the earth. Also, a measure of pressure (atm.) equal to the pressure of air at sea level, 14.7 pounds per square inch.

Atmospheric deposition: Removal of pollutants from the atmosphere onto land, vegetation, water bodies or other objects, by absorption, sedimentation, Brownian diffusion, impaction, or precipitation in rain.

Atomic absorption spectrometry: A measurement method based on the absorption of radiant energy by gaseous ground-state atoms. The amount of absorption depends on the population of the ground state which is related to the concentration of the sample being analyzed.

Atropine: A poisonous white crystalline alkaloid, $C_{17}H_{23}NO_3$, from belladonna and related plants, used to relieve spasms and to dilate the pupil of the eye.

Autocorrelation: Statistical interdependence of variables being analyzed; produces problems, for example, when observations may be related to previous measurements or other conditions.

Autoimmune disease: A condition in which antibodies are produced against the subject's own tissues.

Autologous: A term referring to cellular elements, such as red blood cells and alveolar macrophage, from the same organism; also, something natually and normally ocurring in some part of the body.

Autotrophic: A term applied to those microorganisms which are able to maintain life without an exogenous organic supply of energy, or which only need carbon dioxide or carbonates and simple inorganic nitrogen.

Autotrophic bacteria: A class of microorganisms which require only carbon dioxide or carbonates and a simple inorganic nitrogen compound for carrying on life processes.

Auxin: An organic substance that causes lengthening of the stem when applied in low concentrations to shoots of growing plants.

Awn: One of the slender bristles that terminate the glumes of the spikelet in some cereals and other grasses.

Azo dye: Dyes in which the azo group is the chromophore and joins benzene or napthalene rings.

Background measurement: A measurement of pollutants in ambient air due to natural sources; usually taken in remote areas.

Bactericidal activity: The process of killing bacteria.

Barre: Bars or stripes in a fabric, caused by uneven weaving, irregular yarn or uneven dye distribution.

Basal cell: One of the innermost cells of the deeper epidermis of the skin.

Benzenethiol: A compound of benzene and a hydrosulfide group.

Beta (b)-lipoprotein: A biochemical complex or compound containing both lipid and protein and characterized by having a large molecular weight, rich in cholesterol. Found in certain fractions of human plasma.

Bilateral renal sclerosis: A hardening of both kidneys of chronic inflammatory origin.

Biomass: That part of a given habitat consisting of living matter.

Biosphere: The part of the earth's crust, waters and atmosphere where living organisms can subsist.

Biphasic: Having two distinct successive stages.

Bleb: A collection of fluid beneath the skin; usually smaller than bullae or blisters.

Blood urea: The chief end product of nitrogen metabolism in mammals, excreted in human urine in the amount of about 32 grams (1 oz.) a day.

Bloom: A greenish-gray appearance imparted to silk and pile fabrics either by nature of the weave or by the finish; also, the creamy white color observed on some good cottons.

Blue-green algae: A group of simple plants which are the only N_2-fixing organisms which photosynthesize as do higher plants.

Brightener: A compound such as a dye, which adheres to fabrics in order to provide better brightness or whiteness by converting ultraviolet radiation to visible light. Sometimes called optical bleach or whitening agent. The dyes used are of the florescent type.

Broad bean: The large flat edible seed of an Old World upright vetch (*Vicia faba*), or the plant itself, widely grown for its seeds and for fodder.

Bronchi: The first subdivisions of the trachea which conduct air to and from the bronchioles of the lungs.

Bronchiole: One of the finer subdivisions of the bronchial (trachea) tubes, less than 1 mm in diameter, and having no cartilage in its wall.

Bronchiolitis: Inflammation of the smallest bronchial tubes.

Bronchiolitis fibrosa obliterans syndrome: Obstruction of the bronchioles by fibrous granulation arising from an ulcerated mucosa; the condition may follow inhalation of irritant gases.

Bronchitis: Inflammation of the mucous membrane of the bronchial tubes. It may aggravate an existing asthmatic condition.

Bronchoconstrictor: An agent that causes a reduction in the caliber (diameter) of a bronchial tube.

Bronchodilator: An agent which causes an increase in the caliber (diameter) of a bronchus or bronchial tube.

Bronchopneumonia: Acute inflammation of the walls of the smaller bronchial tubes, with irregular area of consolidation due to spread of the inflammation into peribronchiolar alveoli and the alveolar ducts.

Brownian diffusion: Diffusion by random movement of particles suspended in liquid or gas, resulting from the impact of molecules of the fluid surrounding the particles.

Buffer: A substance in solution capable of neutralizing both acids and bases and thereby maintaining the original pH of the solution.

Buffering capacity: Ability of a body of water and its watershed to neutralize introduced acid.

Butanol: A four-carbon, straight-chain alcohol, C_4H_9OH, also known as butyl alcohol.

Butylated hydroxytoluene (BHT): A crystalline phenolic antioxidant.

Butylated hydroxyanisol (BHA): An antioxidant.

^{14}C labeling: Use of a radioactive form of carbon as a tracer, often in metabolic studies.

^{14}C-proline: An amino acid which has been labeled with radioactive carbon.

Calcareous: Resembling or consisting of calcium carbonate (lime), or growing on limestone or lime-containing soils.

Calorie: Amount of heat required to raise temperature of 1 gram of water at $15^{o}C$ by 1 degree.

Cannula: A tube that is inserted into a body cavity, or other tube or vessel, usually to remove fluid.

Capillary: The smallest type of vessel; resembles a hair. Usually in reference to a blood or lymphatic capillary vessel.

Carbachol: A chemical compound (carbamoylcholine chloride, $C_6H_{15}ClN_2O_2$) that produces a constriction of the bronchi; a parasympathetic stimulant used in veterinary medicine and topically in glaucoma.

Carbon monoxide: An odorless, colorless, toxic gas with a strong affinity for hemoglobin and cytochrome; it reduces oxygen absorption capacity, transport and utilization.

Carboxyhemoglobin: A fairly stable union of carbon monoxide with hemoglobin which interferes with the normal transfer of carbon dioxide and oxygen during circulation of blood. Increasing levels of carboxyhemoglobin result in various degrees of asphyxiation, including death.

Carcinogen: Any agent producing or playing a stimulatory role in the formation of a malignancy.

Carcinoma: Malignant new growth made up of epithelial cells tending to infiltrate the surrounding tissues and giving rise to metastases.

Cardiac output: The volume of blood passing through the heart per unit time.

Cardiovascular: Relating to the heart and the blood vessels or the circulation.

Carotene: Lipid-soluble yellow-to-orange-red pigments universally present the photosynthetic tissues of higher plants, algae, and the photosynthetic bacteria.

Cascade impactor: A device for measuring the size distribution of particulates and/or aerosols, consisting of a series of plates with orifices of graduated size which separate the sample into a number of fractions of decreasing aerodynamic diameter.

Catabolism: Destructive metabolism involving the release of energy and resulting in breakdown of complex materials in the organism.

Catalase: An enzyme (EC 1.11.1.6) catalyzing the decomposition of hydrogen peroxide to water and oxygen.

Catalysis: A modification of the rate of a chemical reaction by some material which is unchanged at the end of the reaction.

Catalytic converter: An air pollution abatement device that removes organic contaminants by oxidizing them into carbon dioxide and water.

Catecholamine: A pyrocatechol with an alkalamine side chain, functioning as a hormone or neurotransmitter, such as epinephrine, morepinephrine, or dopamine.

Cathepsins: Enzymes which have the ability to hydrolyze certain proteins and peptides; occur in cellular structures known as lysosomes.

Cation: A positively charged ion.

Cellular permeability: Ability of gases to enter and leave cells; a sensitive indicator of injury to deep-lung cells.

Cellulose: The basic substance which is contained in all vegetable fibers and in certain man-made fibers. It is a carbohydrate and constitutes the major substance in plant life. Used to make cellulose acetate and rayon.

Cellulose acetate: Commonly refers to fibers or fabrics in which the cellulose is only partially acetylated with acetate groups. An ester made by reacting cellulose with acetic anhydride with SO_4 as a catalyst.

Cellulose rayon: A regenerated cellulose which is chemically the same as cellulose except for physical differences in molecular weight and crystallinity.

Cellulose triacetate: A cellulose fiber which is completely acetylated. Fabrics of triacetate have higher heat resistance than acetate and may be safely ironed at higher temperature. Such fabrics have improved ease-of-care characteristics because after heat treatment during manufacture, a change in the crystalline structure of the fiber occurs.

Cellulosics: Cotton, viscose rayon and other fibers made of natural fiber raw materials.

Celsius scale: The thermometric scale in which freezing point of water is 0 and boiling point is 100.

Central hepatic necrosis: The pathologic death of one or more cells, or of a portion of the liver, involving the cells adjacent to the central veins.

Central nervous system (CNS): The brain and the spinal cord.

Centroacinar area: The center portion of a grape-shaped gland.

Cerebellum: The large posterior brain mass lying above the pons and medulla and beneath the posterior portion of the cerebrum.

Cerebral cortex: The layer of gray matter covering the entire surface of the cerebral hemisphere of mammals.

Chain reaction: A reaction that stimulates its own repetition.

Challenge: Exposure of a test organism to a virus, bacteria, or other stress-causing agent, used in conjunction with exposure to a pollutant of interest, to explore possible susceptibility brought on by the pollutant.

Chamber study: Research conducted using a closed vessel in which pollutants are reacted or substances exposed to pollutants.

Chemiluminescence: A measurement technique in which radiation is produced as a result of chemical reaction.

Chemotactic: Relating to attraction or repulsion of living protoplasm by chemical stimuli.

Chlorophyll: A group of closely related green photosynthetic pigments occurring in leaves, bacteria, and organisms.

Chloroplast: A plant cell inclusion body containing chlorophyll.

Chlorosis: Discoloration of normally green plant parts that can be caused by disease, lack of nutrients, or various air pollutants, resulting in the failure of chlorophyll to develop.

Cholesterol: A steroid alcohol $C_{27}H_{45}OH$; the most abundant steroid in animal cells and body fluids.

Cholinesterase (CHE): One (EC 3.1.1.8) of a family of enzymes capable of catalyzing the hydrolysis of acylcholines.

Chondrosarcoma: A malignant neoplasm derived from cartilage cells, occurring most frequently near the ends of long bones.

Chromatid: Each of the two strands formed by longitudinal duplication of a chromosome that becomes visible during an early stage of cell division.

Chromophore: A chemical group that produces color in a molecule by absorbing near ultraviolet or visible radiation when bonded to a nonabsorbing, saturated residue which possesses no unshared, nonbonding valence electrons.

Chromosome: One of the bodies (46 in man) in the cell nucleus that is the bearer and carrier of genetic information.

Chronic respiratory disease (CRD): A persistent or long-lasting intermittent disease of the respiratory tract.

Cilia: Motile, often hairlike extensions of a cell surface.

Ciliary action: Movements of cilia in the upper respiratory tract, which move mucus and foreign material upward.

Ciliogenesis: The formation of cilia.

Citric acid (Krebs) cycle: A major biochemical pathway in cells, involving terminal oxidation of fatty acids and carbohydrates. It yields a major portion of energy needed for essential body functions and is the major source of CO_2. It couples the glycolytic breakdown of sugar in the cytoplasm with those reactions producing ATP in the mitochondria. It also serves to regulate the synthesis of a number of compounds required by a cell.

Clara cell: A nonciliated mammalian cell.

Closing volume (CV): The lung volume at which the flow from the lower parts of the lungs becomes severely reduced or stops during expiration, presumably because of airway closure.

Codon: A sequence of three nucleotides which encodes information required to direct the synthesis of one or more amino acids.

Coefficient of haze (COH): A measurement of visibility interference in the atmosphere.

Cohort: A group of subjects included in a test or experiment; usually characterized by age, class or other characteristic.

Collagen: The major protein of the white fibers of connective tissue, cartilage, and bond. Comprises over half the protein of the mammal.

Collisional deactivation: Reduction in energy of excited molecules caused by collision with other molecules or other objects such as the walls of a container.

Colorimetric: A chemical analysis method relying on measurement of the degree of color produced in a solution by reaction with the pollutant of interest.

Community exposure: A situation in which people in a sizeable area are subjected to ambient pollutant concentrations.

Compliance: A measure of the change in volume of an internal organ (e.g. lung, bladder) produced by a unit of pressure.

Complement: Thermolabile substance present in serum that is destructive to certain bacteria and other cells which have been sensitized by specific complement-fixing antibody.

Compound: A substance with its own distinct properties, formed by the chemical combination of two or more elements in fixed proportion.

Concanavalin-A: One of two crystalline globulins occurring in the jack bean; a potent hemagglutinin.

Conifer: A plant, generally evergreen, needle-leafed, bearing naked seeds singly or in cones.

Converter: See catalytic converter.

Coordination number: The number of bonds formed by the central atom in a complex.

Copolymer: The product of the process of polymerization in which two or more monomeric substances are mixed prior to polymerization. Nylon is a copolymer.

Coproporphyrin: One of two porphyrin compounds found normally in feces as a decomposition product of bilirubin (a bile pigment). Porphyrin is a widely-distributed pigment consisting of four pyrrole nuclei joined in a ring.

Cordage: A general term which includes banding, cable, cord, rope, string, and twine made from fibers. Synthetic fibers used in making cordage include nylon and dacron.

Corrosion: Destruction or deterioration of a material because of reaction with its environment.

Corticosterone: A steroid obtained from the adrenal cortex. It induces some deposition of glycogen in the liver, sodium conservation, and potassium excretion.

Cosmopolitan: In the biological sciences, a term denoting worldwide distribution.

Coulometric: Chemical analysis performed by determining the amount of a substance released in electrolysis by measuring the number of coulombs used.

Coumarin: A toxic white crystalline lactone ($C_9H_6O_2$) found in plants.

Coupler: A chemical used to combine two others in a reaction, e.g. to produce the azo dye in the Griess-Saltzman method for NO_2.

Crevice corrosion: Localized corrosion occurring within crevices on metal surfaces exposed to corrosives.

Crosslink: To connect, by an atom or molecule, parallel chains in a complex chemical molecule, such as a polymer.

Cryogenic trap: A pollutant sampling method in which a gaseous pollutant is condensed out of sampled air by cooling (e.g. traps in one method for nitrosamines are maintained below -79°C, using solvents maintained at their freezing points).

Cuboidal: Resembling a cube in shape.

Cultivar: An organism produced by parents belonging to different species or to different strains of the same species, originating and persisting under cultivation.

Cuticle: A thin outer layer, such as the thin continuous fatty film on the surface of many higher plants.

Cyanosis: A dark bluish or purplish coloration of the skin and mucous membrane due to deficient oxygenation of the blood.

Cyclic GMP: Guanosine 5'-phosphoric acid.

Cytochrome: A class of hemoprotein whose principal biological function is electron and/or hydrogen transport.

Cytology: The anatomy, physiology, pathology and chemistry of the cell.

Cytoplasm: The substance of a cell exclusive of the nucleus.

Dacron: The trade name for polyester fibers made by E.I. du Pont de Nemours and Co., Inc., made from dimethyl terephthalate and ethylene glycol.

Dark adaptation: The process by which the eye adjusts under reduced illumination and the sensitivity of the eye to light is greatly increased.

Dark respiration: Metabolic activity of plants at night; consuming oxygen to use stored sugars and releasing carbon dioxide.

Deciduous plants: Plants which drop their leaves at the end of the growing season.

Degradation (textiles): The decomposition of fabric or its components or characteristics (color, strength, elasticity) by means of light, heat, or air pollution.

Denitrification: A bacterial process occurring in soils, or water, in which nitrate is used as the terminal electron acceptor and is reduced primarily to N_2. It is essentially an anaerobic process; it can occur in the presence of low levels of oxygen only if the microorganisms are metabolizing in an anoxic microzone.

De novo: Over again.

Deoxyribonucleic acid (DNA): A nucleic acid considered to be the carrier of genetic information coded in the sequence of purine and pyrimidine bases (organic bases). It has the form of a double-stranded helix of a linear polymer.

Depauperate: Falling short of natural development or size.

Derivative spectrophotometer: An instrument with an increased capability for detecting overlapping spectral lines and bands and also for suppressing instrumentally scattered light.

Desorb: To release a substance which has been taken into another substance or held on its surface; the opposite of absorption or adsorption.

Desquamation: The shedding of the outer layer of any surface.

Detection limit: A level below which an element or chemical compound cannot be reliably detected by the method or measurement being used for analysis.

Detritus: Loose material that results directly from disintegration.

DeVarda alloy: An alloy of 50 percent Cu, 45 percent Al, 5 percent Zn.

Diastolic blood pressure: The blood pressure as measured during the period of filling the cavities of the heart with blood.

Diazonium salt: A chemical compound (usually colored) of the general structure $ArN_2^+Cl^-$, where Ar refers to an aromatic group.

Diazotizer: A chemical which, when reacted with amines (RNH_2, for example), produces a diazonium salt (usually a colored compound).

Dichotomous sampler: An air-sampling device which separates particulates into two fractions by particle size.

Differentiation: The process by which a cell, such as a fertilized egg, divides into specialized cells, such as the embryonic types that eventually develop into an entire organism.

Diffusion: The process by which molecules or other particles intermingle as a result of their random thermal motion.

Diffusing capacity: Rate at which gases move to or from the blood.

Dimer: A compound formed by the union of two like radicals or molecules.

Dimerize: Formation of dimers.

1,6-diphosphofructose aldolase: An enzyme (EC 4.1.1.13) cleaving fructose 1,6-bisphosphate to dihydroxyacetone phosphate and glyceraldehyde-3-phosphate.

D-2,3-diphosphoglycerate: A salt or ester of 2,3-diphosphoglyceric acid, a major component of certain mammalian erythrocytes involved in the release of O_2 from HbO_2. Also a postulated intermediate in the biochemical pathway involving the conversion of 3- to 2-phosphoglyceric acid.

<u>Diplococcus</u> <u>pneumoniae</u>: A species of spherical-shaped bacteria belonging to the genus Streptococcus. May be a causal agent in pneumonia.

Direct dye: A dye with an affinity for most fibers; used mainly when color resistance to washing is not important.

Disperse dyes: Also known as acetate dyes; these dyes were developed for use on acetate fabrics, and are now also used on synthetic fibers.

Distal: Far from some reference point such as median line of the body, point of attachment or origin.

Diurnal: Having a repeating pattern or cycle 24 hours long.

DL_{CO}: The diffusing capacity of the lungs for carbon monoxide. The ability of the lungs to transfer carbon monoxide from the alveolar air into the pulmonary capillary blood.

Dorsal hyphosis: Abnormal curvative of the spine; hunch-back.

Dose: The quantity of a substance to be taken all at one time or in fractional amounts within a given period; also the total amount of a pollutant delivered or concentration per unit time times time.

Dose-response curve: A curve on a graph based on responses occurring in a system as a result of a series of stimuli intensities or doses.

Dry deposition: The processes by which matter is transferred to ground from the atmosphere, other than precipitation; includes surface absorption of gases and sedimentation, Brownian diffusion and impaction of particles.

Dyeing: A process of coloring fibers, yarns, or fabrics with either natural or synthetic dyes.

Dynamic calibration: Testing of a monitoring system using a continuous sample stream of known concentration.

Dynamic compliance (C_{Ldyn}): Volume change per unit of transpulmonary pressure minus the pressure of pulmonary resistance during airflow.

Dynel: A trademark for a modacrylic staple fiber spun from a copolymer of acrylonitrile and vinyl chloride. It has high strength, quick-drying properties, and resistance to alkalies and acids.

Dyspepsia: Indigestion, upset stomach.

Dyspnea: Shortness of breath; difficulty or distress in breathing; rapid breathing.

Ecosystem: The interacting system of a biological community and its environment.

Eddy: A current of water or air running contrary to the main current.

Edema: Pressure of excess fluid in cells, intercellular tissue or cavities of the body.

Elastomer: A synthetic rubber product which has the physical properties of natural rubber.

Electrocardiogram: The graphic record of the electrical currents that initiate the heart's contraction.

Electrode: One of the two extremities of an electric circuit.

Electrolyte: A non-metallic electric conductor in which current is carried by the movement of ions; also a substance which displays these qualities when dissolved in water or another solvent.

Electronegativity: Measure of affinity for negative charges or electrons.

Electron microscopy: A technique which utilizes a focused beam of electrons to produce a high-resolution image of minute objects such as particulate matter, bacteria, viruses, and DNA.

Electronic excitation energy: Energy associated in the transition of electrons from their normal low-energy orbitals or orbitals of higher energy.

Electrophilic: Having an affinity for electrons.

Electrophoresis: A technique by which compounds can be separated from a complex mixture by their attraction to the positive or negative pole of an applied electric potential.

Eluant: A liquid used in the process of elution.

Elute: To perform an elution.

Elution: Separation of one material from another by washing or by dissolving one in a solvent in which the other is not soluble.

Elutriate: To separate a coarse, insoluble powder from a finer one by suspending them in water and pouring off the finer powder from the upper part of the fluid.

Emission spectrometry: A rapid analytical technique based on measurement of the characteristic radiation emitted by thermally or electrically excited atoms or ions.

Emphysema: An anatomic alteration of the lung, characterized by abnormal enlargement of air spaces distal to the terminal bronchioles, due to dilation or destructive changes in the alveolar walls.

Emphysematous lesions: A wound or injury to the lung as a result of emphysema.

Empirical modeling: Characterization and description of a phenomena based on experience or observation.

Encephalitis: Inflammation of the brain.

Endoplasmic reticulum: An elaborate membrane structure extending from the nuclear membrane or eucaryotic cells to the cytoplasmic membrane.

Endothelium: A layer of flat cells lining especially blood and lymphatic vessels.

Entropy: A measure of disorder or randomness in a system. Low entropy is associated with highly ordered systems.

Enzyme: Any of numerous proteins produced by living cells which catalyze biological reactions.

Enzyme Commission (EC): The International Commission on Enzymes, established in 1956, developed a scheme of classification and nomenclature under which each enzyme is assigned an EC number which identifies it by function.

Eosinophils: Leukocytes (white blood cells) which stain readily with the dye, eosin.

Epidemiology: A study of the distribution and determinants of disease in human population groups.

Epidermis: The outermost living layer of cells of any organism.

Epididymal fat pads: The fatty tissue located near the epididymis. The epididymis is the first convoluted portion of the excretory duct of the testis.

Epiphyte: A plant growing on another plant but obtaining food from the atmosphere.

Epithelial: Relating to epithelium, the membranous cellular layer which covers free surfaces or lines tubes or cavities of an animal body, which encloses, protects, secretes, excretes and/or assimilates.

Erosion corrosion: Acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Characterized by grooves, gullies, or waves in the metal surface.

Erythrocyte: A mature red blood cell.

Escherichia coli: A short, gram-negative, rod-shaped bacteria common to the human intestinal tract. A frequent cause of infections in the urogenital tract.

Esophageal: Relating to the portion of the digestive tract between the pharynx and the stomach.

Estrus: That portion or phase of the sexual cycle of female animals characterized by willingness to permit coitus.

Estrus cycle: The series of physiologic uterine, ovarian and other changes that occur in higher animals.

Etiolation: Paleness and/or altered development resulting from the absence of light.

Etiology: The causes of a disease or condition; also, the study of causes.

Eucaryotic: Pertaining to those cells having a well-defined nucleus surrounded by a double-layered membrane.

Euthrophication: Elevation of the level of nutrients in a body of water, which can contribute to accelerated plant growth and filling.

Excited state: A state of higher electronic energy than the ground state, usually a less stable one.

Expiratory (maximum) flow rate: The maximum rate at which air can be expelled from the lungs.

Exposure level: Concentration of a contaminant to which an individual or a population is exposed.

Extinction coefficient: A measure of the space rate of diminution, or extinction, of any transmitted light, thus, it is the attenuation coefficient applied to visible radiation.

Extramedullary hematopoiesis: The process of formation and development of the various types of blood cells and other formed elements not including that occurring in bone marrow.

Extravasate: To exclude from or pass out of a vessel into the tissues; applies to urine, lymph, blood and similar fluids.

Far ultraviolet: Radiation in the range of wavelengths from 100 to 190 nanometers.

Federal Reference Method (FRM): For NO_2, the EPA-approved analyzers based on the gas-phase chemiluminescent measurement principle and associated calibration procedures; regulatory specifications prescribed in Title 40, Code of Federal Regulations, Part 50, Appendix F.

Fenestrae: Anatomical aperatures often closed by a membrane.

Fiber: A fine, threadlike piece, as of cotton, jute, or asbestos.

Fiber-reactive dye: A water-soluble dyestuff which reacts chemically with the cellulose in fibers under alkaline conditions; the dye contains two chlorine atoms which combine with the hydroxyl groups of the cellulose.

Fibrin: A white insoluble elastic filamentous protein derived from fibrinogen by the action of thrombin, especially in the clotting of blood.

Fibroadenoma: A benign neoplasm derived from glandular epithelium, involving proliferating fibroblasts, cells found in connective tissue.

Fibroblast: An elongated cell with cytoplasmic processes present in connective tissue, capable of forming collagen fibers.

Fibrosis: The formation of fibrous tissue, usually as a reparative or reactive process and not as a normal constituent of an organ or tissue.

Flocculation: Separation of material from a solution or suspension by reaction with a flocculant to create fluffy masses containing the material to be removed.

Fly ash: Fine, solid particles of noncombustible ash carried out of a bed of solid fuel by a draft.

Folded-path optical system: A long (e.g. 8-22 m) chamber with multiple mirrors at the ends which can be used to reflect an infrared beam through an ambient air sample many times; a spectrometer can be used with such a system to detect trace pollutants at very low levels.

Forced expiratory flow (FEF): The rate at which air can be expelled from the lungs; see expiratory flow rate.

Forced expiratory volume (FEV): The maximum volume of air that can be expired in a specific time interval when starting from maximal inspiration.

Forced vital capacity (FVC): The greatest volume of air that can be exhaled from the lungs under forced conditions after a maximum inspiration.

Fractional threshold concentration: The portion of the concentration at which an event or a response begins to occur, expressed as a fraction.

Free radical: Any of a variety of highly-reactive atoms or molecules characterized by having an unpaired electron.

Fritted bubbler: A porous glass device used in air pollutant sampling systems to introduce small bubbles into solution.

Functional residual capacity: The volume of gas remaining in the lungs at the end of a normal expiration. It is the sum of expiratory reserve volume and residual volume.

Gas exchange: Movement of oxygen from the alveoli into the pulmonary capillary blood as carbon dioxide enters the alveoli from the blood.

Gas chromatography (GC): A method of separating and analyzing mixtures of chemical substances. A flow of gas causes the components of a mixture to migrate differentially from a narrow starting zone in a special porous, insoluble sorptive medium. The pattern formed by zones of separated pigments and of colorless substances in this process is called a chromatogram, and can be analyzed to obtain the concentration of identified pollutants.

Gas-liquid chromatography: A method of separating and analyzing volatile organic compounds, in which a sample is vaporized and swept through a column filled with solid support material covered with a nonvolatile liquid. Components of the sample can be identified and their concentrations determined by analysis of the characteristics of their retention in the column, since compounds have varying degrees of solubility in the liquid medium.

Gastric juice: A thin watery digestive fluid secreted by glands in the mucous membrane of the stomach.

Gastroenteritis: Inflammation of the mucous membrane of stomach and intestine.

Genotype: The type of genes possessed by an organism.

Geometric mean: An estimate of the average of a distribution. Specifically, the nth root of the product of n observations.

Geometric standard deviation: A measure of variability of a distribution. It is the antilogarithm of the standard deviation of the logarithms of the observations.

Globulins (a, b, q): A family of proteins precipitated from plasma (or serum) by half-saturation with ammonium sulfate, or separable by electrophoresis. The main groups are the a, b, q fractions, differing with respect to associated lipids and carbohydrates and in their content of antibodies (immunoglobulins).

Glomular nephrotic syndrome: Dysfunction of the kidneys characterized by excessive protein loss in the urine, accumulation of body fluids and alteration in albumin/globulin ratio.

Glucose: A sugar which is a principal source of energy for man and other organisms.

Glucose-6-phosphate dehydrogenase: An enzyme (EC 1.1.1.49) catalyzing the dehydrogenation of glucose-6-phosphate to 6-phosphogluconolactone.

Glutamic-oxaloacetic transaminase (SGOT): An enzyme (EC 2.6.1.1) whose serum level increases in myocardial infarction and in diseases involving destruction of liver cells. Also known as aspartate aminotransferase.

Glutamic-pyruvic transaminase (SGPT): Now known as alanine aminotransferase (EC 2.6.1.2), the serum levels of this enzyme are used in liver function tests.

Glutathione (GSH): A tripeptide composed of glycine, cystine, and glutamic acid.

Glutathione peroxidase: An enzyme (EC 1.11.1) which catalyzes the destruction of hydroperoxides formed from fatty acids and other substances. Protects tissues from oxidative damage. It is a selenium-containing protein.

Glutathione reductase: The enzyme (EC 1.6.4.2) which reduces the oxidized form of glutathione.

Glycolytic pathway: The biochemical pathway by which glucose is converted to lactic acid in various tissues, yielding energy as a result.

Glycoside: A type of chemical compound formed from the condensation of a sugar with another chemical radical via a hemiacetal linkage.

Goblet cells: Epithelial cells that have been distended with mucin and when this is discharged as mucus, a goblet-shaped shell remains.

Golgi apparatus: A membrane system involved with secretory functions and transport in a cell. Also known as a dictyosome.

Grana: The lamellar stacks of chlorophyll-containing material in plant chloroplasts.

Griege carpet: A carpet in its unfinished state, i.e. before it has been scoured and dyed. The term also is used for woven fabrics in the unbleached and unfinished state.

Ground state: The state of minimum electronic energy of a molecule or atom.

Guanylate cyclase (GC): An enzyme (EC 4.6.2.1) catalyzing the transformation of guanosine triphosphate to guanosine 3':5'-cyclic phosphate.

H-Thymidine: Thymine deoxyribonucleoside: One of the four major nucleosides in DNA. ^{3}H-thymidine has been uniformly labeled with tritium, a radioactive form of hydrogen.

Haze: Fine dust, smoke or fine vapor reducing transparency of air.

Hemagglutination: The agglutination of red blood cells. Can be used as as a measurement of antibody concentration.

Hematocrit: The percentage of the volume of a blood sample occupied by cells.

Hematology: The medical specialty that pertains to the blood and blood-forming tissues.

Hemochromatosis: A disease characterized by pigmentation of the skin possibly due to inherited excessive absorption of iron.

Hemoglobin (Hb): The red, respiratory protein of the red blood cells, hemoglobin transports oxygen from the lungs to the tissues as oxy-hemoglobin (HbO_2) and returns carbon dioxide to the lungs as hemoglobin carbamate, completing the respiratory cycle.

Hemolysis: Alteration or destruction of red blood cells, causing hemoglobin to be released into the medium in which the cells are suspended.

Hepatectomy: Complete removal of the liver in an experimental animal.

Hepatic: Relating to the liver.

Hepatocyte: A liver cell.

Heterogeneous process: A chemical reaction involving reactants of more than one phase or state, such as one in which gases are absorbed into aerosol droplets, where the reaction takes place.

Heterologous: A term referring to donor and recipient cellular elements from different organisms, such as red blood cells from sheep and alveolar macrophage from rabbits.

Hexose monophosphate shunt: Also called the phosphogluconate oxidative pathway of glucose metabolism which affords a total combustion of glucose independent of the citric acid cycle. It is the important generator of NADPH necessary for synthesis of fatty acids and the operation of various enzymes. It serves as a source of ribose and 4- and 7-carbon sugars.

High-volume sampler (Hi-vol): Device for taking a sample of the particulate content of a large amount of air, by drawing air through a fiber filter at a typical rate of 2,000 m^3/24 hr (1.38 m^3/min), or as high as 2,880 m^3/24 hr (2 m^3/min).

Histamine: An amine derived from the amino acid, histidine. It is a powerful stimulant of gastric secretion and a constrictor of bronchial smooth muscle. It is a vasodilator and causes a fall in blood pressure.

Homogenate: Commonly refers to tissue ground into a creamy consistency in which the cell structure is disintegrated.

Host defense mechanism: Inherent means by which a biologic organism protects itself against infection, such as antibody formation, macrophage action, ciliary action, etc.

Host resistance: The resistance exhibited by an organism, such as man, to an infecting agent, such as a virus or bacteria.

Humoral: Relating to the extracellular fluids of the body, blood and lymph.

Hybrid: An organism descended from parents belonging to different varieties or species.

Hydrocarbons: A vast family of compounds containing carbon and hydrogen in various combinations; found especially in fossil fuels. Some contribute to photochemical smog.

Hydrolysis: Decomposition involving splitting of a bond and addition of the H and OH parts of water to the two sides of the split bond.

Hydrometeor: A product of the condensation of atmospheric water vapor (e.g. fog, rain, hail, snow).

Hydroxyproline: An amino acid found among the hydrolysis products of collagen.

Hygroscopic: Pertaining to a marked ability to accelerate the condensation of water vapor.

Hyperplasia: Increase in the number of cells in a tissue or organ excluding tumor formation.

Hyperplastic: Relating to hyperplasia; an increase in the number of cells.

Hypertrophy: Increase in the size of a tissue element, excluding tumor formation.

Hypertension: Abnormally elevated blood pressure.

Hypolimnia: Portions of a lake below the thermocline, in which water is stagnant and uniform in temperature.

Hypoxia: A lower than normal amount of oxygen in the air, blood or tissues

Immunoglobulin (Ig): A class of structurally related proteins consisting of two pairs of polypeptide chains. Antibodies are Ig's and all Ig's probably function as antibodies.

Immunoglobulin A (IgA): A type of antibody which comprises approximately 10 to 15 percent of the total amount of antibodies present in normal serum.

Immunoglobulin G (IgG): A type of antibody which comprises approximately 80 percent of the total amount of antibodies present in normal serum. Subfractions of IgG are fractions G_1, and G_2.

Immunoglobulin M (IgM): A type of antibody which comprises approximately 5 to 10 percent of the total amount of antibodies present in normal serum.

Impaction: An impinging or striking of one object against another; also, the force transmitted by this act.

Impactor: An instrument which collects samples of suspended particulates by directing a stream of the suspension against a surface, or into a liquid or a void.

Index of proliferation: Ratio of promonocytes to polymorphic monocytes in the blood.

Infarction: Sudden insufficiency of arterial or venous blood supply due to emboli, thrombi, or pressure.

Infectivity model: A testing system in which the susceptibility of animals to airborne infectious agents with and without exposure to air pollutants is investigated to produce information related to the possible effects of the pollutant on man.

Inflorescence: The arrangement and development of flowers on an axis; also, a flower cluster or a single flower.

Influenza A_2/Taiwan Virus: An infectious viral disease, believed to have originated in Taiwan, characterized by sudden onset, chills, fevers, headache, and cough.

Infrared: Light invisible to the human eye, between the wavelengths of 7×10^{-7} and 10^{-3} m (7000 and 10,000,000 A).

Infrared laser: A device that utilizes the natural oscillations of atoms or molecules to generate coherent electromagnetic radiation in the infrared region of the spectrum.

Infrared spectrometer: An instrument for measuring the relative amounts of radiant energy in the infrared region of the spectrum as a function of wavelength.

Ingestion: To take in for digestion.

In situ: In the natural or original position.

Instrumental averaging time: The time over which a single sample or measurement is taken, resulting in a measurement which is an average of the actual concentrations over that period.

Insult: An injury or trauma.

Intercostal: Between the ribs, especially of a leaf.

Interferant: A substance which a measurement method cannot distinguish completely from the one being measured, which therefore can cause some degree of false response or error.

Interferon: A macromolecular substance produced in response to infection with active or inactivated virus, capable of inducing a state of resistance.

Intergranular corrosion: A type of corrosion which takes place at and adjacent to grain boundaries, with relatively little corrosion of the grains.

Interstitial edema: An accumulation of an excessive amount of fluids in a space within tissues.

Interstitial pneumonia: A chronic inflammation of the interstitial tissue of the lung, resulting in compression of air cells.

Intraluminal mucus: Mucus that collects within any tubule.

Intraperitoneal injection: An injection of material into the serous sac that lines the abdominal cavity.

In utero: Within the womb; not yet born.

In vitro: Refers to experiments conducted outside the living organism.

In vivo: Refers to experiments conducted within the living organism.

Irradiation: Exposure to any form of radiation.

Ischemia: Local anemia due to mechanical obstruction (mainly arterial narrowing) of the blood supply.

Isoenzymes: Also called isozymes. One of a group of enzymes that are very similar in catalytic properties, but may be differentiated by variations in physical properties, such as isoelectric point or electrophoretic mobility. Lactic acid dehydrogenase is an example of an enzyme having many isomeric forms.

Isopleth: A line on a map or chart connecting points of equal value.

Jacobs-Hochheiser method: The original Federal Reference Method for NO_2, currently unacceptable for air pollution work.

Klebsiella pneumoniae: A species of rod-shaped bacteria found in soil, water, and in the intestinal tract of man and other animals. Certain types may be causative agents in pneumonia.

Kyphosis: An abnormal curvature of the spine, with convexity backward.

Lactate: A salt or ester of lactic acid.

Lactic acid (lactate) dehydrogenase (LDH): An enzyme (EC 1.1.1.27) with many isomeric forms which catalyzes the oxidation of lactate to pyruvate via transfer of H to NAD. Isomeric forms of LDH in the blood are indicators of heart damage.

Lamellar bodies: Arranged in plates or scales. One of the characteristics of Type II alveolar cells.

Lavage fluid: Any fluid used to wash out hollow organs, such as the lung.

Lecithin: Any of several waxy hygroscopic phosphatides that are widely distributed in animals and plants; they form colloidal solutions in water and have emulsifying, wetting and hygroscopic properties.

Legume: A plant with root nodules containing nitrogen fixing bacteria.

Lesion: A wound, injury or other more or less circumscribed pathologic change in the tissues.

Leukocyte: Any of the white blood cells.

Lewis base: A base, defined in the Lewis acid-base concept, is a substance that can donate an electron pair.

Lichens: Perennial plants which are a combination of two plants, an alga and a fungus, growing together in an association so intimate that they appear as one.

Ligand: Those molecules or anions attached to the central atom in a complex.

Light-fastness: The ability of a dye to maintain its original color under natural or indoor light.

Linolenic acid: An unsaturated fatty acid essential in nutrition.

Lipase: An enzyme that accelerates the hydrolysis or synthesis of fats or the breakdown of lipoproteins.

Lipids: A heterogeneous group of substances which occur widely in biological materials. They are characterized as a group by their extractability in nonpolar organic solvents.

Lipofuscin: Brown pigment granules representing lipid-containing residues of lysosomal digestion. Proposed to be an end product of lipid oxidation which accumulates in tissue.

Lipoprotein: Complex or protein containing lipid and protein.

Loading rate: The amount of a nutrient available to a unit area of body of water over a given period of time.

Locomotor activity. Movement of an organism from one place to another of its own volition.

Long-pathlength infrared absorption: A measurement technique in which a system of mirrors in a chamber is used to direct an infrared beam through a sample of air for a long distance (up to 2 km); the amount of infrared absorbed is measured to obtain the concentrations of pollutants present.

Lung compliance (C_L): The volume change produced by an increase in a unit change in pressure across the lung, i.e., between the pleural surface and the mouth.

Lycra: A spandex textile fiber created by E. I. du Pont de Nemours & Co., Inc., with excellent tensile strength, a long flex life and high resistance to abrasion and heat degradation. Used in brassieres, foundation garments, surgical hosiery, swim suits and military and industrial uses.

Lymphocytes: White blood cells formed in lymphoid tissue throughout the body, they comprise about 22 to 28 percent of the total number of leukocytes in the circulating blood and function in immunity.

Lymphocytogram: The ratio, in the blood, of lymphocyte with narrow cytoplasm to those with broad cytoplasm.

Lysosomes: Organelles found in cells of higher organisms that contain high concentrations of degradative enzymes and are known to destroy foreign substances that cells engulf by pinocytosis and phyocytosis. Believed to be a major site where proteins are broken down.

Lysozymes: Lytic enzymes destructive to cell walls of certain bacteria. Present in some body fluids, including tears and serum.

Macaca speciosa: A species of monkeys used in research.

Macrophage: Any large, ameboid, phagocytic cell having a nucleus without many lobes, regardless of origin.

Malaise: A feeling of general discomfort or uneasiness, often the first indication of an infection or disease.

Malate dehydrogenase: An enzyme (EC 1.1.1.37) with at least six isomeric forms that catalyze the dehydrogenation of malate to oxaloacetate or its decarboxylation (removal of a CO_2 group) to pyruvate. Malate, oxaloacetate, and pyruvate are intermediate components of biochemical pathways.

Mannitol: An alcohol derived from reduction of the sugar, fructose. Used in renal function testing to measure glomerular (capillary) filtration.

Manometer: An instrument for the measurement of pressure of gases or vapors.

Mass median diameter (MMD): Geometric median size of a distribution of particles based on weight.

Mass spectrometry (MS): A procedure for identifying the various kinds of particles present in a given substance, by ionizing the particles and subjecting a beam of the ionized particles to an electric or magnetic field such that the field deflects the particles in angles directly proportional to the masses of the particles.

Maximum flow (V_{max}): Maximum rate or expiration, usually expressed at 50 or 25 percent of vital capacity.

Maximum mid-expiratory flow rate (MMFR): The mean rate of expiratory gas flow between 25 and 75 percent of the forced expiratory vital capacity.

Mean (arithmetic): The sum of observations divided by sample size.

Median: A value in a collection of data values which is exceeded in magnitude by one-half the entries in the collection.

Mesoscale: Of or relating to meteorological phenomena from 1 to 100 kilometers in horizontal extent.

Messenger RNA: A type of RNA which conveys genetic information encoded in the DNA to direct protein synthesis.

Metaplasia: The abnormal transformation of an adult, fully differentiated tissue of one kind into a differentiated tissue of another kind.

Metaproterenol: A bronchodilator used for the treatment of bronchial asthma.

Metastases: The shifting of a disease from one part of the body to another; the appearance of neoplasms in parts of the body remote from the seat of the primary tumor.

Meteorology: The science that deals with the atmosphere and its phenomena.

Methemoglobin: A form of hemoglobin in which the normal reduced state of iron (Fe^{2+}) has been oxidized to Fe^{3+}. It contains oxygen in firm union with ferric (Fe^{3+}) iron and is not capable of exchanging oxygen in normal respiratory processes.

Methimazole: An anti-thyroid drug similar in action to propylthiouracil.

Methyltransferase: Any enzyme transferring methyl groups from one compound to another.

Microcoulometric: Capable of measuring millionths of coulombs used in electrolysis of a substance, to determine the amount of a substance in a sample.

Microflora: A small or strictly localized plant.

Micron: One-millionth of a meter.

Microphage: A small phagocyte; a polymorphonuclear leukocyte that is phagocytic.

Millimolar: One-thousandth of a molar solution. A solution of one-thousandth of a mole (in grams) per liter.

Minute volume: The minute volume of breathing; a product of tidal volume times the respiratory frequency in one minute.

Mitochondria: Organelles of the cell cytoplasm which contain enzymes active in the conservation of energy obtained in the aerobic part of the breakdown of carbohydrates and fats, in a process called respiration.

Mobile sources: Automobiles, trucks and other pollution sources which are not fixed in one location.

Modacrylic fiber: A manufactured fiber in which the fiber-forming substance is any long chain synthetic polymer composed of less than 85 percent but at least 35 percent by weight of acrylonitrite units.

Moeity: One of two or more parts into which something is divided.

Mole: The mass, in grams, numerically equal to the molecular weight of a substance.

Molecular correlation spectrometry: A spectrophotometric technique which is used to identify unknown absorbing materials and measure their concentrations by using preset wavelengths.

Molecular weight: The weight of one molecule of a substance obtained by adding the gram-atomic weights of each of the individual atoms in the substance.

Monocyte: A relatively large mononuclear leukocyte, normally constituting 3 to 7 percent of the leukocytes of the circulating blood.

Mordant: A substance which acts to bind dyes to a textile fiber of fabric.

Morphological: Relating to the form and structure of an organism or any of its parts.

Moving average: A procedure involving taking averages over a specific period prior to and including a year in question, so that successive averaging periods overlap; e.g. a three-year moving average would include data from 1967 through 1969 for the 1969 average and from 1968 through 1970 for 1970.

Mucociliary clearance: Removal of materials from the upper respiratory tract via ciliary action.

Mucociliary transport: The process by which mucus is transported, by ciliary action, from the lungs.

Mucosa: The mucous membrane; it consists of epithelium, lamina propria and, in the digestive tract, a layer of smooth muscle.

Mucous membrane: A membrane secreting mucus which lines passages and cavities communicating with the exterior of the body.

Murine: Relating to mice.

Mutagen: A substance capable of causing, within an organism, biological changes that affect potential offspring through genetic mutation.

Mutagenic: Having the power to cause mutations. A mutation is a change in the character of a gene (a sequence of base pairs in DNA) that is perpetuated in subsequent divisions of the cell in which it occurs.

Myocardial infarction: Infarction of any area of the heart muscle usually as a result of occlusion of a coronary artery.

Nares: The nostrils.

Nasopharyngeal: Relating to the nasal cavity and the pharynx (throat).

National Air Surveillance Network (NASN): Network of monitoring stations for sampling air to determine extent of air pollution; established jointly by federal and state governments.

Near ultraviolet: Radiation of the wavelengths 2000-4000 Angstroms.

Necrosis: Death of cells that can discolor areas of a plant or kill the entire plant.

Necrotic: Pertaining to the pathologic death of one or more cells, or of a portion of tissue or organ, resulting from irreversible damage.

Neonate: A newborn.

Neoplasm: An abnormal tissue that grows more rapidly than normal; synonymous with tumor.

Neoplasia: The pathologic process that results in the formation and growth of a tumor.

Neutrophil: A mature white blood cell formed in bone marrow and released into the circulating blood, where it normally accounts for 54 to 65 percent of the total number of leukocytes.

Ninhydrin: An organic reagent used to identify amino acids.

Nitramine: A compound consisting of a nitrogen attached to the nitrogen of amine.

Nitrate: A salt or ester of nitric acid (NO_3^-).

Nitrification: The principal natural source of nitrate in which ammonium (NH_4^+) ions are oxidized to nitrites by specialized microorganisms. Other organisms oxidize nitrites to nitrates.

Nitrite: A salt or ester of nitrous acid ($NO_2^=$).

Nitrocellulose: Any of several esters of nitric acid formed by its action on cellulose, used in explosives, plastics, varnishes and rayon; also called cellulose nitrate.

Nitrogen cycle: Refers to the complex pathways by which nitrogen-containing compounds are moved from the atmosphere into organic life, into the soil, and back to the atmosphere.

Nitrogen fixation: The metabolic assimilation of atmospheric nitrogen by soil microorganisms, which becomes available for plant use when the microorganisms die; also, industrial conversion of free nitrogen into combined forms used in production of fertilizers and other products.

Nitrogen oxide: A compound composed of only nitrogen and oxygen. Components of photochemical smog.

Nitrosamine: A compound consisting of a nitrosyl group connected to the nitrogen of an amine.

Nitrosation: Addition of a nitrosyl group.

N-Nitroso compounds: Compounds carrying the functional nitrosyl group.

Nitrosyl: A group composed of one oxygen and one nitrogen atom (-N=O).

Nitrosylhemoglobin (NOHb): The red, respiratory protein of erythrocytes to which a nitrosyl group is attached.

N/P Ratio: Ratio of nitrogen to phosphorous dissolved in lake water, important due to its effect on plant growth.

Nucleolus: A small spherical mass of material within the substance of the nucleus of a cell.

Nucleophilic: Having an affinity for atomic nuclei; electron-donating.

Nucleoside: A compound that consists of a purine or pyrimidine base combined with deoxyribose or ribose and found in RNA and DNA.

5'-Nucleotidase: An enzyme (EC 3.1.3.5) which hydrolyzes nucleoside 5'-phosphates into phosphoric acid (H_3PO_4) and nucleosides.

Nucleotide: A compound consisting of a sugar (ribose or deoxyribose), a base (a purine or a pyrimidine), and a phosphate; a basic structural unit of RNA and DNA.

Nylon: A generic name chosen by E. I. du Pont de Nemours & Co., Inc. for a group of protein-like chemical products classed as synthetic linear polymers; two main types are Nylon 6 and Nylon 66.

Occlusion: A point which an opening is closed or obstructed.

Olefin: An open-chain hydrocarbon having at least one double bond.

Olfactory: Relating to the sense of smell.

Olfactory epithelium: The inner lining of the nose and mouth which contains neural tissue sensitive to smell.

Oligotrophic: A body of water deficient in plant nutrients; also generally having abundant dissolved oxygen and no marked stratification.

Oribitals: Areas of high electron density in an atom or molecule.

Orlon: An acrylic fiber produced by E. I. du Pont de Nemours and Co., Inc., based on a polymer of acrylonitrite; used extensively for outdoor uses, it is resistant to chemicals and withstands high temperatures.

Osteogenic osteosarcoma: The most common and malignant of bone sarcomas (tumors). It arises from bone-forming cells and affects chiefly the ends of long bones.

Ovarian primordial follicle: A spheroidal cell aggregation in the ovary in which the primordial oocyte (immature female sex cell) is surrounded by a single layer of flattened follicular cells.

Oxidant: A chemical compound which has the ability to remove electrons from another chemical species, thereby oxidizing it; also, a substance containing oxygen which reacts in air to produce a new substance, or one formed by the action of sunlight on oxides of nitrogen and hydrocarbons.

Oxidation: An ion or molecule undergoes oxidation by donating electrons.

Oxidative deamination: Removal of the NH_2 group from an amino compound by reaction with oxygen.

Oxidative phosphorylation: The mitochondrial process by which "high-energy" phosphate bonds form from the energy released as a result of the oxidation of various substrates. Principally occurs in the tricarboxylic acid pathway.

Oxyhemoglobin: Hemoglobin in combination with oxygen. It is the form of hemoglobin present in arterial blood.

Ozone layer: A layer of the stratosphere from 20 to 50 km above the earth's surface characterized by high ozone content produced by ultraviolet radiation.

Ozone scavenging: Removal of O_3 from ambient air or plumes by reaction with NO, producing NO_2 and O_2.

Paired electrons: Electrons having opposite intrinsic spins about their own axes.

Parenchyma: The essential and distinctive tissue of an organ or an abnormal growth, as distinguished from its supportive framework.

Parenchymal: Referring to the distinguishing or specific cells of a gland or organ.

Partial pressure: The pressure exerted by a single component in a mixture of gases.

Particulates: Fine liquid or solid particles such as dust, smoke, mist, fumes or smog, found in the air or in emissions.

Pascal: A unit of pressure in the International System of Units. One pascal is equal to 7.4×10^{-3} torr. The pascal is equivalent to one newton per square meter.

Pathogen: Any virus, microorganism, or other substance causing disease.

Pathophysiological: Derangement of function seen in disease; alteration in function as distinguished from structural defects.

Peptide bond: The bond formed when two amino acids react with each other.

Percentiles: The percentage of all observations exceeding or preceding some point; thus, 90th percentile is a level below which will fall 90 percent of the observations.

Perfusate: A liquid, solution or colloidal suspension that has been passed over a special surface or through an appropriate structure.

Perfusion: Artificial passage of fluid through blood vessels.

Permanent-press fabrics: Fabrics in which applied resins contribute to the easy care and appearance of the fabric and to the crease and seam flat-
ness by reacting with the cellulose on pressing after garment manufacture.

Permeation tube: A tube which is selectively porous to specific gases.

Peroxidation: Refers to the process by which certain organic compounds are converted to peroxides.

Peroxyacetyl nitrate (PAN): Pollutant created by action of sunlight on hydrocarbons and NO_x in the air; an ingredient of photochemical smog.

pH: A measure of the acidity or alkalinity of a material, liquid, or solid. pH is represented on a scale of 0 to 14 with 7 being a neutral state, 0 most acid, and 14 most alkaline.

Phagocytosis: Ingestion, by cells such as macrophages, of other cells, bacteria, foreign particles, etc.; the cell membrane engulfs solid or liquid particles which are drawn into the cytoplasm and digested.

Phenotype: The observable characteristics of an organism, resulting from the interaction between an individual genetic structure and the environment in which development takes place.

Phenylthiourea: A crystalline compound, $C_7H_8N_2S$, that is bitter or tasteless depending on a single dominant gene in the tester.

Phlegm: Viscid mucus secreted in abnormal quantity in the respiratory passages.

Phosphatase: Any of a group of enzymes that liberate inorganic phosphate from phosphoric esters (E.C. sub-subclass 3.1.3).

Phosphocreatine kinase: An enzyme (EC 2.7.3.2) catalyzing the formation of creatine and ATP, its breakdown is a source of energy in the contraction of muscle; also called creatine phosphate.

Phospholipid: A molecule consisting of lipid and phosphoric acid group(s). An example is lecithin. Serves as an important structural factor in biological membranes.

Photochemical oxidants: Primary ozone, NO_2, PAN with lesser amounts of other compounds formed as products of atmospheric reactions involving organic pollutants, nitrogen oxides, oxygen, and sunlight.

Photochemical smog: Air pollution caused by chemical reaction of various airborne chemicals in sunlight.

Photodissociation: The process by which a chemical compound breaks down into simpler components under the influence of sunlight or other radiant energy.

Photolysis: Decomposition upon irradiation by sunlight.

Photomultiplier tube: An electron multiplier in which electrons released by photoelectric emission are multiplied in successive stages by dynodes that produce secondary emissions.

Photon: A quantum of electromagnetic energy.

Photostationary: A substance or reaction which reaches and maintains a steady state in the presence of light.

Photosynthesis: The process in which green parts of plants, when exposed to light under suitable conditions of temperature and water supply, produce carbohydrates using atmospheric carbon dioxide and releasing oxygen.

Phytotoxic: Poisonous to plants.

Phytoplankton: Minute aquatic plant life.

Pi π bonds: Bonds in which electron density is not symmetrical about a line joining the bonded atoms.

Pinocytotic: Refers to the cellular process (pinocytosis) in which the cytoplasmic membrane forms invaginations in the form of narrow channels leading into the cell. Liquids can flow into these channels and the membrane pinches off pockets that are incorporated into the cytoplasm and digested.

Pitting: A form of extremely localized corrosion that results in holes in the metal. One of the most destructive forms of corrosion.

Pituary: A stalk-like gland near the base of the brain which is attached to the hypothalmus. The anterior portion is a major repository for for hormones that control growth, stimulate other glands, and regulate the reproductive cycle.

Placenta: The organ in the uterus that provides metabolic interchange between the fetus and mother.

Plasmid: Replicating unit, other than a nucleus gene, that contains nucleoprotein and is involved in various aspects of metabolism in organisms; also called paragenes.

Plasmolysis: The dissolution of cellular components, or the shrinking of plant cells by osmotic loss of cytoplasmic water.

Plastic: A plastic is one of a large group of organic compounds synthesized from cellulose, hydrocarbons, proteins or resins and capable of being cast, extruded, or molded into various shapes.

Plasticizer: A chemical added to plastics to soften, increase malleability or to make more readily deformable.

Platelet (blood): An irregularly-shaped disk with no definite nucleus; about one-third to one-half the size of an erythrocyte and containing no hemoglobin. Platelets are more numerous than leukocytes, numbering from 200,000 to 300,000 per cu. mm. of blood.

Plethysmograph: A device for measuring and recording changes in volume of a part, organ or the whole body; a body plethysmograph is a chamber apparatus surrounding the entire body.

Pleura: The serous membrane enveloping the lungs and lining the walls of the chest cavity.

Plume: Emission from a flue or chimney, usually distributed stream-like downwind of the source, which can be distinguished from the surrounding air by appearance or chemical characteristics.

Pneumonia (interstitial): A chronic inflammation of the interstitial tissue of the lung, resulting in compression of the air cells. An acute, infectious disease.

Pneumonocytes: A nonspecific term sometimes used in referring to types of cells characteristic of the respiratory part of the lung.

Podzol: Any of a group of zonal soils that develop in a moist climate, especially under coniferous or mixed forest.

Point source: A single stationary location of pollutant discharge.

Polarography: A method of quantitative or qualitative analysis based on current-voltage curves obtained by electrolysis of a solution with steadily increasing voltage.

Pollution gradient: A series of exposure situations in which pollutant concentrations range from high to low.

Polyacrylonitrile: A polymer made by reacting ethylene oxide and hydrocyanic acid. Dynel and Orlon are examples.

Polyamides: Polymerization products of chemical compounds which contain amino ($-NH_2$) and carboxyl ($-COOH$) groups. Condensation reactions between the groups form amides ($-CONH_2$). Nylon is an example of a polyamide.

Polycarbonate: Any of various tough transparent thermoplastics characterized by high impact strength and high softening temperature.

Polycythemia: An increase above the normal in the number of red cells in the blood.

Polyester fiber: A man-made or manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of an ester of a dihydric alcohol and terephthalic acid. Dacron is an example.

Polymer: A large molecule produced by linking together many like molecules.

Polymerization: In fiber manufacture, converting a chemical monomer (simple molecule) into a fiber-forming material by joining many like molecules into a stable, long-chain structure.

Polymorphic monocyte: Type of leukocyte with a multi-lobed nucleus.

Polymorphonuclear leukocytes: Cells which represent a secondary non-specific cellular defense mechanism. They are transported to the lungs from the bloodstream when the burden handled by the alveolar macrophages is too large.

Polysaccharides: Polymers made up of sugars. An example is glycogen which consists of repeating units of glucose.

Polystyrene: A thermoplastic plastic which may be transparent, opaque, or translucent. It is light in weight, tasteless and odorless, it also is resistant to ordinary chemicals.

Polyurethane: Any of various polymers that contain NHCOO linkages and are used especially in flexible and rigid foams, elastomers and resins.

Pores of Kohn: Also known as interalveolar pores; pores between air cells. Assumed to be pathways for collateral ventilation.

Precipitation: Any of the various forms of water particles that fall from the atmosphere to the ground, rain, snow, etc.

Precursor: A substance from which another substance is formed; specifically, one of the anthropogenic or natural emissions or atmospheric constituents which reacts under sunlight to form secondary pollutants comprising photochemical smog.

Probe: In air pollution sampling, the tube or other conduit extending into the atmosphere to be sampled, through which the sample passes to treatment, storage and/or analytical equipment.

Proline: An amino acid, $C_5H_9NO_2$, that can be synthesized from glutamate by animals.

Promonocyte: An immature monocyte not normally seen in the circulating blood.

Proteinuria: The presence of more than 0.3 gm of urinary protein in a 24-hour urine collection.

Pulmonary: Relating to the lungs.

Pulmonary edema: An accumulation of excessive amounts of fluid in the lungs.

Pulmonary lumen: The spaces in the interior of the tubular elements of the lung (bronchioles and alveolar ducts).

Pulmonary resistance: Sum of airway resistance and viscous tissue resistance.

Purine bases: Organic bases which are constituents of DNA and RNA, including adenine and guanine.

Purulent: Containing or forming pus.

Pyrimidine bases: Organic bases found in DNA and RNA. Cytosine and thymine occur in DNA and cytosine and uracil are found in RNA.

QRS: Graphical representation on the electrocardiogram of a complex of three distinct waves which represent the beginning of ventricular contraction.

Rainout: Removal of particles and/or gases from the atmosphere by their involvement in cloud formation (particles act as condensation nuclei, gases are absorbed by cloud droplets), with subsequent precipitation.

Rayleigh scattering: Coherent scattering in which the intensity of the light of wavelength g, scattered in any direction making an angle with the incident direction, is directly proportional to $1 + \cos^2 r$ and inversely proportional to g^4.

Reactive dyes: Dyes which react chemically with cellulose in fibers under alkaline conditions. Also called fiber reactive or chemically reactive dyes.

Reduction: Acceptance of electrons by an ion or molecule.

Reference method (RM): For NO_2, an EPA-approved gas-phase chemiluminescent analyzer and associated calibration techniques; regulatory specifications are described in Title 40, Code of Federal Regulations, Part 50, Appendix F. Formerly, Federal Reference Method.

Residual capacity: The volume of air remaining in the lungs after a maximum expiratory effort; same as residual volume.

Residual volume (RV): The volume of air remaining in the lungs after a maximal expiration. RV = TLC - VC

Resin: Any of various solid or semi-solid amorphous natural organic substances, usually derived from plant secretions, which are soluble in organic solvents but not in water; also any of many synthetic substances with similar properties used in finishing fabrics, for permanent press shrinkage control or water repellency.

Ribosomal RNA: The most abundant RNA in a cell and an integral constituent of ribosomes.

Ribosomes: Discrete units of RNA and protein which are instrumental in the synthesis of proteins in a cell. Aggregates are called polysomes.

Runoff: Water from precipitation, irrigation or other sources that flows over the ground surface to streams.

Sclerosis: Pathological hardening of tissue, especially from overgrowth of fibrous tissue or increase in interstitial tissue.

Selective leaching: The removal of one element from a solid alloy by corrosion processes.

Septa: A thin wall dividing two cavities or masses of softer tissue.

Seromucoid: Pertaining to a mixture of watery and mucinous material such as that of certain glands.

Serum antiprotease: A substance, present in serum, that inhibits the activity of proteinases (enzymes which destroy proteins).

Sigma (s) bonds: Bonds in which electron density is symmetrical about a line joining the bonded atoms.

Silo-filler's disease: Pulmonary lesion produced by oxides of nitrogen produced by fresh silage.

Single breath nitrogen elimination rate: Percentage rise in nitrogen fraction per unit of volume expired.

Single breath nitrogen technique: A procedure in which a vital capacity inspiration of 100 percent oxygen is followed by examination of nitrogen in the vital capacity expirate.

Singlet state: The highly-reactive energy state of an atom in which certain electrons have unpaired spins.

Sink: A reactant with or absorber of a substance.

Sodium arsenite: Na_3AsO_3, used with sodium hydroxide in the absorbing solution of a 24-hour integrated manual method for NO_2.

Sodium dithionite: A strong reducing agent (a supplier of electrons).

Sodium metabisulfite: $Na_2S_2O_5$, used in absorbing solutions of NO_2 analysis methods.

Sorb: To take up and hold by absorption or adsorption.

Sorbent: A substance that takes up and holds another by absorption or adsorption.

Sorbitol dehydrogenase: An enzyme that interconverts the sugars, sorbitol and fructose.

Sorption: The process of being sorbed.

Spandex: A manufactured fiber in which the fiber forming substance is a long chain synthetic elastomer composed of at least 85 percent of a segmented polyurethane.

Spectrometer: An instrument used to measure radiation spectra or to determine wavelengths of the various radiations.

Spectrophotometry: A technique in which visible, UV, or infrared radiation is passed through a substance or solution and the intensity of light transmitted at various wavelengths is measured to determine the spectrum of light absorbed.

Spectroscopy: Use of the spectrometer to determine concentrations of an air pollutant.

Spermatocytes: A cell destined to give rise to spermatozoa (sperm).

Sphingomyelins: A group of phospholipids found in brain, spinal cord, kidney and egg yolk.

Sphygomenometer: An apparatus, consisting of a cuff and a pressure gauge, which is used to measure blood pressure.

Spirometry: Also called pneometry. Testing the air capacity of the lungs with a pneometer.

Spleen: A large vascular organ located on the upper left side of the abdominal cavity. It is a blood-forming organ in early life. It is a storage organ for red corpuscles and because of the large number of macrophages, acts as a blood filter.

Sputum: Expectorated matter, especially mucus or mucopurulent matter expectorated in diseases of the air passages.

Squamous: Scale-like, scaly.

Standard deviation: Measure of the dispersion of values about a mean value. It is calculated as the positive square root of the average of the squares of the individual deviations from the mean.

Standard temperature and pressure: $0^{o}C$, 760 mm mercury.

<u>Staphylococcus aureus</u>: A spherically-shaped, infectious species of bacteria found especially on nasal mucous membrane and skin.

Static lung compliance (C_{Lstat}): Measure of lung's elastic recoil (volume change resulting from change in pressure) with no or insignificant airflow.

Steady state exposure: Exposure to air pollutants whose concentration remains constant for a period of time.

Steroids: A large family of chemical substances comprising many hormones and vitamins and having large ring structures.

Stilbene: An aromatic hydrocarbon $C_{14}H_{12}$ used as a phosphor and in making dyes.

Stoichiometric factor: Used to express the conversion efficiency of a non-quantitative reaction, such as the reaction of NO_2 with azo dyes in air monitoring methods.

Stoma: A minute opening or pore (plural is stomata).

Stratosphere: That region of the atmosphere extending from 11 km above the surface of the earth to 50 km. At 50 km above the earth temperature rises to a maximum of 0^oC.

Streptococcus pyogenes: A species of bacteria found in the human mouth, throat and respiratory tract and in inflammatory exudates, blood stream, and lesions in human diseases. It causes formation of pus or even fatal septicemias.

Stress corrosion cracking: Cracking caused by simultaneous presence of tensile stress and a specific corrosive medium. The metal or alloy is virtually unattached over most of its surface, while fine cracks progress through it.

Strong interactions: Forces or bond energies holding molecules together. Thermal energy will not disrupt the formed bonds.

Sublobular hepatic necrosis: The pathologic death of one or more cells, or of a portion of the liver, beneath one or more lobes.

Succession: The progressive natural development of vegetation towards a climax, during which one community is gradually replaced by others.

Succinate: A salt of succinic acid involved in energy production in the citric acid cycle.

Sulfadiazine: One of a group of sulfa drugs. Highly effective against pneumococcal, staphlococcal, and streptococcal infections.

Sulfamethazine: An antibacterial agent of the sulfonamide group, active against homolytic streptococci, staphytococci, pneumococci and meningococci.

Sulfanilimide: A crystalline sulfonamide ($C_6H_8N_2O_2S$), the amide of sulfanilic acid and parent compound of most sulfa drugs.

Sulfhydryl group: A chemical radical consisting of sulfur and hydrogen which confers reducing potential to the chemical compound to which it is attached (-SH).

Sulfur dioxide (SO_2): Colorless gas with pungent odor released primarily from burning of fossil fuels, such as coal, containing sulfur.

Sulfur dyes: Used only on vegetable fibers, such as cottons. They are insoluble in water and must be converted chemically in order to be soluble. They are resistant (fast) to alkalies and washing and fairly fast to sunlight.

Supernatant: The clear or partially clear liquid layer which separates from the homogenate upon centrifugation or standing.

Surfactant: A substance capable of altering the physiochemical nature of surfaces, such as one used to reduce surface tension of a liquid.

Symbiotic: A close association between two organisms of different species in which at least one of the two benefits.

Synergistic: A relationship in which the combined action or effect of two or more components is greater than that of the components acting separately.

Systolic: Relating to the rhythmical contraction of the heart.

Tachypnea: Very rapid breathing.

Terragram (Tg): One million metric tons, 10^{12} grams.

Teratogenesis: The disturbed growth processes resulting in a deformed fetus.

Teratogenic: Causing or relating to abnormal development of the fetus.

Threshold: The level at which a physiological or psychological effect begins to be produced.

Thylakoid: A membranous lamella of protein and lipid in plant chloroplasts where the photochemical reactions of photosynthesis take place.

Thymidine: A nucleoside ($C_{10}H_{14}N_2O_5$) that is composed of thymine and deoxyribose; occurs as a structural part of DNA.

Tidal volume (V_T): The volume of air that is inspired or expired in a single breath during regular breathing.

Titer: The standard of strength of a volumetric test solution. For example, the titration of a volume of antibody-containing serum with another volume containing virus.

Tocopherol: a-d-tocopherol is one form of Vitamin E prepared synthetically. The a form exhibits the most biological activity. It is an antioxidant and retards rancidity of fats.

Torr: A unit of pressure sufficient to support a 1 mm column of mercury; 760 torr = 1 atmosphere.

Total lung capacity (TLC): The sum of all the compartments of the lung, or the volume of air in the lungs at maximum inspiration.

Total suspended particulates (TSP): Solid and liquid particles present in the atmosphere.

Trachea: Commonly known as the windpipe, a cartilaginous air tube extending from the larnyx (voice box) into the thorax (chest) where it divides, serving as the entrance to each of the lungs.

Transaminase: Aminotransferase; an enzyme transferring an amino group from an a-amino acid to the carbonyl carbon atom of an a-keto acid.

Transmissivity (UV): The percent of ultraviolet radiation passing through a a medium.

Transmittance: The fraction of the radiant energy entering an absorbing layer which reaches the layer's further boundary.

Transpiration: The process of the loss of water vapor from plants.

Triethanolamine: An amine, $(HOCH_2CH_2)_3N$, used in the absorbing solution of one analytical method for NO_2.

Troposphere: That portion of the atmosphere in which temperature decreases rapidly with altitude, clouds form, and mixing of air masses by convection takes place. Generally extends to about 7 to 10 miles above the earth's surface.

Type 1 epithelial cells: Squamous cells which provide a continuous lining to the alveolar surface.

Type I pneumonocytes: Pulmonary surface epithelial cells.

Type II pneumonocytes: Great alveolar cells.

Ultraviolet: Light invisible to the human eye of wavelengths between $4x10^{-7}$ and $5x10^{-9}$ m (4000 to 50A).

Urea-formaldehyde resin: A compound composed of urea and formaldehyde in an arrangement that conveys thermosetting properties.

Urobilinogen: One of the products of destruction of blood cells; found in the liver, intestines and urine.

Uterus: The womb; the hollow muscular organ in which the impregnated ovum (egg) develops into the fetus.

Vacuole: A minute space in any tissue.

Vagal: Refers to the vagus nerve. This mixed nerve arises near the medulla oblongata and passes down from the cranial cavity to supply the larynx, lungs, heart, esophagus, stomach, and most of the abdominal viscera.

Valence: The number of electrons capable of being bonded or donated by an atom during bonding.

Van Slyke reactions: Reaction of primary amines, including amino acids, with nitrous acid, yielding molecular nitrogen.

Variance: A measure of dispersion or variation of a sample from its expected value; it is usually calculated as the square root a sum of squared deviations about a mean divided by the sample size.

Vat dyes: Dyes which have a high degree of resistance to fading by light, NO_x and washing. Widely used on cotton and viscose rayon. Colors are brilliant and of almost any shade. The name was originally derived from their application in a vat.

Venezuelan equine encephalomyelitis: A form of equine encephalomyelitis found in parts of South America, Panama, Trinidad, and the United States, and caused by a virus. Fever, diarrhea, and depression are common. In man, there is fever and severe headache after an incubation period of 2 to 5 days.

Ventilatory volume (V_E): The volume of gas exchanged between the lungs and the atmosphere that occurs in breathing.

Villus: A projection from the surface, especially of a mucous membrane.

Vinyl chloride: A gaseous chemical suspected of causing at least one type of cancer. It is used primarily in the manufacture of polyvinyl chloride, a plastic.

Viscose rayon: Filaments of regenerated cellulose coagulated from a solution of cellulose xanthate. Raw materials can be cotton linters or chips of spruce, pine, or hemlock.

Visible region: Light between the wavelengths of 4000-8000 Å.

Visual range: The distance at which an object can be distinguished from background.

Vital capacity: The greatest volume of air that can be exhaled from the lungs after a maximum inspiration.

Vitamin E: Any of several fat-soluble vitamins (tocopherols), essential in nutrition of various vertibrates.

Washout: The capture of gases and particles by falling raindrops.

Weak interactions: Forces, electrostatic in nature, which bind atoms and/or molecules to each other. Thermal energy will disrupt the interaction. Also called van der Waal's forces.

Wet deposition: The process by which atmospheric substances are returned to earth in the form of rain or other precipitation.

Wheat germ lipase: An enzyme, obtained from wheat germ, which is capable of cleaving a fatty acid from a neutral fat; a lipolytic enzyme.

X-ray fluorescence spectrometry: A nondestructive technique which utilizes the principle that every element emits characteristic x-ray emissions when excited by high-energy radiation.

Zeolites: Hydrous silicates analogous to feldspars, occurring in lavas and various soils.

Zooplankton: Minute animal life floating or swimming weakly in a body of water.