External Review Draft No. 2
February 1981

Draft
Do Not Quote or Cite

Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume III

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

*

NOTE TO READER

The Environmental Protection Agency is revising the existing criteria documents for particulate matter and sulfur oxides (PM/SO_x) under Sections 108 and 109 of the Clean Air Act, 42 U.S.C. §§ 7408, 7409. The first external review draft of a revised combined PM/SO_x criteria document was made available for public comment in April 1980.

The Environmental Criteria and Assessment Office (ECAO) filled more than 4,000 public requests for copies of the first external review draft. Because all those who received copies of the first draft from ECAO will be sent copies of the second external review draft, there is no need to resubmit a request.

To facilitate public review, the second external review draft will be released in five volumes on a staggered schedule as the volumes are completed. Volume I (containing Chapter 1), Volume II (containing Chapters 2, 3, 4, and 5), Volume III (containing Chapters 6, 7, and 8), Volume IV (containing Chapters 9 and 10), and Volume V (containing Chapters 11, 12, 13, and 14) will be released during January-February, 1981. As noted earlier, they will be released as volumes are completed, not in numerical order by volume.

The first external review draft was announced in the Federal Register of April 11, 1980 (45 FR 24913). ECAO received and reviewed 89 comments from the public, many of which were quite extensive. The Clean Air Scientific Advisory Committee (CASAC) of the Science Advisory Board also provided advice and comments on the first external review draft at a public meeting of August 20-22, 1980 (45 FR 51644, August 4, 1980).

As with the first external review draft, the second external review draft will be submitted to CASAC for its advice and comments. ECAO is also soliciting written comments from the public on the second external review draft and requests that an original and three copies of all comments be submitted to: Project Officer for PM/SO_x, Environmental Criteria and Assessment Office, MD-52, U.S. Environmental Protection Agency, Research Triangle Park, N. C. 27711. To facilitate ECAO's consideration of comments on this lengthy and complex document, commentators with extensive comments should index the major points which they intend ECAO to address, by providing a list of the major points and a cross-reference to the pages in the document. Comments should be submitted during the forthcoming comment period, which will be announced in the Federal Register once all volumes of the second external review draft are available.

External Review Draft No. 2
February 1981

Draft
Do Not Quote or Cite

Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume III

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

*

PREFACE

This document is a revision of External Review Draft No. 1, Air Quality Criteria for Particulate Matter and Sulfur Oxides, released in April 1980. Comments received during a public comment period from April 15, 1980 through July 31, 1980, and recommendations made by the Clean Air Scientific Advisory Committee in August have been addressed here.

Volume III contains Chapters 6, 7, and 8, which cover atmospheric chemistry and dispersion modeling, acidic deposition, and vegetation effects of sulfur oxides and particulate matter. A Table of Contents for Volumes I, II, III, IV, and V follows.

*

CONTENTS

VOLUMES I, II, III, IV, AND V

		Page
Volume I.		
Chapter 1.	Executive Summary	1-1
Volume II.		
Chapter 2.	Physical and Chemical Properties of Sulfur Oxides and Particulate Matter	2-1
Chapter 3.	Techniques for the Collection and Analysis of Sulfur Oxides, Particulate Matter, and Acidic Precipitation	3-1
Chapter 4.	Sources and Emissions	4-1
Chapter 5.	Environmental Concentrations and Exposure	5-1
Volume III.		
Chapter 6.	Atmospheric Transport, Transformation and Deposition	6-1
Chapter 7.	Acidic Deposition	7-1
Chapter 8.	Effects on Vegetation	8-1
Volume IV.		
Chapter 9.	Effects on Visibility and Climate	9-1
Chapter 10.	Effects on Materials	10-1
Volume V.		
Chapter 11.	Respiratory Deposition and Biological Fate of Inhaled Aerosols and SO_2	11-1
Chapter 12.	Toxicological Studies	12-1
Chapter 13.	Controlled Human Studies	13-1
Chapter 14.	Epidemiology Studies on the Effects of Sulfur Oxides and Particulate Matter on Human Health	14-1

*

CONTENTS

		Page
6.	ATMOSPHERIC TRANSPORT, TRANSFORMATION AND DEPOSITION	6-1
	6.1 INTRODUCTION	6-1
	6.2 CHEMICAL TRANSFORMATION PROCESSES	6-3
	6.2.1 Chemical Transformation of SO_2 and Particulate Matter	6-3
	6.2.2 Field Measurements on the Rate of SO_2 Oxidation	6-4
	6.3 PHYSICAL REMOVAL PROCESSES	6-4
	6.3.1 Dry Deposition	6-7
	6.3.1.1 Sulfur Dioxide Dry Deposition	6-9
	6.3.1.2 Particle Dry Deposition	6-10
	6.3.2 Precipitation Scavenging	6-13
	6.3.2.1 SO_2 Wet Removal	6-16
	6.3.2.2 Particle Wet Removal	6-19
	6.4 TRANSPORT AND DIFFUSION	6-20
	6.4.1 The Planetary Boundary Layer	6-24
	6.4.2 Horizontal Transport and Pollutant Residence Times.	6-26
	6.5 AIR QUALITY SIMULATION MODELING	6-29
	6.5.1 Gaussian Plume Modeling Techniques	6-30
	6.5.2 Long Range Air Pollution Modeling	6-31
	6.5.3 Model Evaluation and Data Bases	6-35
	6.5.4 Atmospheric Budgets	6-36
	6.6 SUMMARY	6-36
	6.7 REFERENCES	6-38
7.	ACIDIC DEPOSITION	7-1
	7.1 INTRODUCTION	7-1
	7.1.1 Overview of the Problem	7-1
	7.1.2 Ecosystem Dynamics	7-5
	7.2 CAUSES OF ACIDIC PRECIPITATION	7-12
	7.2.1 Emissions of Sulfur and Nitrogen Oxides	7-12
	7.2.2 Transport of Nitrogen and Sulfur Oxides	7-14
	7.2.3 Formation	7-20
	7.2.3.1 Composition and pH of Precipitation	7-21
	7.2.3.2 Geographic Extent of Acidic Precipitation	7-28
	7.2.4 Acidic Deposition	7-34
	7.3 EFFECTS OF ACIDIC DEPOSITION	7-36
	7.3.1 Aquatic Ecosystems	7-36
	7.3.1.1 Acidification of lakes and streams	7-36
	7.3.1.2 Effects on decomposition	7-45
	7.3.1.3 Effect on primary producers and primary productivity	7-48
	7.3.1.4 Effects on invertebrates	7-54
	7.3.1.5 Effects on fish	7-57
	7.3.1.6 Effects on vertebrates other than fish	7-64
	7.3.2 Terrestrial Ecosystems	7-68
	7.3.2.1 Effects on soils	7-68
	7.3.2.2 Effects on vegetation	7-78
	7.3.2.2.1 Direct effects on vegetation	7-79
	7.3.2.3 Effects on Human Health	7-89
	7.3.2.4 Effects of Acidic Precipitation on Materials	7-89

7.4 ASSESSMENT OF SENSITIVE AREAS 7-92
7.4.1 Aquatic Ecosystems 7-92
7.4.2 Terrestrial Ecosystems 7-98
7.5 SUMMARY 7-102
7.6 REFERENCES 7-106

8. EFFECTS ON VEGETATION 8-1
8.1 GENERAL INTRODUCTION AND APPROACH 8-1
8.2 REACTION OF PLANTS TO SO_2 EXPOSURES 8-2
8.2.1 Introduction to Terminology 8-2
8.2.2 Wet and Dry Deposition of Sulfur Compounds on Leaf Surfaces 8-3
8.2.3 Routes and Methods of Entry Into the Plant 8-3
8.2.4 Cellular and Biochemical Changes 8-6
8.2.5 Acute Foliar Injury 8-6
8.2.6 Chronic Foliar Injury 8-8
8.2.7 Classification of Plant Sensitivity to SO_2 8-9
8.2.8 Beneficial "Fertilizer" Effects 8-12
8.2.9 Foliar Versus Whole Plant Responses 8-14
8.3 DOSE-RESPONSE RELATIONSHIPS - SO_2 8-16
8.4 EFFECTS OF MIXTURES OF SO_2 AND OTHER POLLUTANTS INCLUDING PARTICULATE MATTER 8-42
8.4.1 Sulfur Dioxide and Ozone 8-42
8.4.2 Sulfur and Nitrogen Dioxide 8-46
8.4.3 Sulfur Dioxide and Hydrogen Fluoride 8-46
8.4.4 Sulfur Dioxide, Nitrogen Dioxide and Ozone 8-46
8.4.5 Summary 8-48
8.5 EFFECTS OF NON-POLLUTANT ENVIRONMENTAL FACTORS ON SO_2 PLANT EFFECTS 8-48
8.5.1 Temperature 8-48
8.5.2 Relative Humidity 8-49
8.5.3 Light 8-49
8.5.4 Edaphic Factors 8-50
8.5.5 SO_2 and Biotic Plant Pathogen Interactions 8-50
8.6 PLANT EXPOSURE TO PARTICULATE MATTER 8-51
8.6.1 Deposition Rates 8-51
8.6.2 Routes and Methods of Entry Into Plants 8-52
8.7 REACTION OF PLANTS TO PARTICULATE EXPOSURE 8-53
8.7.1 Symptomatology of Particle-Induced Injury 8-53
8.7.2 Classification of Plant Sensitivity--Particles 8-56
8.8 DOSE-RESPONSE RELATIONSHIPS--PARTICULATES 8-57
8.9 INTERACTIVE EFFECTS ON PLANTS WITH THE ENVIRONMENT--PARTICULATE MATTER 8-58
8.9.1 Biotic Interactions 8-58
8.10 EFFECTS OF SULFUR DIOXIDE AND PARTICULATES ON NATURAL ECOSYSTEMS 8-58
8.10.1 Sulfur Dioxide in Terrestrial Ecosystems 8-59
8.10.2 Ecosystem Response to Sulfur Dioxide 8-62
8.10.3 Response of Natural Ecosystems to Particulate Matter 8-67
8.11 SUMMARY 8-69
8-12 REFERENCES 8-73

*

LIST OF FIGURES

Figure		Page
6-1	Pathway processes of airborne pollutants	6-2
6-2	Predicted deposition velocities at 1 m for μ_*=30 cms^{-1} and particle densities of 1,4, and 11.5 g cm^{-3}	6-14
6-3	Basic factors influencing precipitation scavenging	6-15
6-4	Abundance of dissolved SO_2 species as a function of pH (25°C)	6-18
6-5	Relationship between rain scavenging rates and particle size	6-22
6-6	Percentages of aerosol particles of various sizes removed by precipitation scavenging	6-23
6-7	Estimated residence times for select pollutant species and their associated horizontal transport scale	6-27
6-8	Trajectory modeling approaches	6-33
7-1	The nitrogen cycle. Organic phase shaded	7-9
7-2	Law of tolerence	7-11
7-3	Historical patterns of fossil fuel consumption in the United States	7-13
7-4	Forms of coal usage in the United States	7-15
7-5a	Trends in emissions of sulfur dioxides	7-16
7-5b	Trends in emissions of nitrogen oxides	7-16
7-6	Point sources of sulfur oxides emissions over 100 tons per year.	7-17
7-7	Point sources of nitrogen oxides emissions over 100 tons per year	7-18
7-8	Trends in mean annual concentrations of sulfate, ammonium, and nitrate in precipitation	7-22
7-9	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 (◇,○), Pennsylvania (Δ), and Virginia (□)	7-26
7-10	Seasonal variations in pH (A) and ammonium and nitrate concentrations (B) in wet-only precipitation at Gainesville, Florida	7-27
7-11	Seasonal variation of precipitation pH in the New York Metropolitan Area	7-30
7-12	History of acidic precipitation at various sites in and adjacent to State of New York	7-31
7-13	Location of acidic precipitation monitoring stations	7-33
7-14	Annual mass transfer rates of sulfate expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand	7-35
7-15	Schematic representation of the hydrogen ion cycle	7-38
7-16	pH and calcium concentrations in lakes in norther and northwestern Norway sampled as part of the regional survey of 1975, in lakes in northwestern Norway sampled in 1977 (o) and in lakes in southernmost and southeastern Norway sampled in 1974 (o)	7-42
7-17	The pH value and sulfur loads in lake waters with extremely sensitive surroundings (curve 1) and with slightly less sensitive surroundings (curve 2)	7-43

*

7-18 Total dissolved Al as a function of pH level in lakes in acidified areas in Europe and North America..... 7-44
7-19 pH levels in Little Moose Lake, Adirondack region of New York State, at a depth of 3 meters and at the lake outlet..... 7-46
7-20 Numbers of phytoplankton species in 60 lakes having different pH values on the Swedish West Coast, August 1976..... 7-50
7-21 Percentage distribution of phytoplankton species and their biomasses..... 7-51
7-22 The number of species of crustacean zooplankton observed in 57 lakes during a synoptic survey of lakes in southern Norway... 7-55
7-23 Frequency distribution of pH and fish population status in Adirondack Mountain lakes greater than 610 meters elevation..... 7-59
7-24 Frequency distribution of pH and fish population status in 40 Adirondack lakes greater than 610 meters elevation, surveyed during the period 1929-1937 and again in 1975..... 7-60
7-25 Norwegian salmon fishery statistics for 68 unacidified and 7 acidified rivers..... 7-61
7-26 Showing the exchangeable ions of a soil with pH 7, the soil solution composition, and the replacement of Na^+ and H^+ from acid rain..... 7-69
7-27 Regions in North America with lakes that are sensitive to acidification by acid precipitation by virtue of their underlying bedrock characteristics..... 7-94
7-28 Equivalent percent composition of major ions in Adirondack lake surface waters (215 lakes) sampled in June 1975..... 7-96
7-29 Percent frequency distribution of sulfate concentrations in surface water from lakes in sensitive regions..... 7-97
7-30 Soils of the Eastern United States sensitive to acid rainfall... 7-100

8-1 A conceptual model of potential responses by plants following exposure to various doses of sulfur dioxide..... 8-4
8-2 Exposure thresholds for minimum, maximum and average sensitivity of 33 plant species to visible foliar injury by SO_2..... 8-11
8-3 Map of the United States indicating major areas of sulfur deficient soils..... 8-13
8-4 Conceptual model of the factors involved in air pollution effects (dose-response) on vegetation..... 8-19
8-5 Percentage of plant species visibly injured as a function of peak, 1-hr, and 3-hr SO_2 concentrations..... 8-21
8-6 Regression of yield response vs. transformed dose (ppm hr) for controlled exposures using field chambers (zero and positive effects excluded from regression analysis)..... 8-37
8-7 Regression of yield effects vs. transformed dose (ppm hr) for laboratory and greenhouse studies using agricultural, ornamental, and native herbs..... 8-38
8-8 Yield responses vs. SO_2 dose for Norway spruce (Keller, 1980) and white pine (Linzon, 1971)..... 8-40
8-9 The sulfur cycle..... 8-60

LIST OF TABLES

Table		Page
6-1	Field measurements on the rates of SO_2 oxidation in plumes	6-5
6-2	Average dry deposition velocity of SO_2 by surface type	6-9
6-3	Laboratory measurements of deposition velocities of particles	6-11
6-4	Field measurements of deposition velocities of particles	6-12
6-5	Predicted particle deposition velocities	6-16
6-6	Field measurements of scavenging coefficients of particles	6-21
6-7	Summary of long range transport air pollution models	6-34
7-1	Composition of ecosystems	7-7
7-2	Deposition of sulfuric and nitric acids in precipitation in eastern North America	7-23
7-3	Mean pH values in the New York metropolitan area	7-29
7-4	Storm type classification	7-29
7-5	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)	7-39
7-6	pH levels identified in field surveys as critical to long-term survival of fish populations	7-62
7-7	Changes in aquatic biota likely to occur with increasing acidity	7-65
7-8	Summary of effects on aquatic organisms associated with a range in pH	7-66
7-9	Potential effects of acid precipitation on soils	7-70
7-10	Types of direct, visible injury reported in response to acidic wet deposition	7-80
7-11	Thresholds for visible injury and growth effects associated with experimental studies of wet deposition of acidic substances (after Jacobson, 1980a,b)	7-83
7-12	Lead and copper concentration and pH of water from pipes carrying outflow from Hinckley Basin and Hanns and Steele Creek Basin, near Amsterdam, New York	7-90
7-13	Composition of rain and hoarfrost at Headingley, Leeds	7-92
7-14	The sensitivity to acid precipitation based on: buffer capacity against pH-change, retention of H^+, and adverse effects on soils	7-99
8-1	Relationship of biochemical response to visual symptoms of plant injury	8-7
8-2	Sulfur dioxide concentrations causing visible injury to various sensitivity groupings of vegetation	8-10
8-3	Summary of studies reporting results of SO_2 exposures using exposure systems and/or chambers over plants under field conditions	8-23
8-4	Summary of studies reporting results of SO_2 exposure under laboratory conditions for agronomic and horticultural crops	8-25
8-5	The degree of injury of eastern white pine observed at various distances from the Sudbury smelters for 1953-63	8-29

*

8-6 Summary of studies reporting results of SO_2 exposure under laboratory conditions for various tree species..... 8-30
8-7 Dose-response information summarized from literature pertaining to native plants as related to foliar, yield and specific effects by increasing SO_2 dose..... 8-33
8-8 Effects of mixtures of SO_2 and O_3 on plants..... 8-44
8-9 Effects of mixtures of SO_2 and NO_2 on plants..... 8-47
8-10 Plants sensitive to heavy metals, arsenic, and boron as accumulated in soils and typical symptoms expressed..... 8-55

7. ACIDIC DEPOSITION

7.1 INTRODUCTION

The occurrence of acidic precipitation in many regions of the United Sates, Canada, northern Europe, Taiwan and Japan has become a major environmental concern. Acidic precipitation in the Adirondack Mountains of New York State, in the eastern Precambrian Shield area of Canada, in southern Norway and in southwest Sweden has been associated with the acidification of waters in ponds, lakes and streams with a resultant disappearance of animal and plant life. Acidic precipitation (rain and snow), also is believed to have the potential for leaching elements from sensitive soils, causing direct and indirect injury to forests. It also has the potential for damaging monuments and buildings made of stone, for corroding metals and for deteriorating paint.

The story of acidic precipitation is an ever-changing one. New information concerning the phenomenon is forthcoming nearly every day. The sections that follow emphasize the effects of wet deposition of sulfur and nitrogen oxides and their products on aquatic and terrestrial ecosystems. Dry deposition also plays an important role, but contributions by this process have not been quantified. Because sulfur and nitrogen oxides are so closely linked in the formation of acidic precipitation, no attempt has been made to limit the discussion which follows to the main topic of this document, sulfur oxides.

7.1.1 Overview of the Problem

The generally held hypothesis is that sulfur and nitrogen compounds are largely responsible for the acidity of precipitation. The emissions of the sulfur and nitrogen compounds involved in acidification are attributed chiefly to the combustion of fossil fuels. Emissions may occur at ground level, as from automobile exhausts, or from stacks of 1000 feet or more in height. Emissions from natural sources are also involved; however, in highly industrialized areas, emissions from man-made sources well exceed those from natural sources. In the eastern United States the highest emissions of sulfur oxides are from electric power generators using coal, while in the West, emissions of nitrogen oxides, chiefly from automotive sources, predominate.

The fate of sulfur and nitrogen oxides, as well as other pollutants emitted into the atmosphere, depends on their dispersion, transport, transformation and deposition. Sulfur and nitrogen oxides may be deposited locally or transported long distances from the emission sources. Therefore, residence time in the atmosphere will be brief if the emissions are deposited locally or may extend to days or even weeks if long range transport occurs. The chemical form in which emissions ultimately reach the receptor is determined by the complex chemical transformations that take place between the emission sources and the receptor. Long range transport over distances of hundreds or even thousands of miles allows time for a greater number of chemical transformations to occur.

Sulfates and nitrates are among the products of the chemical transformations of sulfur and nitrogen oxides. Ozone and other photochemical oxidants are believed to be involved in

*
the chemical processes that form them. When sulfates and nitrates combine with atmospheric water, dissociated forms of sulfuric (H_2SO_4) and nitric (HNO_3) acids result. When these acids are brought to earth in rain and snow, acidic precipitation occurs. Because of long range transport, acidic precipitation in a particular state or region can be the result of emissions from sources in states or regions many miles away, rather than from local sources. To date, however, the complex nature of the chemical transformation processes has not made it possible to demonstrate a direct cause and effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation.

Acidic precipitation is arbitrarily defined as precipitation with a pH less than 5.6. This value has been selected because precipitation formed in a geochemically clean environment would have a pH of approximately 5.6 due to the combining of carbon dioxide with air to form carbonic acid.

Acidity of solutions is determined by the concentration of hydrogen ions (H^+) present and is expressed in terms of pH units--the negative logarithm of the concentration of hydrogen ions. The pH scale ranges from 0 to 14, with a value of 7 representing a neutral solution. Solutions with values less than 7 are acidic, while values greater than 7 are basic. Because pH is a logarithmic scale, a change of one unit represents a tenfold change in acidity, hence pH 3 is ten times as acidic as pH 4. Currently the acidity of precipitation in the northeastern United States normally ranges from pH 3.0 to 5.0; in other regions of the United States precipitation episodes with a pH as low as 3.0 have been reported. For comparison, the pH of some familiar substances are: cow's milk, 6.6; tomato juice, 4.3; cola (soft drink) 2.8, and lemon juice, 2.3.

The pH of precipitation can vary from event to event, from season to season and from geographical area to geographical area. Substances in the atmosphere can cause the pH to shift by making it more acidic or more basic. Dust and debris swept up in small amounts from the ground into the atmosphere may become components of precipitation. In the West and Midwest soil particles tend to be more basic, but in the eastern United States they tend to be acidic. Gaseous ammonia from decaying organic matter makes precipitation more acidic, so in areas where there are large stockyards or other sources of organic matter, acidic precipitation would be more likely to occur.

In the eastern United States sulfur oxide emissions are greater than nitrogen oxides, therefore, sulfates are greater contributors to the formation of acids in precipitation in this region. The ratio between the two emissions, however, has been decreasing. Sulfate concentrations are greater in summer than in winter in the eastern United States. In California, however, around some of the larger cities, nitrates contribute more to the formation of acidity in rainfall. In coastal areas sea spray strongly influences percipitation chemistry by contributing calcium, potassium, chlorine and sulfates. In the final analysis, the pH of precipitation is a measure of the relative contributions of all of these components.

*

The impact of acidic precipitation on lakes, streams, ponds, forests, fields and manmade objects, therefore, is not the result of a single, or even of several precipitation events, but the result of continued additions of acids or acidifying substances over time. When did precipitation become acidic? Some scientists state that it began with the industrial revolution and the burning of large amounts of coal; others say it began in the United States with the introduction of tall stacks in power plants in the 1950's; other scientists disagree completely and state that rain has always been acidic. In other words, no definitive answer to the question exists at the present time, nor is there data to indicate with any accuracy pH trends in precipitation. The pH of rain has not been continuously monitored in the United States for any period of time, so no data exist. In Scandinavia, on the other hand, the pH of rain has been monitored for many years, therefore a determination of the time of origin can be made.

Though acidic precipitation (wet deposition) is usually emphasized, it is not the only process by which acids or acidifying substances are added to bodies of water or to the land. Dry deposition also occurs. During wet deposition substances such as sulfur and nitrogen oxides are scavenged by precipitation (rain and snow) and deposited on the surface of the earth. Dry deposition processes include gravitational sedimentation of particles, impaction of aerosols and the sorption and absorption of gases by objects at the earth's surface or by the soil or water. Gases, particles and solid and liquid aerosols can be removed by both wet and dry deposition. Dew, fog and frost are also involved in the deposition processes but do not strictly fall into the category of wet or dry deposition. Dry deposition processes are not as well understood as wet deposition at the present time, however, all of the deposition processes contribute to the gradual accumulation of acidic or acidifying substances in the environment. In any event, percipitation at the present time is acidic and has been associated with changes in ponds, lakes and streams that are considered by humans to be detrimental to their welfare.

The most visible changes associated with acidic deposition, that is both wet and dry processes, are those observed in the lakes and streams of the Adirodack Mountains in New York State, the Pre-cambrian Shield areas of Canada and in the Scandinavian countries. In these regions the pH of the fresh water bodies has decreased, causing changes in animal and plant populations. The most readily observable has been the decrease in fish populations.

The chemistry of fresh waters is determined primarily by the geological structure (soil system and bedrock) of the lake or stream catchment basin, by the ground cover and by land use. Near coastal areas (up to 100 miles) marine salts also may be important in determining the chemical composition of the stream, river or lake.

Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition plus the same factors--the soil system of the drainage basin, the canopy effects of the ground cover and the composition of the waterbed bedrock--that determine the chemical composition of fresh water bodies. The capability, however, of a lake and its drainage basin to neutralize incoming acidic substances is determined largely by the composition of the bedrocks.

*

Soft water lakes, those most sensitive to additions of acidic substances, are usually found in areas with igneous bedrock which contributes few solids to the surface waters, whereas hard waters contain large concentrations of alkaline earths (chiefly bicarbonates of calcium and sometimes magnesium) derived from limestones and calcareous sandstones in the drainage basin. Alkalinity is associated with the increased capacity of lakes to neutralize or buffer the incoming acids. The extent to which acidic precipitation contributes to the acidification process has yet to be determined.

The disappearance of fish populations from freshwater lakes and streams is usually one of the most readily observable signs of lake acidification. Death of fish in acidified waters has been attributed to the modification of a number of physiological processes by a change in pH. Two patterns of pH change have been observed. The first involves a sudden short-term drop in pH and the second, a gradual decrease in pH with time. Sudden short-term drops in pH often result from a winter thaw or the melting of the snow pack in early spring and the release of the acidic constituents of the snow into the water. Fish may be killed at pH levels above those normally causing death.

A gradual decrease in pH, particularly below 5, can interfere with reproduction and spawning of fish until elimination of the population occurs. In some lakes, aluminum mobilization in fresh waters at a pH below 5 has resulted in fish mortality .

Although the disappearance of and/or reductions in fish populations are usually emphasized as significant results of lake and stream acidification, changes of equal or greater importance are the effects on other aquatic organisms ranging from waterfowl to bacteria. Organisms at all tropic (feeding) levels in the food web appear to be affected. Species reduction in number and diversity may occur, biomass (total number of living organisms in a given volume of water) may be altered and processes such as primary production and decomposition impaired.

Primary production and decomposition are the bases of the two major food webs (grazing and detrital) within an ecosystem by which energy is passed along from one organism to another through a series of steps of eating and being eaten. Green plants, through the process of photosynthesis, are the primary energy producers in the grazing web, while bacteria initiate the detrital food web by feeding on dead organic matter. Disruption of either of these two food webs results in a decrease in the supply of minerals and nutrients, interferes with their cycling and also reduces energy flow within the affected ecosystems. Acidification of lakes and streams affects both these processes when alteration of the species composition and structure of the pondweed and algae plant communities occurs due to a slowing down in the rate of microbial decomposition.

At present there are no documented observations or measurements of changes in natural terrestrial ecosystems that can be directly attributed to acidic precipitation. The information available is an accumulation of the results of a wide variety of controlled research

*
approaches largely in the laboratory, using in most instances some form of "simulated" acidic rain, frequently dilute sulfuric acid. The simulated "acid rains" have deposited hydrogen (H^+), sulfate ($SO_4^=$) and nitrate (NO_3^-) ions on vegetation and have caused nicrotic lesions in a wide variety of plants species under greenhouse and laboratory conditions. Such results must be interpreted with caution, however, because the growth and morphology of leaves under greenhouse conditions are often not typical of field conditions. Based on laboratory studies, the sensitivity of plants to acidic deposition seems to be associated with the wettability of leaf surfaces. The shorter the time of contact, the lower the resulting dose and the less likelihood of injury.

Soils may become gradually acidified from an influx of hydrogen (H^+) ions. Leaching of the mobilizable forms of mineral nutrients may occur. The rate of leaching is determined by the buffering capacity of the soil and the amount and composition of precipitation. Unless the buffering capacity of the soil is strong and/or the salt content of precipitation is high, leaching will in time result in acidification. At present there are no studies showing this process has occurred because of acidic precipitation.

Damage to monuments and buildings made of stone, corrosion of metals and deterioration of paint can result from acidic precipitation. Because sulfur compounds are a dominant component of acidic precipitation and are deposited during dry deposition also, the effects resulting from the two processes cannot be distinguished. In addition, the deposition of sulfur compounds on stone surfaces provides a medium for microbial growth that can result in deterioration.

Human health effects due to the acidification of lakes and rivers have been postulated. Fish in acidified water may contain toxic metals mobilized due to the acidity of the water. Drinking water may contain toxic metals or leach lead from the pipes bringing water into the homes. Humans eating contaminated fish or drinking contaminated water could become ill. No instances of these effects having occurred have been documented.

Several aspects of the acidic precipitation problem remain subject to debate because exisitng 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 nitrogen and sulfur 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 relative contribution of wet and dry deposition to the acidification of lakes and streams.

7.1.2 Ecosystem Dynamics

The emission of sulfur and nitrogen oxides into the atmosphere, their transformation, transport and deposition, either as acidic precipitation or in dry form, as well as the

*
responses of aquatic and terrestrial ecosystems to acidic deposition are all natural phenomena that have been in existence as long as humans can remember. Environmental problems arise because the natural systems are being overloaded by emissions from the combustion of fossil fuels from anthropogenic sources.

Life on the planet Earth depends on the movement of energy and minerals through the biosphere, that thin layer of life surrounding the earth. The living systems (forest, grasslands, cultivated fields, lakes, rivers, estuaries and oceans) within the biosphere obtain energy from the sun, nutrients from the earth's crust, the lithosphere, gases from the atmosphere and water from the hydrosphere. All of the living systems are interdependent. Energy and nutrients move from one to another. The living systems together with their physical environment, the lithosphere, hydrosphere and atmosphere, make up the ecosystem that is the planet Earth (Billings, 1978; Boughey, 1971; Odum, 1971; Smith, 1980).

Ecosystems are basically energy processing systems "whose components have evolved together over a long period of time. The boundaries of the system are determined by the environment, that is, by what forms of life can be sustained by the environmental conditions of a particular region. Plant and animal populations within the system represent the objects through which the system functions." (Smith, 1980)

Ecosystems are composed of biotic (living) and abiotic (non-living) components. The biotic component consists of: (a) producers, green plants that capture the energy of the sun; (b) consumers that utilize the food stored by the producers for their energy; and (c) the decomposers who break down dead organic matter and convert it into inorganic compounds again. (See Table 7-1). The abiotic components are the soil matrix, sediment, particulate matter, dissolved organic matter and nutrients in aquatic systems, and dead or inactive organic matter in terrestrial systems (See Table 7-1) (Billings, 1978; Boughey, 1971; Smith, 1980).

Ecosystems are open systems that receive both abiotic (gases, nutrients and radient energy) and biotic contributions from their environment and in turn contribute energy, water, gases and nutrients. Energy flows through the system while water, gases and nutrients are usually recycled and fed back into the system and to some extent control its functioning. Populations are the structural elements of the ecosystem through which energy flows and nutrients cycle (Smith, 1980).

Energy from the sun is the driving force in ecosystems. If the sun's energy were cut off all ecosystems would cease to function. The energy of the sun is captured by green plants through the process of photosynthesis and stored in plant tissues. This stored energy is passed along through ecosystems by a series of feeding steps, known as food chains, in which organisms eat and are eaten. Energy flows through ecosystems in two major food chains, the grazing food chain and the detrital food chain. The amount of energy that passes through the two food chains varies from community to community. The detrital food chain is dominant in most terrestrial and shallow-water ecosystems. The grazing food chain may be dominant in deep-water aquatic ecosystems (Smith, 1980). The two fundamental processes involved in these two

*

TABLE 7-1. COMPOSITION OF ECOSYSTEMS

Component	Description
Biotic (biological):	
Individuals	Plants, animals (man), and microorganisms. These are either producers, consumers, or decomposers.
Producers	Green plants.
Consumers	Herbivores, carnivores.
Decomposers	Macroorganisms (mites, earthworms, millipedes, and slugs) and microorganisms (bacteria and fungi).
Populations	Groups of interbreeding organisms of the same kind, producers, consumers or decomposers, occupying a particular habitat.
Communities	Interacting populations linked together by their responses to a common environment.
Abiotic (physical):	
Energy	Radiation, light, temperature, and heat flow.
Water	Liquid, ice, etc.
Atmosphere	Gases and wind.
Fire	Combustion.
Topography	Surface features.
Geological strata	Soil, a complex system. Nutrients. (Minerals)

*
food chains are photosynthesis, the capture of energy from the sun by green plants, and decomposition, the final dissipation of energy and the reduction of organic matter into inorganic nutrients.

In addition to the flow of energy, the existence of the living world depends upon the circulation of nutrients through the ecosystems. Both energy and nutrients move through the ecosystem as organic matter. It is not possible to separate one from the other. Both influence the abundance of organisms, the metabolic rate at which they live and the complexity and structure of the ecosystem (Smith, 1980). Nutrients, unlike energy, after moving from the living to the non-living return to the living components of the ecosystem in a perpetual cycle. It is through the cycling of nutrients that plants and animals obtain the minerals necessary for their existence.

The gaseous and sedimentary cycles are the two basic types of nutrient or biogeochemical cycles. The gaseous cycles involve carbon, oxygen and nitrogen. Water, also, is sometimes considered as belonging to the gaseous cycle. In the gaseous cycles, the main nutrient reservoir is the atmosphere and the ocean. In the sedimentary cycle, to which phosphorus belongs, the soil and rocks of the earth's crust is the reservoir. The sulfur cycle is a combination of the two cycles because it has reservoirs in the atmosphere and the earth's crust.

Nitrogen, sulfur and water cycles are involved in acidic deposition. Nitrogen, through the agency of plants (chiefly legumes and blue green algae), moves from the atmosphere to the soil and back (see Figure 7-1). Human intrusion into the nitrogen cycles include the addition of nitrogen oxides to the atmosphere and nitrates to aquatic ecosystems. Sulfur enters the atmosphere from volcanic eruptions, from the surface of the ocean, from gases released in the decomposition processes and from the combustion of fossil fuels (see Chapter 8 for details). Both the nitrogen and sulfur cycles have been overloaded by the combustion of fossil fuels by man. For these cycles to function, an ecosystem must possess a number of structured relationships among its components. By changing the amounts of nitrogen and sulfur moving through the cycles, humans have perturbed or upset the structured relationships that have existed for thousands of years and altered the movement of the elements through the ecosystems. The pathways the elements take through the system depend upon the interaction of the populations and their relationships to each other in terms of eating and being eaten.

Change is one of the basic characteristics of our environment. Weather changes from day to day, temperatures rise and fall, rains come and go, soils erode, volcanoes erupt, and winds blow across the land. These are natural phenomena. Significant environmental changes also result when human beings clear forests, build cities and factories, and dam rivers. All of these environmental changes influence the organisms that live in the ecosystems where the changes are occurring (Moran et al., 1980).

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 the basic biotic responses of an ecosystem to

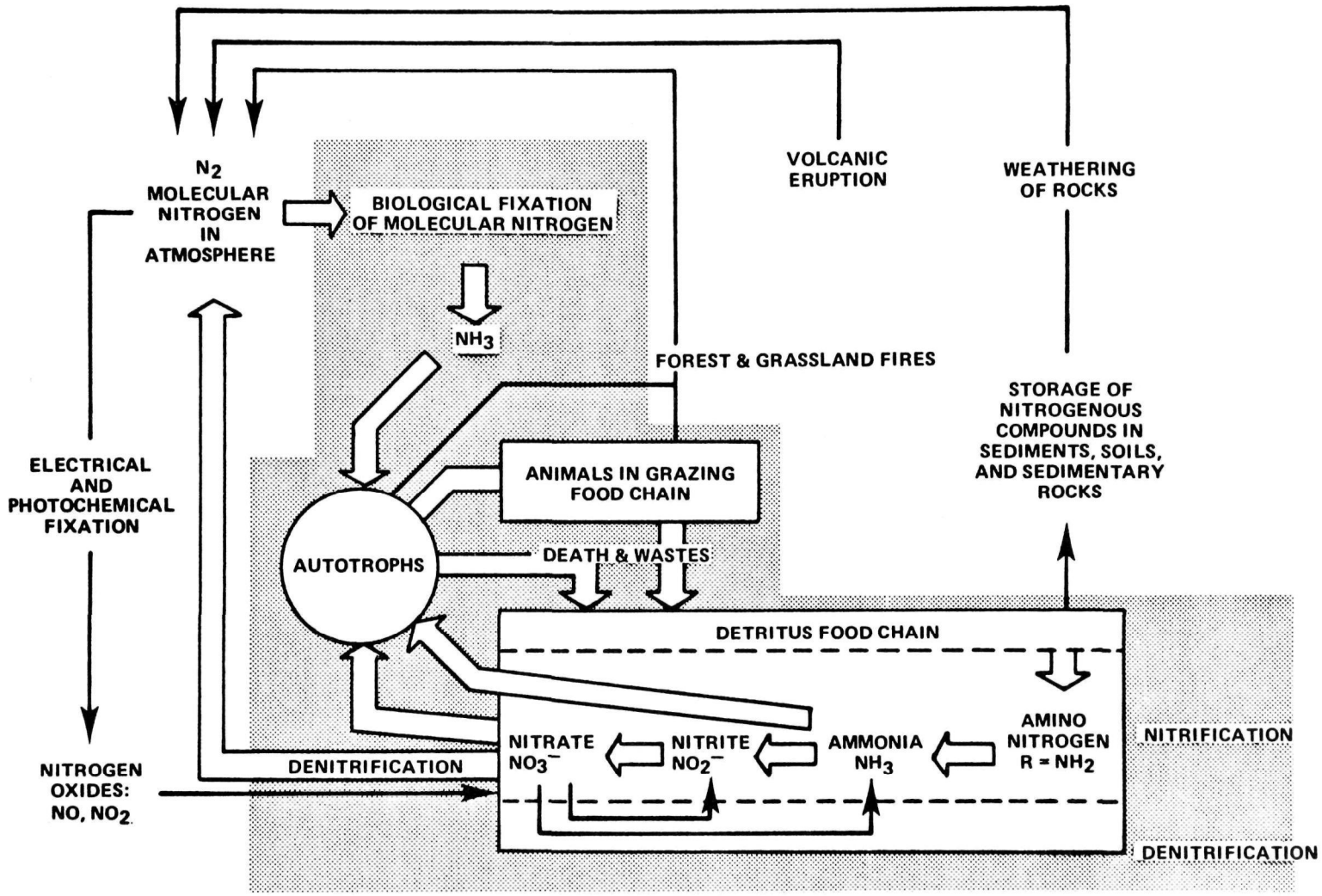


Figure 7-1. The nitrogen cycle. Organic phase shaded.

*
disturbances such as caused by environmental stress (Woodwell, 1970; Woodwell, 1962; Odum, 1965; Garrett, 1967). These responses to disturbance are (1) removal of sensitive organisms at the species and subspecies level due to differential kill; (2) reduction in the number of plants and animals (standing crop); (3) inhibition of growth or reduction in productivity; (4) disruption of food chains; (5) return to a previous state of development; and (6) modification in the rates of nutrient cycling.

Ecosystems can respond to environmental changes or perturbations only through the response of the populations of organisms of which they are composed (Smith, 1980). Species of organisms sensitive to environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior. The success with which an organism copes with environmental changes is determined by its ability to produce reproducing offspring. The size and success of a population depends upon the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that adjust best contribute most to future generations because they have the greatest number of progeny in the population (Smith, 1980; Billings, 1978; Woodwell, 1970, 1962; Odum, 1971).

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition or polluted air follows the principle of limiting factors (Billings, 1978; Odum, 1971; Moran et al., 1980; Smith, 1980). According to this principle, for each physical factor in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and in extreme cases a species (Billing, 1978; Smith, 1980; Boughey, 1971; Odum, 1971; Moran et al., 1980). The range of tolerance (see Figure 7-2) of an organism may be broad for one factor and narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth or growth form of an organism. Limiting factors are, therefore, factors which, when scarce or overabundant, limit the growth, reproduction and/or distribution of an organism (Billings, 1978; Smith, 1980; Boughey, 1971; Odum, 1971; Moran et al., 1980). The increasing acidity of water in lakes and streams is such a factor.

Organisms can exist only within their range of tolerance. Some populations of organisms, annual plants, insects, and mice, for example, respond rapidly. They increase in numbers under favorable conditions and decline rapidly when conditions are unfavorable. Populations of other organisms, such as trees and wolves, fluctuate less in response to favorable or unfavorable conditions. Ecosystems that contain both types of populations are more stable bacause they are able to absorb changes and still persist because the structure of the ecosystem permits it to persist even though populations within it fluctuate widely in response to environmental changes (Smith 1980; Holling, 1973). Other ecosystems are resistant; their structure enables

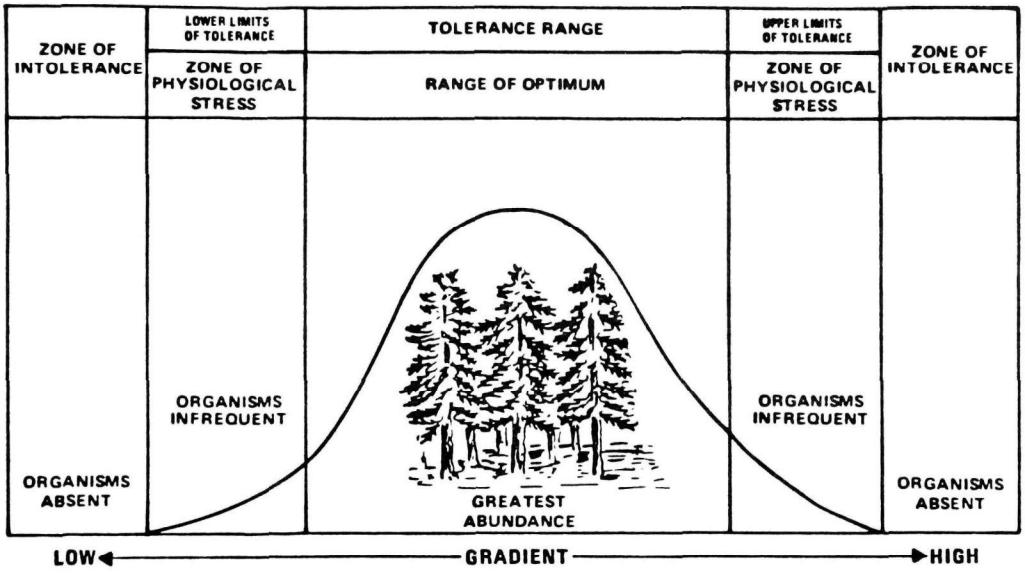


Figure 7-2. Law of tolerance.

Source: Adapted from Smith (1980).

*
them to resist changes. Typically, most resistant ecosystems have large living components, trees for example, and store nutrients and energy in the standing biomass. Such resistant systems, such as forests, once highly disturbed are very slow in returning to their original state (Smith, 1980).

Aquatic ecosystems which lack components in which energy and nutrients may be stored for long periods of time usually are not very resistant to environmental changes (Smith, 1980). For example, an influx of pollutants such as effluents from sewage disrupts the system because more nutrients enter the system than it can handle. However, since the nutrients are not retained or recycled within the system it returns to its original state in a relatively short time after the perturbation is removed.

No barriers exist between the various environmental factors or between an organism or biotic community and its environment. Because an ecosystem is a complex of interacting components, if one factor is changed, almost all will change eventually. "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. 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" (Billings, 1978).

Continued or severe perturbation of an ecosystem can overcome its resistance or prevent its recovery with the result that the original ecosystem will be replaced by a new system. In the Adirondack Mountains of New York State, in eastern Canada and parts of Scandinavia the original aquatic ecosystems have been and are continuing to be replaced by ecosystems different from the original due to acidification of the aquatic habitat. Forest ecosystems appear to be more resistant because, thus far, changes due to stress from acidifying substances have not been detected. The sections that follow discuss the response of aquatic and terrestrial ecosystems to stressing or perturbation by acidic deposition. Sulfur and nitrogen oxide emissions, their transformation, transport and deposition in acidic form is elucidated in the context of the ecosystem processes that were discussed above.

7.2 CAUSES OF ACIDIC PRECIPITATION

7.2.1 Emissions of Sulfur and Nitrogen Oxides

The generally held hypothesis is that increased emissions of sulfur and nitrogen compounds are largely responsible for the acidity of precipitation (Smith, 1872; Bolin et al., 1972; Likens, 1976). The emissions of the sulfur and nitrogen compounds involved in the acidification are attributed chiefly to the combustion of fossil fuels. Emissions from natural sources can also be involved; however, in highly industrialized areas emissions from man-made sources usually exceed those from natural sources (see Chapter 4). In the eastern United States 90 percent of the sulfur oxides in the atmosphere are from anthropogenic sources (see Figure 7-6).

Since 1900 there has been a nearly exponential increase in the consumption of coal, gas, and oil in the United States (see Figure 7-3). Although the total consumption of coal has not increased greatly since about 1925, the consumption of oil and gas has continued to rise

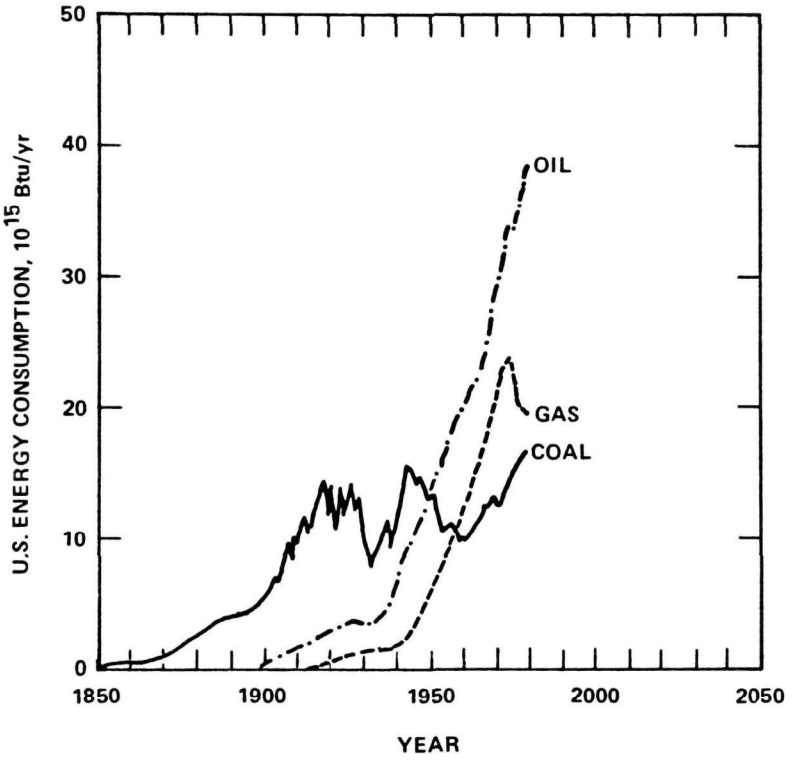


Figure 7-3. Historical patterns of fossil fuel consumption in the United States

Source: Adapted from Hubbert (1976).

precipitously, thus overshadowing coal as the dominant fuel source during the past 50 years (Hubert, 1976). Within this overall increase in fossil-fuel use there have been shifts in the pattern of consumption. Whereas formerly a considerable proportion of coal was used for transportation and heating, these functions have since been taken over by oil and gas. Coal is now predominantly devoted to electric power generation (Figure 7-4). In fact, electric power generation is the primary factor accounting for an absolute increase in coal consumption over the past two decades. (The decline in the use of coal in the 1930s was due to the general economic depression, and the decline in the 1950s was due to the availability of relatively inexpensive oil and gas.) Approximately 550 MM tons (National Research Council, 1978) were used per year during 1918-1928 compared to 672 MM tons/year during 1979 (Hamilton, 1980). 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.

These changes in the pattern of fuel use have been accompanied by changes in the pattern of pollutant emissions. Figure 7-5A and 7-5B illustrate the rise since 1940 in emissions of sulfur and nitrogen oxides, the primary gaseous pollutants resulting from the combustion of fossil fuels. Although there has been a net increase in both categories, the more consistent rise has been in emissions of nitrogen oxides. Almost all (93 percent) emissions of sulfur oxides in the United States arise from stationary point sources, principally industrial and power plant stacks. Nitrogen oxide pollutants, on the other hand, originate about equally from transportation (mobile) sources and from stationary sources, which include not only industrial and power plants, but residential and institutional heating equipment as well (U.S. Environmental Protection Agency, 1978). (see Chapter 5 of Air Quality Criteria for Oxides of Nitrogen for a more detailed discussion.)

The geographic distributions of sources of the gaseous precursors of acidic precipitation are depicted in Figures 7-6 and 7-7. Clearly, the dominant sources of sulfur oxides in the United States are in the eastern half of the country, particularly the northeastern quadrant. Major nitrogen oxide sources also show a tendency to be concentrated somewhat in the northeastern quadrant of the country. Chapter 4 should be consulted for a more detailed account of the sources and emissions of sulfur oxides.

7.2.2 Transport of Nitrogen and Sulfur Oxides

Among the factors influencing the formation as well as the location where acidic deposition occurs is the long-range transport of nitrogen and sulfur oxides. Neither the gases nor their transformation products always remain near the sources from which they have been emitted. They may be transported for long distances downwind (Altshuller and McBean, 1979; Pack et al., 1978; Cogbill and Likens, 1974).

The geographic picture of the problem of acidic precipitation in North America can be better understood in the light of some information on prevailing wind patterns. Winds transport the precursors of acidic precipitation from their points of origin to areas where the

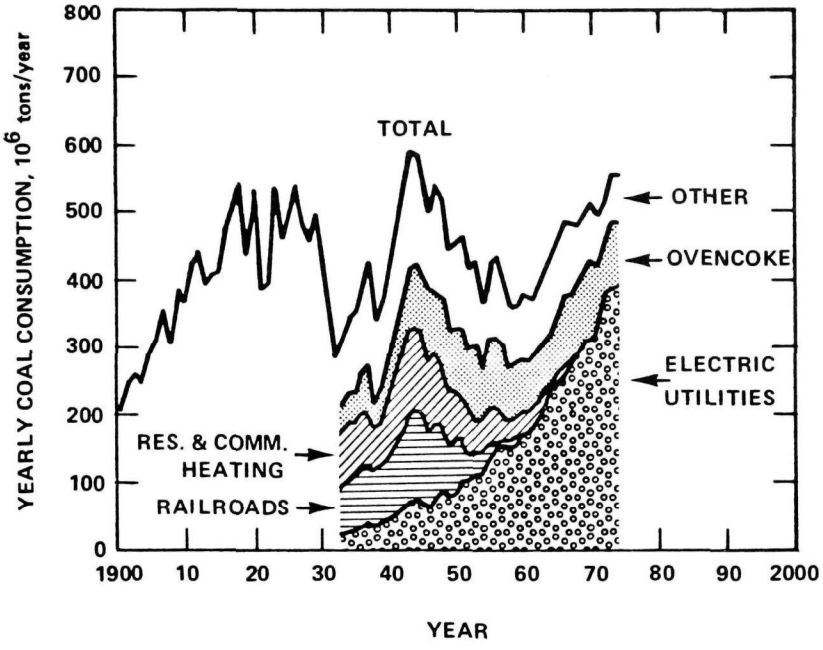
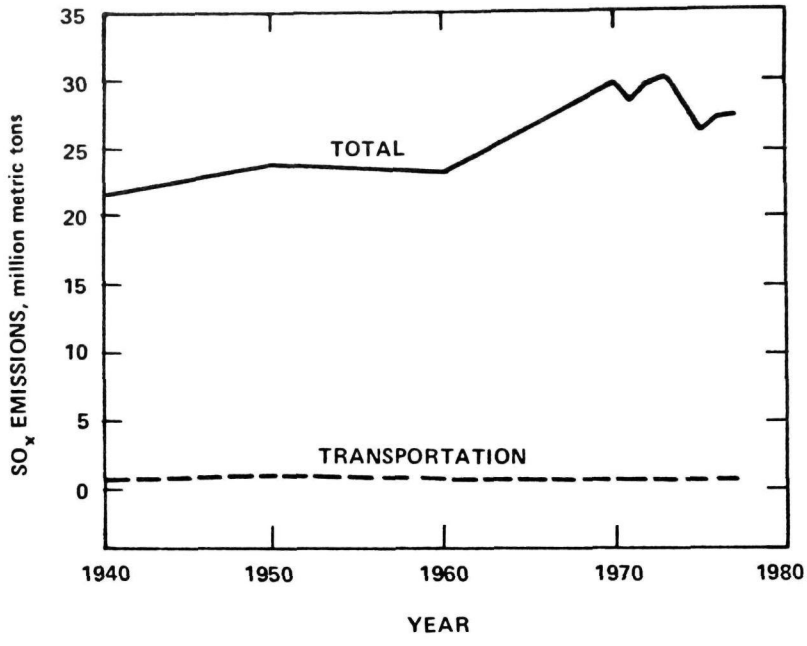


Figure 7-4. Forms of coal usage in the United States. Electric power generation is currently the primary user of coal. (Data from U.S. Bureau of Mines, Minerals Yearbooks 1933--1974).

Source: U.S. Bureau of Mines (1954, 1976).



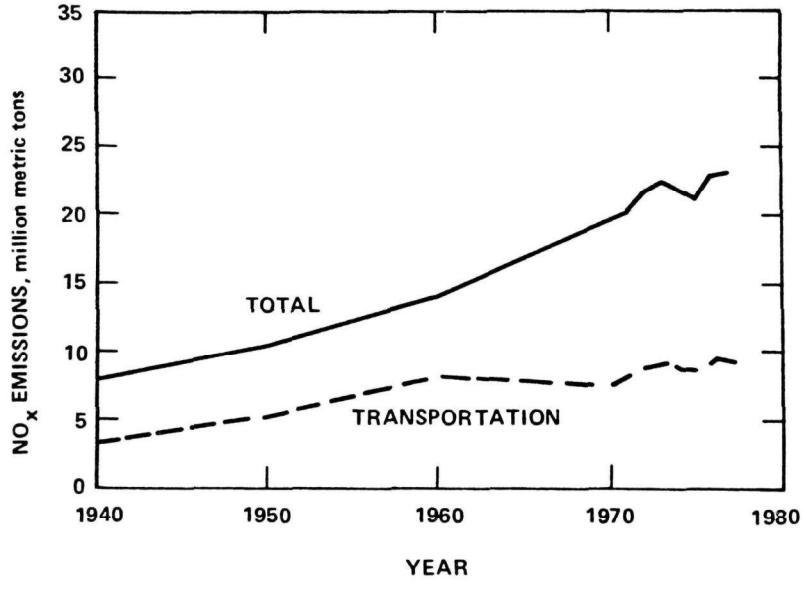


Figure 7-5a. Trends in emissions of sulfur dioxides.

Figure 7-5b. Trends in emissions of nitrogen oxides.

Source: U.S. Environmental Protection Agency (1978).

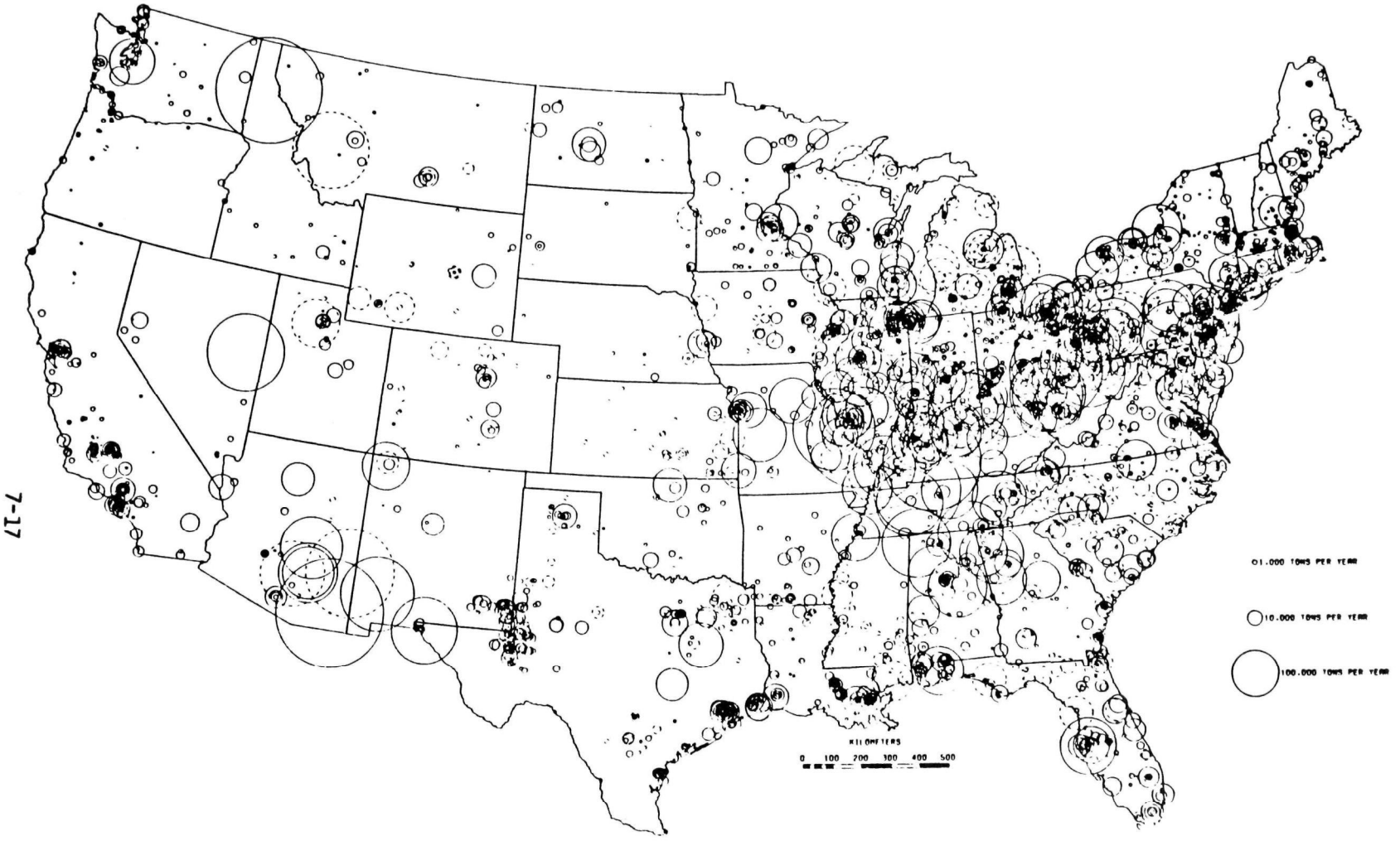


Figure 7-6. Point sources of sulfur oxides emissions over 100 tons per year. Broken circles represent estimated locations of point sources.

Source: U.S. Environmental Protection Agency (1978).

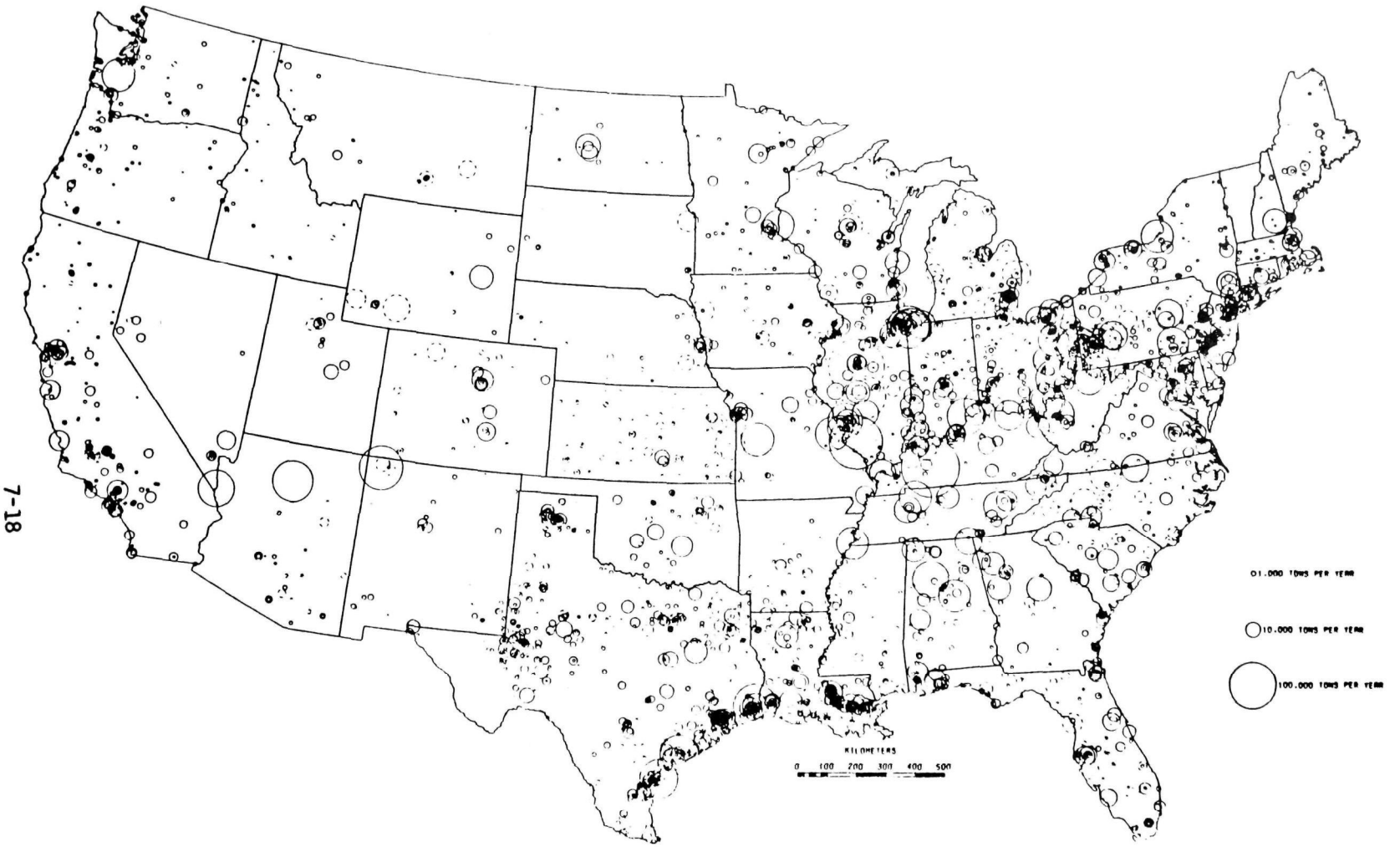


Figure 7-7. Point sources of nitrogen oxides emissions over 100 tons per year. Broken circles represent estimated locations of point sources.

Source: U.S. Environmental Protection Agency(1978).

*
acidified rain and snow eventually fall. Prevailing winds in the eastern United States tend to be from the west and southwest. Atmospheric pollutants, therefore, are carried in a generally northeasterly direction. Thus, pollution originating in the Ohio River valley can be carried toward the New England states. Seasonal meteorological patterns, however, can modify the direction of windflow, particularly in the summer. The Maritime Tropical air masses from the Gulf of Mexico that occur in late summer have the greatest potential for the formation and transport of high concentrations of sulfate into the northeastern United States and into eastern Canada (Altshuller and McBean, 1979).

Cogbill and Likens (1974) associated acidic rainfall in central New York during 1972-73 with high altitude air masses transported into the region from the Midwest. They stated that the NO_x and SO_2 that is involved in acidic rain formation may be transported distances of 300 to 1500 km. Reports by Miller et al. (1978), Wolf et al. (1979), and Galvin et al. (1973) all support the concept that the trajectories of the air masses which come from the Midwest carry sulfur and nitrogen compounds which acidify precipitation in New York State.

A significant though disputed factor in this transport picture is the height at which the pollutants are emitted. Industrial and power plant smokestacks emit their effluents into the atmosphere at higher elevations than do motor vehicles or most space heating equipment. In fact, there has been a trend since the 1960s toward building higher stacks as a means of dispersing pollutants and thereby reducing pollutant concentrations in the vicinity of power plants, smelters, and similar sources (Grennard and Ross, 1974). The result has been that sulfur and nitrogen oxides are carried by prevailing winds for long distances and allowed to diffuse over greater areas through the atmosphere. Concomitantly, long-range transport allows greater time for chemical reactions to convert these pollutant gases into particulate forms which are more easily removed by wet processes (Eliassen and Saltbones, 1975; Smith and Jeffrey, 1975; Prahm et al., 1976). Chapter 6 discusses the chemical transformations of wet and dry deposition and transport and diffusion of sulfur oxides in the atmosphere. Sulfates and nitrates combine with atmospheric water to form dissociated forms of nitric (HNO_3) and sulfuric (H_2SO_4) acids. These acids are considered to be the main components of acidic precipitation.

The mechanisms of these chemical reactions are quite complex and depend on a host of variables ranging from physical properties of the pollutants to weather conditions and the presence of catalytic or interacting agents (Fisher, 1978). Although these processes of atmospheric chemistry are not well understood, it does appear that the long-range transport of sulfur compounds can cover 1000 to 2000 km over three to five days (Pack et al., 1978). Thus, the impact of sulfur pollutants in the form of acidic precipitation may be far removed from their points of origin. It is not yet clear whether the atmospheric transport of nitrogen oxide pollutants is comparable to that of sulfur compounds (Pack, 1978), but in the northeast nitrates are currently thought to contribute 15 to 30 percent of the acidity of polluted precipitation. This figure has increased over the past few years and is expected to increase still further in the future (National Research Council, 1978).

*

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 precipitation. The acid rains that have received intensive study in southern Scandinavia have been shown to result primarily from emissions of nitrogen and sulfur oxides in Great Britain and the industrial regions of continental Western Europe (e.g., Holland, Belgium, West Germany) (Brosset, 1973).

7.2.3 Formation

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 the earth surfaces (Smith, 1974). Water moves into the atmosphere by evaporation and transpiration (water vapor lost by vegetation). 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^-). When in equilibrium with normal atmospheric concentrations and pressures of carbon dioxide, the pH of rain and snow is approximately 5.6 (Likens et al., 1979).

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 become a component of 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. Decaying 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 also those most abundant in ocean water (Likens, 1976; Likens et al., 1979).

Gases which enter precipitation, in addition to CO_2, are sulfur dioxide (SO_2) and the nitrogen oxides (NO_x). Some sulfur gases originate from natural sources, e.g. volcanoes and swamps. Others originate from industrial emissions. In the wet atmosphere, both SO_2 and H_2S can be oxidized to sulfuric acid. Nitrogen oxides in the atmosphere are converted to nitric acid (Likens, 1976; Likens et al., 1979). Strong acids dissociate completely in dilute aqueous solutions and lower the pH to less than 5.6. Acidic precipitation has been arbitrarily considered by many scientists to be rain or snow with a pH below 5.6 (Galloway and Cowling, 1978; Wood, 1975; Likens et al., 1979).

Additional acidic or potentially acidifying substances present in both wet and dry deposition are sulfur trioxide ($SO_3^{=}$), sulfate $SO_4^{=}$), nitric oxide (NO), nitrogen dioxide (NO_2), nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), chlorine (Cl^-) hydrochloric acid (HCl), and

*
Brønsted acids [e.g., dissolved iron (Fe) and ammonium (NH_4^+)] (Whelpdale, 1978).

The amounts of the various substances in the atmosphere originating from seawater, desert sands, volcanic islands, or vegetated land influence the chemistry of natural precipitation. In regions with calcareous soils, calcium and bicarbonate may enter precipitation as dust, subsequently increasing the pH of rain or snow to 6.0 or above (Likens et al., 1979).

7.2.3.1 Composition and pH of Precipitation--Sulfur and nitrogen compounds are chiefly responsible for the acidity of precipitation. Continuous measurement of pH in rain by Likens et al. (1972) for the Hubbard Brook Experimental Forest in Hew Hampshire from 1964 to 1971 indicated the precipitation was acid with an annual weighted average pH range of 4.03 to 4.19. (A weighted average takes into account the amount of rain as well as its composition.) Cogbill and Likens (1974), using precipitation from the Ithaca area, and Hubbard Brook reported that their analysis of precipitation which consistently had a pH of less than 4.4 showed that 65 percent of the acidity was due to H_2SO_4, 30 percent to HNO_3, and less than 5 percent was due to HCl.

In 1976, Likens reported that the continued monitoring of precipitation at the Hubbard Brook Forest through 1974 indicated the mean annual pH for the years 1964-1974 ranged from 4.03 to 4.21. No statistically significant trend was noted; however, pH values of 2.1 and 3.0 were observed for individual storms at various locations. The increased deposition of hydrogen ion was due to an increase in nitric acid in the precipitation (rain and snow) falling there. This change in the composition of acidic precipitation suggests that the sources of nitrogen oxide emissions increased while those for sulfur oxides remained constant.

The acidity of precipitation is a reflection of the free hydrogen ions in precipitation. The contribution of sulfate and nitrate anions has changed with time, and analysis indicates that the nitrate anion makes up an ever-increasing fraction of the total negative ion equivalents. Following the reasoning of Granat (1972), Likens et al. (1976) found [assuming $2H^+$ per SO_4^{2-} ion as in H_2SO_4 or one H^+ ion per SO_4^{2-} as in $(NH_4)_2SO_4$] 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.

Data for nitrate, ammonium, and sulfate in rain at Ithaca and Geneva, New York, constitute the longest record of precipitation chemistry in the United States (Likens, 1972). Data are available from 1915 to the present, but long gaps exist in the measurements, especially at the Geneva site. Figures 7-8 (A) to (C) show that marked changes in composition have occurred at Ithaca: a gradual decline in ammonium, 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 (1972) concluded

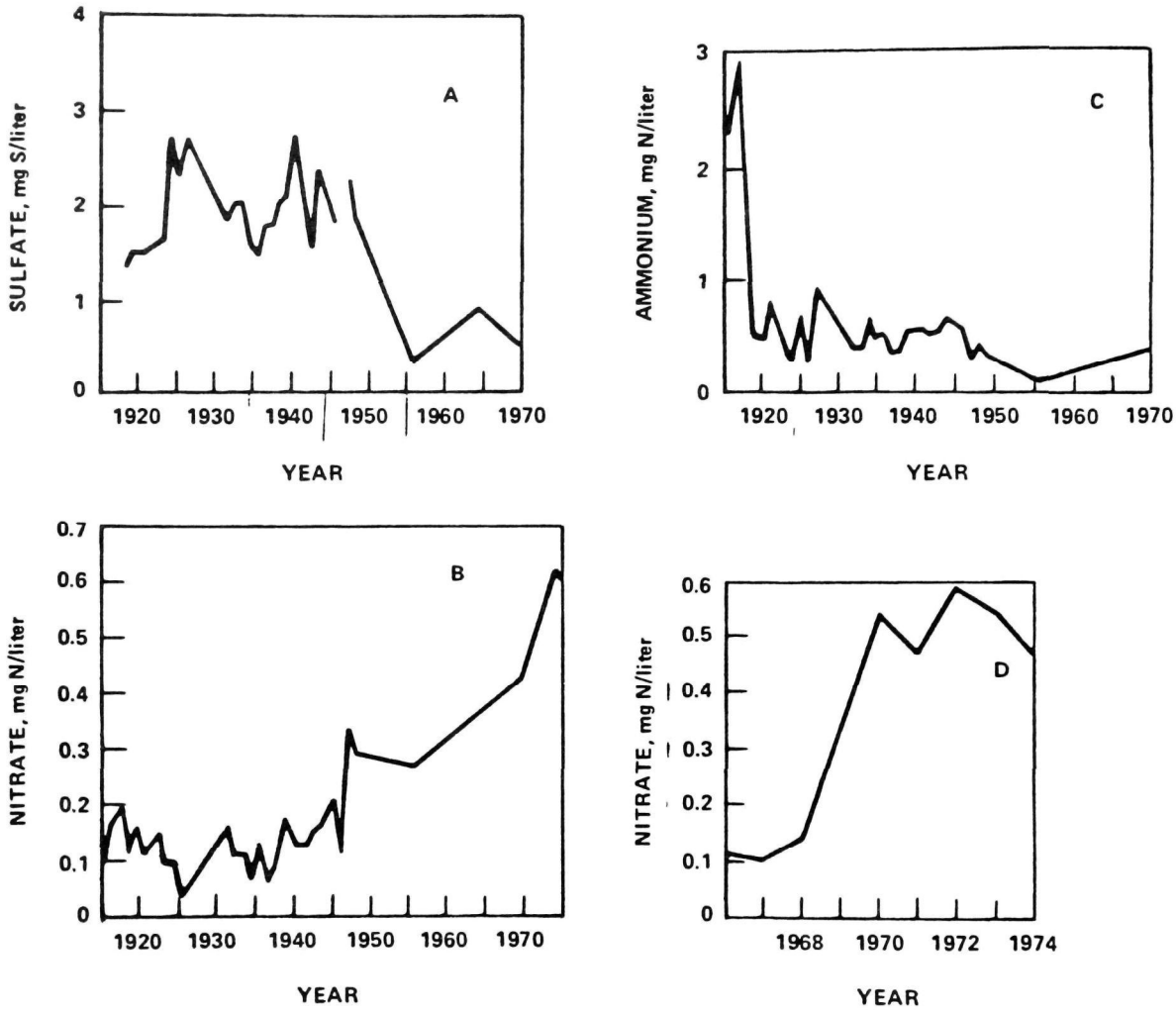


Figure 7-8. Trends in mean annual concentrations of sulfate, ammonium, and nitrate in precipitation. (A), (B), and (C) present long-term data for Ithaca, New York; (D) presents data for eight yearsaaveraged over eight sites in New York and one in Pennsylvania. One point in (A), for 1946--47, is not plotted because it is believed to be an anomaly.

Source: (A), (B), and (C) modified from Likens (1972); (D) modified from Likens (1976).

*
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. On the basis of United States Geological Survey data for nine stations, Likens (1976) reported a sharp increase in nitrate concentrations in New York state during the past decade (Figure 7-8 [D]).

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 (1975), 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 of H^+ deposition attributable to nitrate rose from 19 percent in 1955-1956 to 24 percent in 1972-1973 (Table 7-2), while the deposition attributable to H_2SO_4 decreased from 80 to 73 percent.

TABLE 7-2. 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[a]	10.8[a]	+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 Nisbet (1975).

*

Lindberg et al. (1979) 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 indicated that H^+ constitutes approximately 50 percent of the cationic strength and trace elements account for only 0.2 percent. Sulfate 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 (Lindberg et al., 1979). In Florida, Hendrey (1977) and Hendrey et al. (1980) found that sulfate contributed 69 percent, nitrate 23 percent, and chloride 8 percent of the free acidity in rainfall at Gainesville, Florida, during 1976.

Based on most reports, sulfate (SO_4^{2-}) appears to be the predominant anion in acidic precipitation in the Eastern United States. In the west in California, however, nitrate (NO_3^-) seems to predominate. Liljestrand and Morgan (1978) reported that their analyses of acidic rainfall collected from February 1976 to September 1977 in the Pasedena, CA, area showed that the volume-weighted mean pH was 4.0, with nitric acid being 32 percent more important as a source of acidity than sulfuric acid. The major cations present were H^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} while the major anions were Cl^-, NO_3^- and SO_4^{2-}. McColl and Bush (1978) also noted the strong influence of nitrate on rain in the Berkeley, CA, region. However, they note that in bulk precipitation (wet plus dry fall-out) that sulfate (SO_4^{2-}) constituted 50 percent of the total anions.

Nearly all of the nitrate in rainfall is formed in the atmosphere from NO_x. 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 (National Research Council, 1978). Thus, all atmospherically derived nitrate and sulfate contribute to the acidification of precipitation, 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 acidity of precipitation will be reduced (National Research Council, 1978). However, since much of the ammonium ion reaching soil is converted to nitrate, these neutral salts still have an acidifying effect on the soil.

Seasonal fluctuations in composition as well as pH of rainfall have been reported by many workers. In addition, the composition of rainfall and pH fluctuates from event to event, from locality to locality, and from storm to storm.

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. (1979) found this to be true for the New York Metropolitan Area. Hornbeck et al. (1976) and Miller et al. (1978) both stated that

*
a summer maximum for sulfate was associated with an increase in hydrogen ion concentration in upstate New York, the Hubbard Brook Experimental Forest in New Hampshire, and in portions of Pennsylvania. Pack (1978), using data (1977) from the four original MAP3S (Multistate Atmospheric Power Production Pollution Study) precipitation chemistry networks, plotted the weighted monthly sulfate ion concentrations (Figure 7-9). Maximum sulfate concentrations occurred from June through August. Lindberg et al. (1979), 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. 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 are discussed in some detail in Chapter 5, Section 5.3.4.

Seasonal variations of nitrogen compounds and of pH in precipitation have been reported by several workers, but no simple trends are apparent (see U.S. Environmental Protection Agency Air Quality Criteria for Nitrogen Oxides, 1980). Hoeft et al. (1972) found relatively constant levels of nitrate in rain and snow collected in Wisconsin throughout the year, but deposition of ammonia and organic nitrogen was lowest in winter and highest in spring, perhaps because of the thawing of frozen animal wastes. Haines (1976) reported large random variations, but relatively small seasonal variations, for nitrogen forms in wet-only precipitation at Sapelo Island, Georgia; nitrogen concentrations were lowest during the rainy months of July and September. The highest nitrogen loadings occurred during July and were asosciated with the lowest range in pH, 4.2-4.8. Hendrey (1977) and Hendrey and Brezonik (1980) found relatively smooth seasonal trends in ammonia and nitrate concentrations in both wet-only and bulk collections (wet- and dryfall) at Gainesville, Florida, with lowest concentrations in winter (Figure 7-10). In addition, the pH of the bulk precipitation showed no seasonal trend. Wet-only collections, however, showed the lowest pH value (4.0) during the spring and summer. This historical record suggests there has been an increase in the concentration of inorganic nitrogen in Florida over the past 20 years.

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.

Major ions [chloride (Cl^-) and sulfate ($SO_4^=$)], inorganic forms of nitrogen [nitrate (NO_3^-) and ammonium (NH_4^+)], total phosphorus and pH were measured in rain collected in 5-minute segments within three individual rainstorms. Initially, rapid decreases were observed for nitrate and ammonium and total phosphorus. There was also a decrease in pH from 4.65 to 4.4. Steady state concentrations were reached in 10 minutes. Two other storms sampled in the same manner showed similar but less defined patterns.

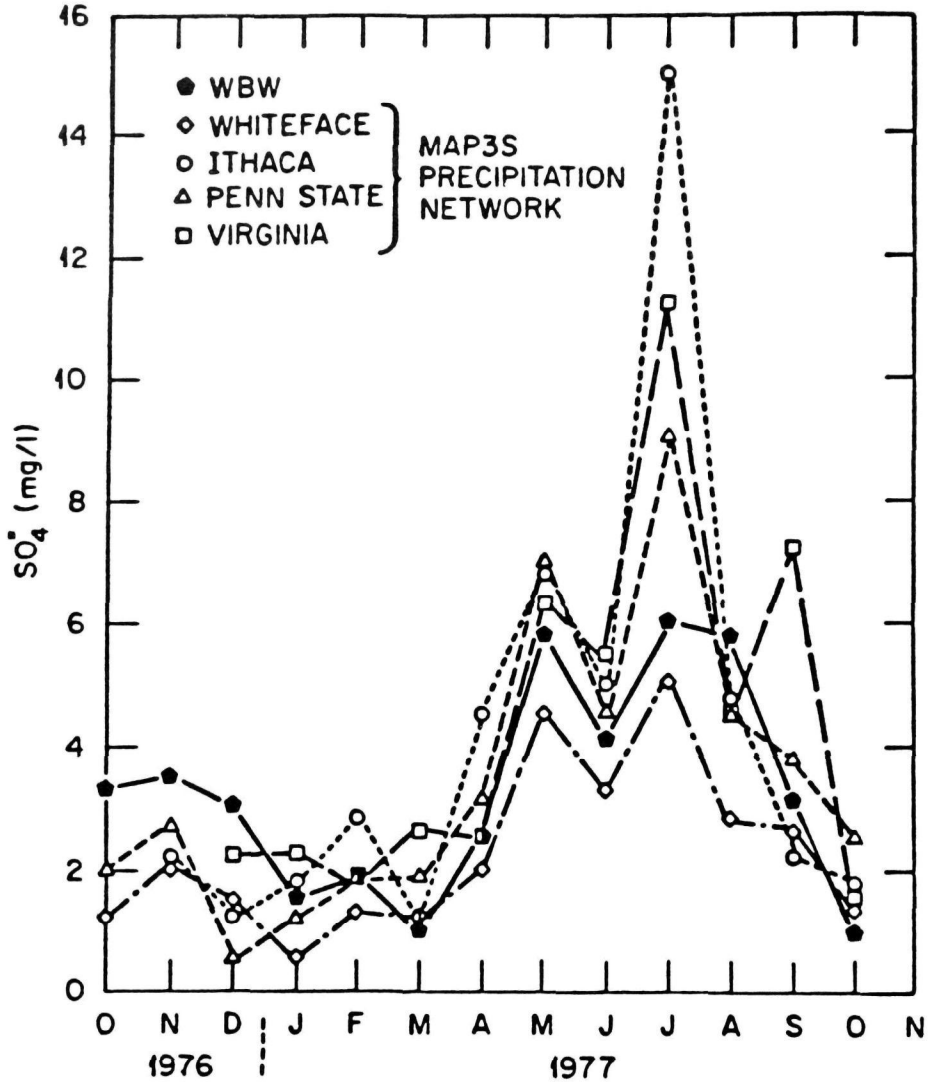


Figure 7-9. Comparison of weighted mean monthly concentrations of sulfate in incident precipitation collected in Walker Branch Watershed, Tenn. (WBW) and four MAP3S precipitation chemistry monitoring stations in New York (◇, 0), Pennsylvania (△), and Virginia (□).

Source: Pack (1978).

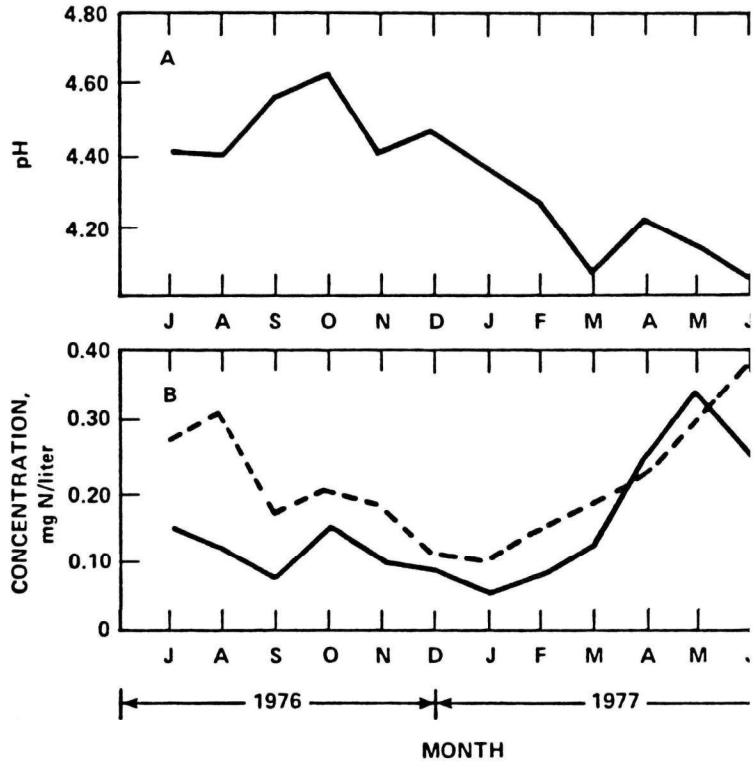


Figure 7-10. Seasonal variations in pH (A) and ammonium and nitrate concentrations (B) in wet-only precipitation at Gainesvil Florida. Values are monthly volume-weighted averages of level in rain from individual storms.

*

Wolf et al. (1979) examined spatial meteorological and seasonal factors associated with the pH of precipitation in the New York Metropolitan Area. Seventy-two events were studied from 1975 through 1977. There was some site-to-site variability among the eight sites they studied in the Manhattan area (Table 7-3). They also noted that the pH varied according to storm type (Table 7-4). 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 (Wolff et al., 1979).

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 7-11). 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 pH of 4.12 for the New York Metropolitan area occurred during the summer months (Wolff et al., 1979). 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 westerly or southwesterly winds (Wolff et al., 1979).

Seasonal variations in pH measured at several sites in New York State 70 km (45 mi.) apart demonstrated a significant difference between seasons (Winter had an average pH of 4.2; summer, 3.9.) but no significant difference between sites. In New Hampshire, however, six summer storms sampled at 4 sites less than 3 km (2 mi.) apart showed a significant difference (3.8 to 4.2) indicating considerable variation in pH may occur in the same storm.

Stensland (1978, 1980) compared the precipitation chemistry for 1954 and 1977 at a site in central Illinois. The pH for the 1954 samples had not been measured, but were calculated and compared with those measured in 1977. The corrected pH for 1954 was 6.05; the pH for 1977 was 4.1. The more basic pH in 1954, according to the author, could have resulted from low levels of acidic ions (e.g. sulfate or nitrate) or from high amounts of basic ions (e.g. calcium and magnesium). Stensland suggests that the higher pH in 1954 was due to calcium (Ca^{++}) and magnesium (Mg^{++}) ions from the soil.

7.2.3.2 Geographic Extent of Acidic Precipitation--Acidic precipitation has been a reality in New York State for an undetermined period of time. Data collected by the United States Geological Survey (Harr and Coffey, 1975) over a ten-year period are presented in Figure 7-12. 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 7-13) represents an area within a given watershed. The pH of precipitation has remained nearly at the same general average during the entire ten-year period; therefore, since data for the years prior to 1965 are lacking, it is difficult to determine when the pH in precipitation first began to decrease (Harr and Coffey, 1975).

*

TABLE 7-3. 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 Wolff, et al., 1979 .

TABLE 7-4. 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 Wolff et al., 1979.

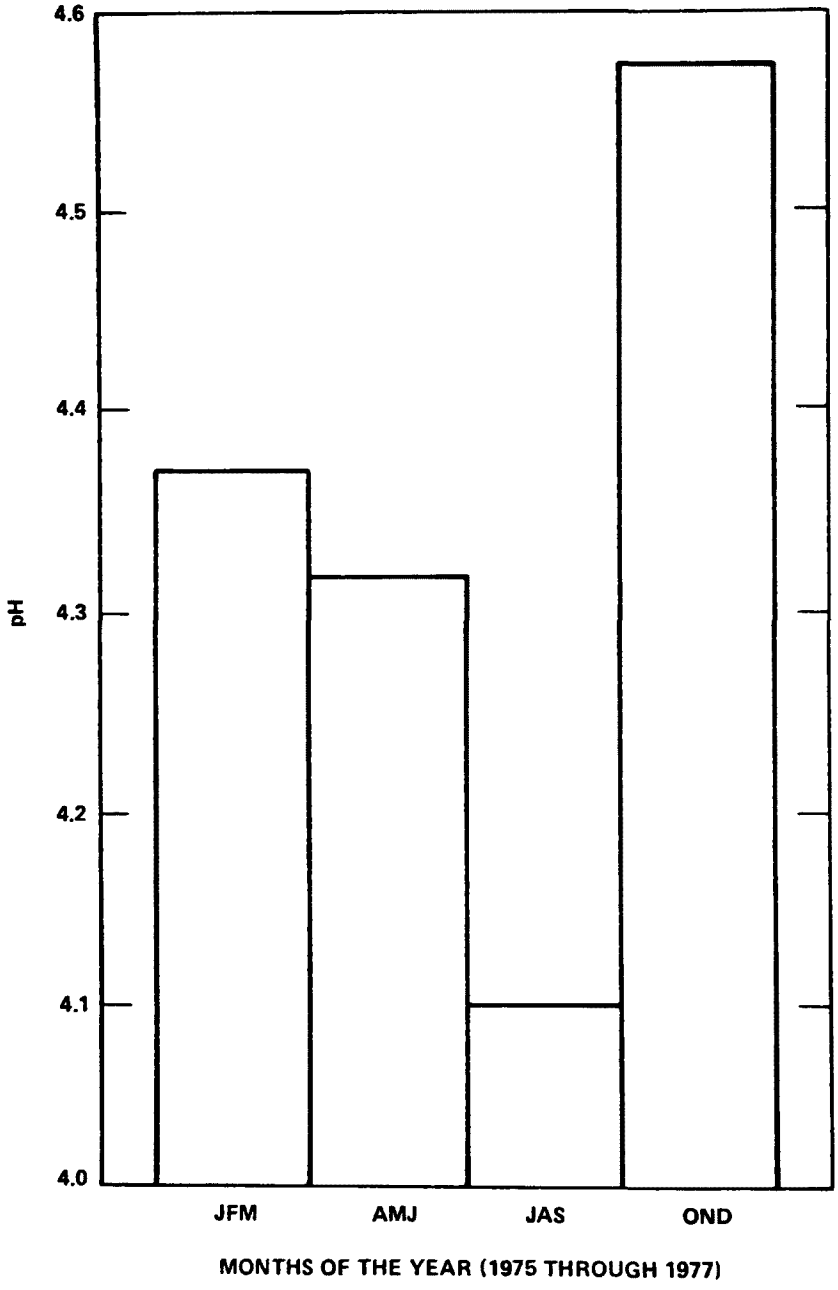


Figure 7-11. Seasonal variation of precipitation pH in the New York Metropolitan Area.

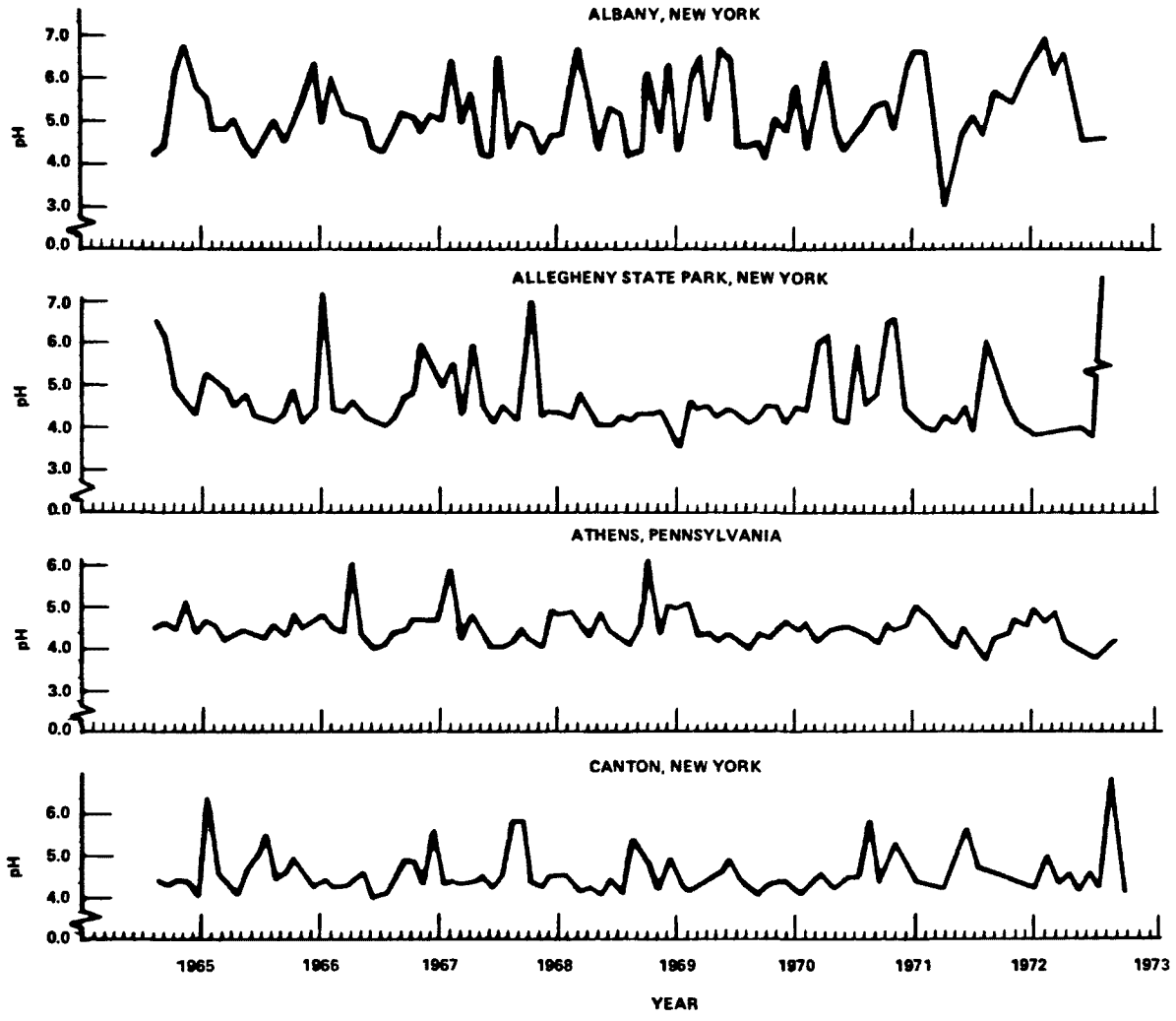


Figure 7-12. History of acidic precipitation at various sites in and adjacent to State of New York.

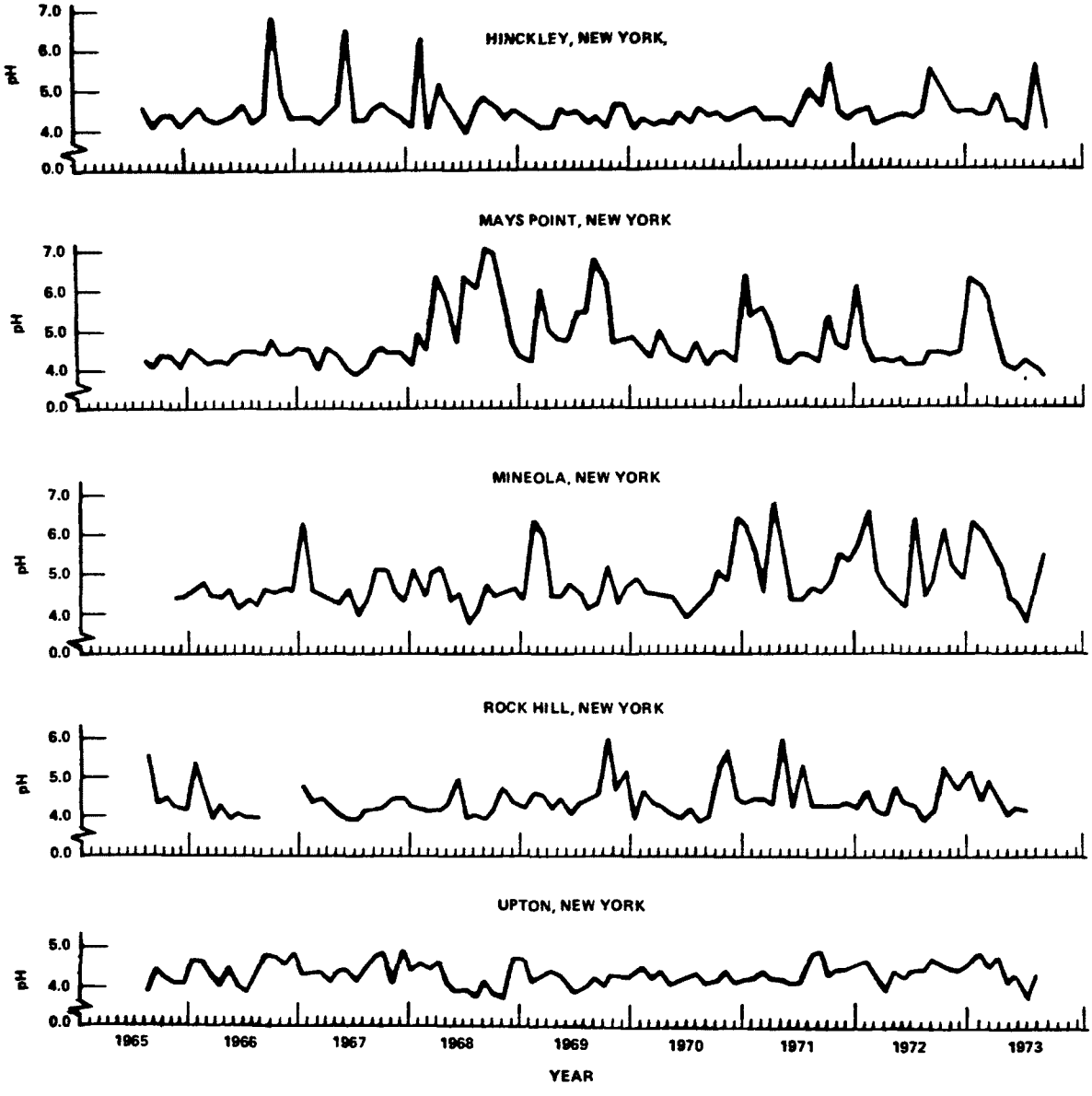


Figure 7-12 (continued). History of acidic precipitation at various sites in and adjacent to State of New York.

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.

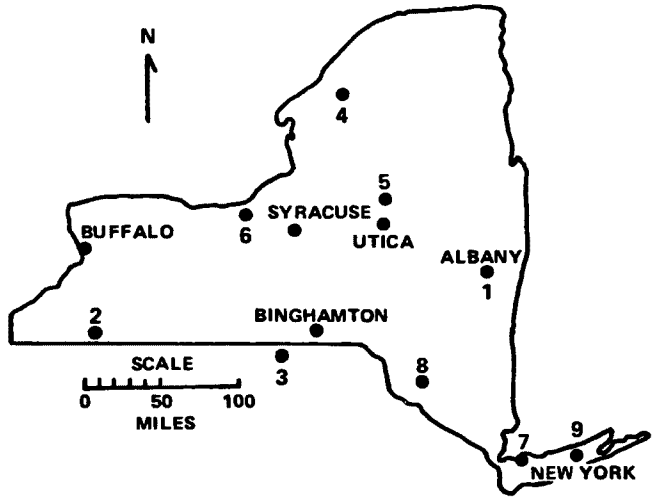


Figure 7-13. Location of acidic precipitation monitoring stations.

*

That precipitation is acidic in parts of the country other than the northeastern United States is apparent. Average pH values around 4.5 have been reported as far south as northern Florida (Likens, 1976; Hendry and Brezonik, 1980), from Illinois (Irving, 1978), the Denver area of Colorado (Lewis and Grant, 1980), the San Francisco Bay area of California (McColl and Bush, 1978; Williams, 1978), Pasadena, California (Liljestrand and Morgan, 1978), the Puget Sound area of Washington (Larsen et al., 1976), and from eastern Canada (Glass et al., 1979; Dillon et al., 1978). Data from the San Francisco Bay area indicate that precipitation has become more acidic in that region since 1957-1958 (McColl and Bush, 1978). The pH decreased from 5.9 during 1957-1958 to 4.0 in 1974, and seems to be related to an increase in the NO_3^- concentration (McColl and Bush, 1978). Another report, using data from the California Air Resources Board (CARB) (Williams, 1978), states that acidic precipitation has been reported from such widespread areas as Pasadena, Palo Alto, Davis, and Lake Tahoe.

Studies in the Great Smoky Mountain National Park (Lipske, 1980) indicate a downward trend in pH has occurred there over the past twenty years. Over a period of 20 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 controversial. 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 a Central Analytical Laboratory in Illinois to be analyzed. This long-term network plans to have 75 to 100 collection sites throughout the United States; 74 are already operational.

7.2.4 Acidic Deposition

The previous sections of this chapter have discussed the formation, composition and geographic distribution of acidic precipitation. Usually when the effects of acidic deposition are discussed, emphasis is placed on the effects resulting from the scavenging of sulfur and nitrogen compounds by precipitation. Dry deposition of gaseous and particulate and aerosol forms of these compounds also occurs and is beginning to receive more emphasis in research (Galloway and Whelpdale, 1980; Schlesinger and Hasey, 1980; Stensland, 1980; Schmel, 1980; Chamberlain, 1980). Gaseous compounds reach the surface of the earth by turbulent transfer while particulate sulfates and nitrates reach the earth's surface by gravitational sedimentation, turbulent transfer and impaction (Galloway and Whelpdale, 1980; Schmel, 1980; Hicks and Wesely, 1980). A comparison of the relative significance of wet and dry deposition is difficult. Dry deposition, however, is always removing pollutants from the atmosphere, while removal by wet deposition is intermittent (Schmel, 1980). Marenco and Fontan (1974) suggest that dry deposition is more important than wet in removing air pollutants from manmade sources.

Lindberg et al. (1979) have calculated the annual mass transfer rates of sulfates to the forest floor in Tennessee (Figure 7-14). Their calculations for $SO_4^=$ suggest wet deposition by incident precipitation to be 27 percent compared with a total dry precipitation of 13

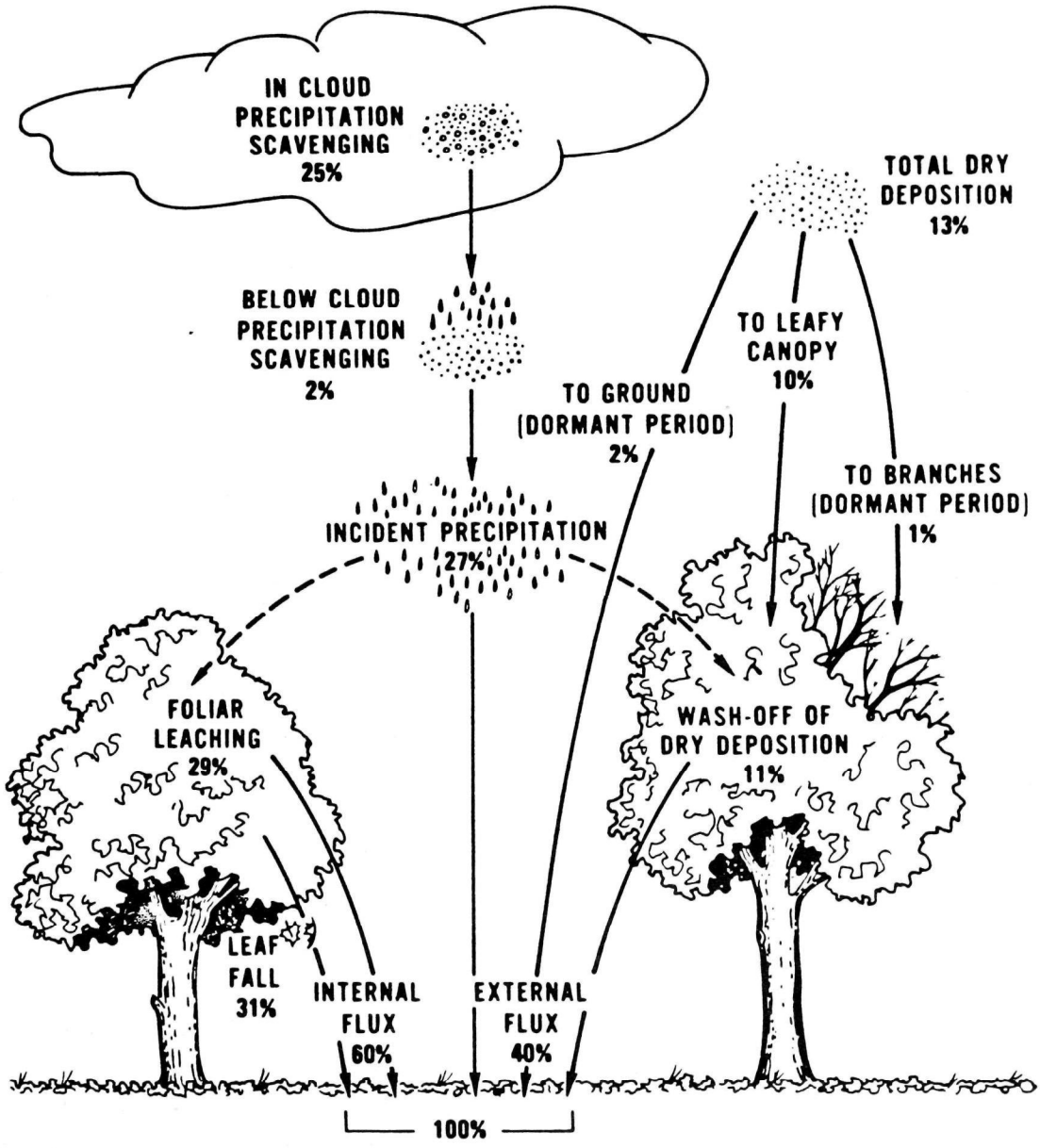


Figure 7-14. Annual mass transfer rates of sulfate expressed as a percentage of the estimated total annual flux of the element to the forest floor beneath a representative chestnut oak stand.

Source: Lindberg et al. (1979).

*
percent. The dry deposition and foliar absorption of SO_2, a very important component, is missing from this calculation. The wet and dry deposition percentages are only an indication of the relative magnitude of the two processes. The percentages do, however, point out that the effects of acidic deposition usually attributed to precipitation scavenging alone are probably a result of both wet and dry deposition. At the present time the accuracy with which dry deposition can be measured is still under question.

The studies of McColl and Bush (1978), Hendrey and Brezonik (1980), and Schlesinger and Hasey (1980) also point out that both wet and dry deposition are important when considering the effects of H^+, SO_4^{2-}, and NO_3^- ions on aquatic and terrestrial receptors.

The effects of the dry deposition of SO_2 and particulate matter on vegetation and terrestrial ecosystems is discussed in Chapter 8. The processes of wet and dry deposition of sulfur oxides are discussed in Chapter 6 of this document; for nitrogen oxides in Chapter 6 of Air Quality Criteria for Nitrogen Oxides.

7.3 EFFECTS OF ACIDIC DEPOSITION

Acidic precipitation has been implicated in the degradation of aquatic ecosystems, the disintegration of stone buildings and monuments and as a potential source of harm to forests and other terrestrial ecosystems. The sections that follow discuss these effects.

7.3.1 Aquatic Ecosystems--Acidification of surface waters is a major problem in regions of southern Scandinavia (Oden, 1968; Almer et al., 1974; Gjessing et al., 1976), Scotland (Wright et al., 1980a), eastern Canada (Beamish and Harvey, 1972; Dillon et al., 1978), and the eastern United States - in the Adirondack Region of New York State (Schofield, 1976; Pfeiffer and Festa, 1980), in Maine (Davis et al., 1978), and in northern Florida (Crisman et al., 1980). Damage to fisheries is the most obvious affect of acidification on freshwater life. The disappearance of fish populations from acidified freshwater lakes and streams was first noted in southern Norway in the 1920's. In 1959, Dannevig proposed that acidic deposition was the probable cause for acidification and thus far the loss of fish populations (Leivestad et al., 1976). Subsequent studies have verified this postulate. Declines in fish populations have been related to acidification of surface waters in southern Norway (Jensen and Snekvik, 1972; Wright and Snekvik, 1978), southwestern Sweden (Almer et al., 1974), southwestern Scotland (Wright et al., 1980a), the Adirondack Region of New York State (Schofield, 1976), and the LaCloche Mountain Region in southern Ontario (Beamish and Harvey, 1972). Acidification may also have serious repercussions on other aquatic biota inhabiting these systems. Changes in the acidity and chemistry of freshwater affect the communities of organisms living there. Pertinent details of these effects are described in the following sections.

7.3.1.1 Acidification of lakes and streams. Precipitation enters lakes directly as rain or snow or indirectly as runoff of seepage water from the surrounding watershed. The relative magnitude of the influents from these two sources is dependent on the surface area and volume of the lake, and the size of the watershed and its soil volume and type. In general, the watershed plays a dominant role in determining the composition of water entering the lake. As

*
a result, the water will be strongly influenced by processes in the edaphic environment of the watershed, such as weathering, ion exchange, uptake and release of ions by plants, carbon dioxide production by vegetation, microbial respiration, and reduction and oxidation reactions of sulfur and nitrogen compounds (Seip, 1980). Precipitation as a direct source of water to the lake plays a relatively greater role when lake areas are large in comparison to the size of the watershed.

Acidification of surface waters results when the sources of hydrogen ion exceed the ability of an ecosystem to neutralize the hydrogen ion. In general, the soils and crust of the earth are composed principally of basic materials with large capacities to buffer acids. However, areas where bedrock is particularly resistant to weathering and soils are thin and poorly developed have much less neutralizing ability. This inability to neutralize hydrogen ion does not arise from a limited soil or mineral buffering capacity. Instead low cation exchange capacity and slow mineral dissolution rates in relation to the relatively short retention time of water within the soil system may result in incomplete neutralization of soil waters and acidification of surface waters (Driscoll, 1980). Characteristics of regions sensitive to surface water acidification are discussed in more detail in Section 7.4.1.

Sources of hydrogen ion to the edaphic-aquatic system include, besides acidic deposition, mechanisms for internal generation of hydrogen ion - oxidation reactions (e.g., pyrite oxidation, nutrification), cation uptake by vegetation (e.g., uptake of NH_4^+ or Ca^{++}), or generation of organic acids from incomplete organic litter decomposition (Figure 7-15). The relative importance of the hydrogen ion content in acidic deposition to the overall hydrogen ion budget of an ecosystem has been discussed by many researchers (Rosenqvist, 1976; SNSF Project, 1977).

The consensus is that changes in internal hydrogen ion generation related to land use or other changes (e.g., Drablos and Sevaldrud, 1980) can not consistently account for the widespread acidification of surface waters occurring in southern Scandinavia, the Adirondack Region of New York, the LaCloche Mountain Area of Ontario, and elsewhere. Driscoll (1980) developed a hydrogen ion budget for the Hubbard Brook Area in New Hampshire. Based on these calculations, atmospheric hydrogen ion sources represent 48 percent of the total Hubbard Brook ecosystem hydrogen ion sources.

As noted above, freshwater ecosystem sensitive to inputs of acids are generally in areas of poor soil development and underlain by highly siliceous types of bedrock resistant to dissolution through weathering (Likens et al., 1979). As a result, surface waters in such areas typically contain very low concentrations of ions derived from weathering. The waters are diluted with low levels of dissolved salts and inorganic carbon, and low in acid neutralizing capacity. The chemical composition of acid lakes is summarized in Table 7-5 for lakes in southern Norway (Gjessing, et al., 1976), the west coast (Hörnstrom et al., 1976) and west-central (Grahn et al., 1976) regions of Sweden, the LaCloche Mountains of southeastern Ontario (Beamish, 1976), and the vicinity of Sudbury, Ontario (Scheider et al., 1976), as well as for

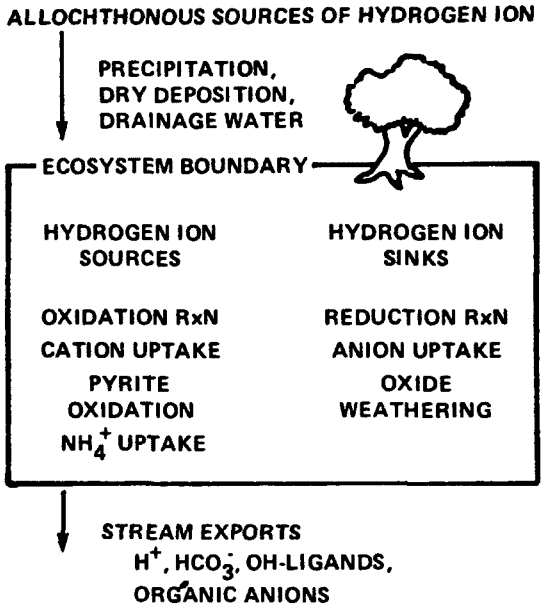


Figure 7-15. Schematic representation of the hydrogen ion cycle.

Source: Driscoll (1980).

TABLE 7-5. 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)

Region		No. of lakes	Specific conductance††	μeq/l H (pH)	Na	K	Ca	Mg	HCO_3	HCl	SO_4	NO_3	Σ cations	Σ anions	Reference
I. LAKES IN ACID AREAS															
Scandinavia															
Southernmost Norway	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	Gjessing
	Less s w*:			18	9	4	50	25	11	0	92	4	106	107	et al., 1976
Westcoast Sweden	Measured:	12	72**	43** (4.37**)	330	20	——— 280 ———		0	440	200	8	673	648	Hornström
	Less s w*:			43**	-50	13	-	-	0	0	155	8	-	-	et al., 1976
West-central Sweden	Measured:	6	47±23	22±15 (4.66)	165±120	15±8	75±10	80±40	-	170±90	200±70	19±4	360	390	Grahn
	Less s w*:			22	20	12	70	50	-	0	180	19	175	200	et al., 1976
North America															
La Cloche Mtns, Ontario	Measured:	4	38±8	20±9 (4.7)	26±4	10±3	150±25	75±8	0	22±6	290±40	-	280	310	Beamish,
	Less s w*:			20	9	10	150	65	0	0	290	-	255	290	1976
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	Armstrong,
	Less s w*:			36	50	40	450	300	8	0	800	-	880	800	1971
II. LAKES IN UNAFFECTED AREAS															
Scandinavia															
West-central Norway	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	Gjessing
	Less s w*:			6	9	3	16	7	13	0	30	5	41	48	et al., 1976
North America															
Experimental Lakes Area, Ontario	Measured:	40	19	0.2-2 (5.6-6.7)	40	10	80	75	60	40	60	<1.5	200	160	Armstrong,
	Less s w*:			0.2-2	4	10	80	65	60	0	55	<1.5	160	120	1971

*Less s w = Concentrations after subtracting the seawater contribution according to the procedure explained by Wright and Gjessing (1976).
**Data for 112 lakes
†Measured after past liming of the lakes
††μS/cm at 20°C

*
lakes not yet affected by acidification but in regions of similar geological substrata in west-central Norway (Gjessing et al., 1976) and the experimental lakes area of northwestern Ontario (Armstrong and Schindler, 1971). Basic cation concentrations (Ca, Mg, Na, K) are low (e.g., calcium levels of 18-450 μeq/liter or 0.4 - 9 mg/liter) relative to world-wide averages (15 mg/liter calcium, Livingstone, 1963). Bicarbonate is the predominant anion in most freshwaters (Stumm and Morgan, 1970). However, in acid lakes in regions affected by acidic deposition, sulfate replaces bicarbonate as the dominant anion (Wright and Gjessing, 1976; Beamish, 1976). With a decreasing pH level in acid lakes, the importance of the hydrogen ion to the total cation content increases.

Surveys to determine the extent of effects of acidic deposition on the chemistry of lakes have been conducted in Norway (Wright and Snekvik, 1978; Wright and Henriksen, 1978), Sweden (Almer et al., 1974; Dickson, 1975), Scotland (Wright et al., 1980a), the LaCloche Mountain area of Ontario (Beamish and Harvey, 1972), the Muskoka-Haliburton Area of south-central Ontario (Dillon et al., 1978), and the Adirondack Region of New York State (Schofield, 1976b), Maine (Davis et al., 1978), and Pennsylvania (Arnold et al., 1980). In regions of similar geological substrata not receiving acidic deposition, lake pH levels average 5.6-6.7 (Armstrong and Schindler, 1971). Of 155 lakes systematically surveyed in southern Norway in October 1974, over 70 percent had pH levels below 6.0, 56 percent below 5.5, and 24 percent below 5.0 (Wright and Henriksen, 1978). Of 700 lakes in the Sørlandet Region of southern Norway surveyed in 1974 to 1975 (May-November), 65 percent had pH levels below 5.0 (Wright and Snekvik, 1978). On the west coast of Sweden, of 321 lakes investigated during 1968-1970, 93 percent had a pH level 5.5 or lower. Fifty-three percent had pH levels between 4.0 and 4.5 (Dickson, 1975). In the LaCloche Mountain Region of Ontario, 47 percent of 150 lakes sampled in 1971 had pH levels less than 5.5, and 22 percent had pH levels below 4.5 (Beamish and Harvey, 1972). In the Adirondacks, 52 percent of the high elevation (> 610 m) lakes had pH values below 5.0 (Schofield, 1976b). In each of these studies, the pH level of an individual lake could be related to, in most cases, the intensity of the acidic deposition and the geologic environment of the watershed. Atmospheric contributions of sea salts are also important in coastal regions.

Several methods have been developed to assess the degree of acidification in a lake and relate it to inputs of hydrogen ion or sulfate. Henriksen (1979) utilized alkalinity-calcium and pH-calcium relationships in lakes to estimate the degree of acidification experienced by a surface water. This technique is based on the premise that when carbonic acid weathering occurs one equivalent of alkalinity (acid neutralizing capacity) is released to the aquatic environment for every equivalent of basic cation (Ca, Mg, K, or Na) dissolved. On the other hand, if mineral acid weathering is occurring, for example as a result of acidic deposition, one equivalent of hydrogen ion is comsumed for every equivalent of cation solubilized. Therefore, for a given basic cation level, there is less aqueous acid neutralizing capacity in lakes in systems experiencing strong acid weathering than in systems experiencing carbonic

*
acid weathering. When comparing alkalinity plots from two watersheds, one experiencing strong acid contributions and the other undergoing largely carbonic acid weathering (assuming both watersheds have similar edaphic environments), the difference in alkalinity between the two plots for a given calcium level (the dominant basic cation) should be indicative of the amount of strong acid the watershed receives and the degree of acidification of the surface water. For waters with pH levels below 5.6, alkalinity is approximately equal to the negative of the hydrogen ion concentration. Therefore, pH level can be substituted for alkalinity, and pH-calcium plots developed (Figure 7-16). Data of this type for Norway indicate that significant acidification of lakes has occurred in areas receiving precipitation with volume-weighted average concentrations of H^+ above 20-25 μeq/liter (pH 4.7-4.6) and sulfate concentrations above 1 mg/liter (20 μeq/liter) (Henriksen, 1979).

Henriksen (1979) also utilized the concentration of excess sulfate in lake water (sulfate in excess of that of marine origin) to estimate acidification. This suggests that bicarbonate anions lost in acidified lakes have been replaced by an equivalent amount of sulfate. Almer et al. (1978) plot pH levels in Swedish lakes as a function of excess sulfur load (excess sulfur in lake water multiplied by the yearly runoff) (Figure 7-17). Based on this relationship, they estimate that the most sensitive lakes in Sweden may resist a load of only about 0.3 g/m^2 of sulfur in lake water each year. At 1 g/m^2 of sulfur, the pH level of the lake will probably decrease below 5.0.

Elevated metal concentrations (e.g., aluminum, zinc, manganese, and/or iron) in surface waters are often associated with acidification (Schofield and Trojnar, 1980; Hutchinson et al., 1978; Wright and Gjessing, 1976; Beamish, 1976). Mobility of all these metals is increased at low pH values (Stumm and Morgan, 1970). For example, an inverse correlation between aluminum concentration and pH level has been identified for lakes in the Adirondack Region of New York State, southern Norway, the west coast of Sweden, and Scotland (Wright, 1980b) (Figure 7-18). Aluminum appears to be the primary element mobilized by strong acid inputs in precipitation and dry deposition (Cronan, 1978).

Aluminum is the third most abundant element by weight in the earth's crust (Foster, 1971). In general, aluminum is extremely insoluble and retained within the edaphic environment. However, with increased hydrogen ion inputs (via acidic deposition or other sources) into the edaphic environment, aluminum is rapidly mobilized. Cronan and Schofield (1979) suggest that input of strong acids may inhibit the historical trend of aluminum accumulation in the B soil horizon. Consequently, aluminum tends to be transported through the soil profile and into streams and lakes. Evidence from field data (Schofield and Trojnar, 1980) and laboratory experiments (Driscoll et al., 1979; Muniz and Leivestad, 1980) suggest that these elevated aluminum levels may be toxic to fish. Concentration of aluminum may be as or more important than pH levels as a factor leading to declining fish populations in acidified lakes. Aluminum toxicity to aquatic biota other than fish has not been assessed.

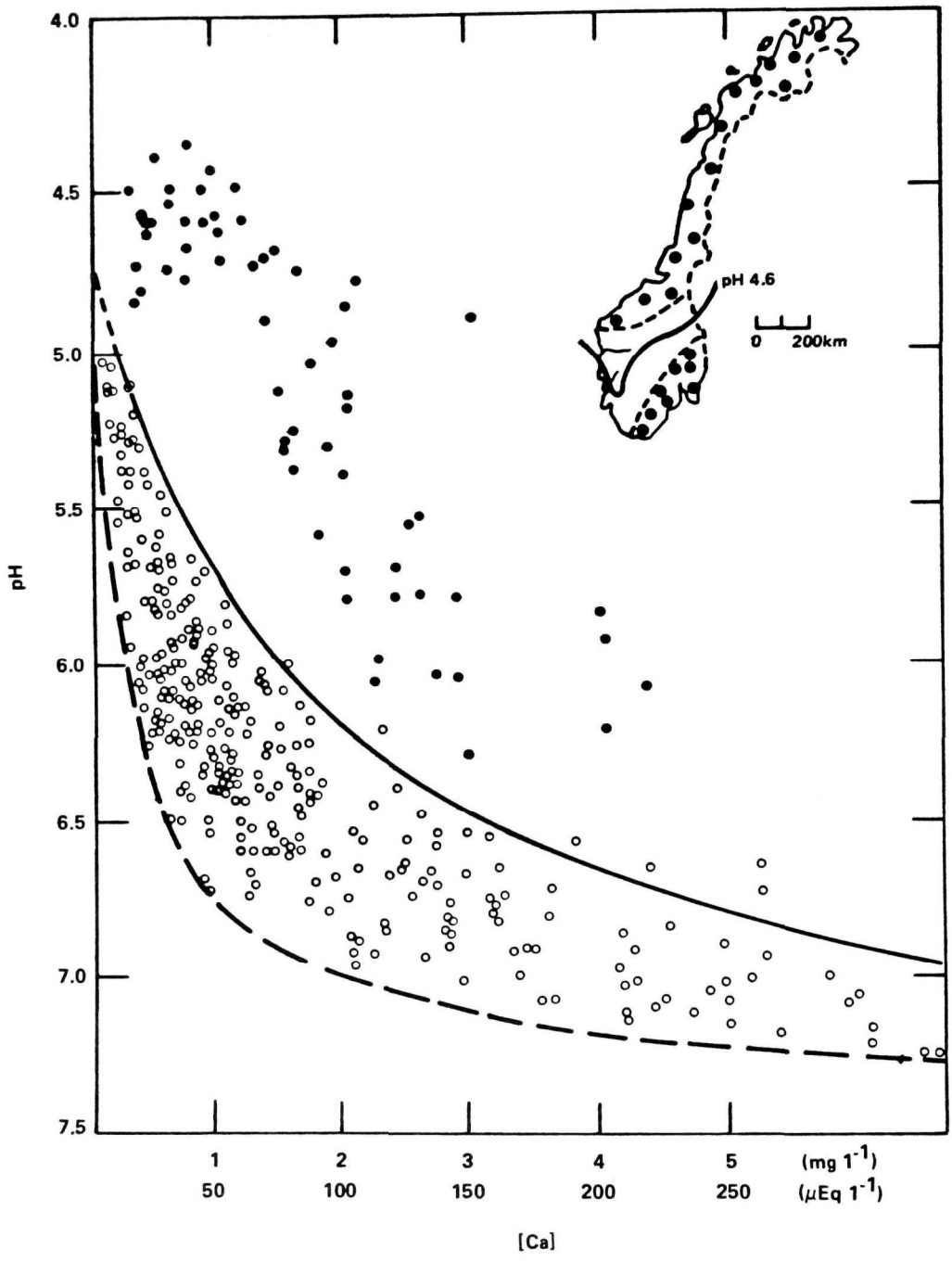


Figure 7-16. pH and calcium concentrations in lakes in northern and northwestern Norway sampled as part of the regional survey of 1975, in lakes in northwestern Norway sampled in 1977 (○) and in lakes in southernmost and southeastern Norway sampled in 1974 (●). Southern Norway receives highly acid precipitation (pH 4.2-4.5) and a large number of lakes have lost their fish populations due to high acidity. Inset shows areas in which these lakes are located. Areas south of isoline receive precipitation more acid than pH 4.6.

Source: Henriksen (1979).

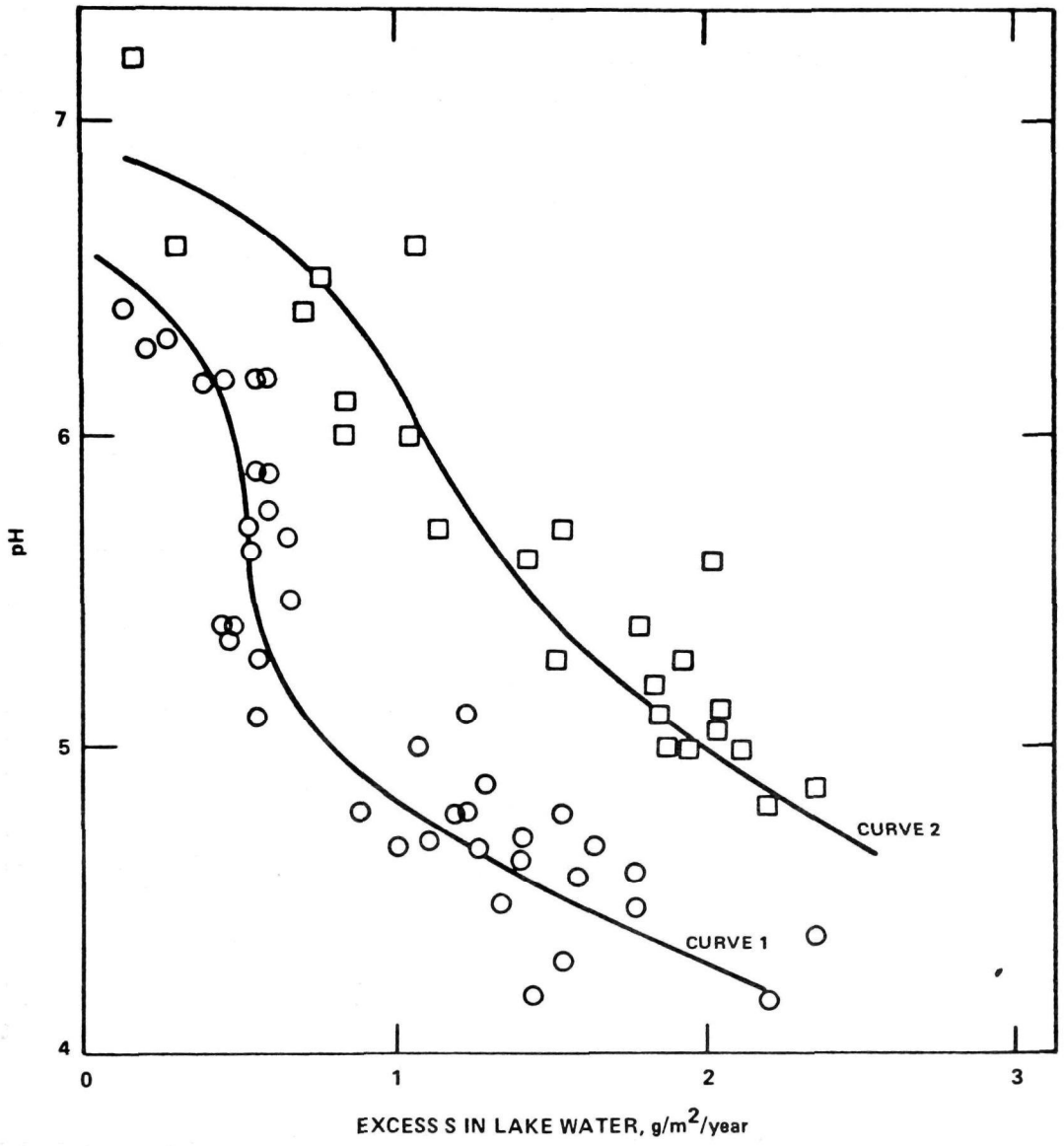


Figure 7-17. The pH value and sulfur loads in lake waters with extremely sensitive surroundings (curve 1) and with slightly less sensitive surroundings (curve 2). (Load = concentration of "excess" sulfur multiplied by the yearly runoff.)

Source: Almer et al. (1978).

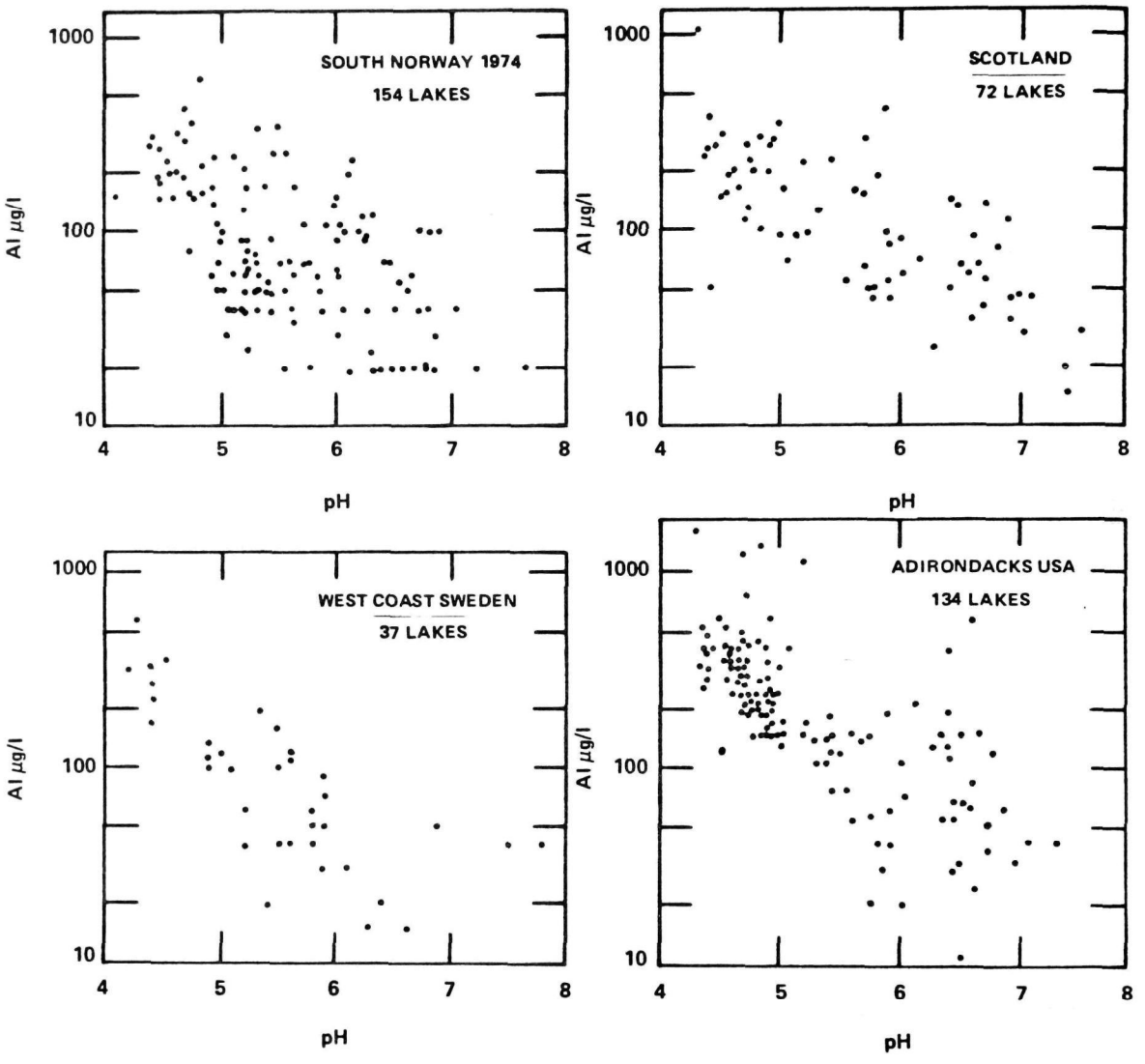


Figure 7-18. Total dissolved Al as a function of pH level in lakes in acidified areas in Europe and North America.

Source: Wright et al. (1980b).

*

Surface water chemistry, particularly in streams and rivers, may be highly variable with time. Since many of the neutralization reactions in soils are kinetically slow, the quality of the leachate from the edaphic system into the aquatic system varies with the retention time of water in the soil (Johnson et al., 1969). The longer the contact period of water with lower soil strata, the greater the neutralization of acid contribution from precipitation and dry deposition. Therefore, during periods of heavy rainfall or snowmelt, and rapid water discharge, pH levels in receiving waters may be relatively depressed.

Many of the regions currently affected by acidification experience freezing temperatures during the winter and accumulation of a snowpack. In the Adirondack Region of New York approximately 55 percent of the annual precipitation occurs during the winter months (Schofield, 1976b). Much of the acid load deposited in winter accumulates in the snowpack, and may be released during a relatively short time period during snowmelt in the spring. In addition, on melting, 50 to 80 percent of the pollutant load (including hydrogen ion and sulfate) may be released in the first 30 percent of the meltwater (Johannessen and Henriksen, 1978). As a result, melting of the snowpack and ice cover can result in a large influx of acidic pollutants into lakes and streams (Figure 7-19) (Gjessing et al., 1976; Schofield and Trojnar, 1980; Hultberg, 1976). The rapid flux of this meltwater through the edaphic environment, and its interaction with only upper soil horizons, limits neutralization of the acid content. As a result, surface waters only moderately acidic during most of the year may experience extreme drops in pH level during the spring thaw. Basic cation concentrations (Ca, Mg, Na, K) may also be lower during this time period (Johannessen et al., 1980). Similar but usually less drastic pH drops in surface waters (particularly streams) may occur during extended periods of heavy rainfall (Driscoll, 1980). These short term changes in water chemistry may have significant impacts on aquatic biota.

7.3.1.2 Effects on decomposition. The processing of dead organic matter (detritus) plays a central role in the energetics of lake and stream ecosystems (Wetzel, 1975). The organic matter may have been generated either internally (autochthonous) via photosynthesis within the aquatic ecosystem or produced outside the lake or stream (allochthonous) and later exported to the aquatic system. Detritus is an important food source for bacteria, fungi, some protozoa, and other animals. These organisms through the utilization of detritus release energy, minerals and other compounds stored in the organic matter back into the environment. Initial processing of coarse particulate detritus is often accomplished by benthic invertebrate fauna. Among other things, the particles are physically broken down into smaller units, increasing their surface area. Biochemical transformations of particulate and dissolved organic matter occur via microbial metabolism and are fundamental to the dynamics of nutrient cycling and energy flux within the aquatic ecosystem.

In general, the growth and reproduction of microorganisms is greatly affected by hydrogen ion concentration (Rheinheimer, 1971). Many bacteria can grow only within the range pH 4-9 and the optimum for most aquatic bacteria is between pH 6.5 and 8.5. There are more acidiphilic fungi than bacteria; consequently in acid waters and sediments the proportion of fungi

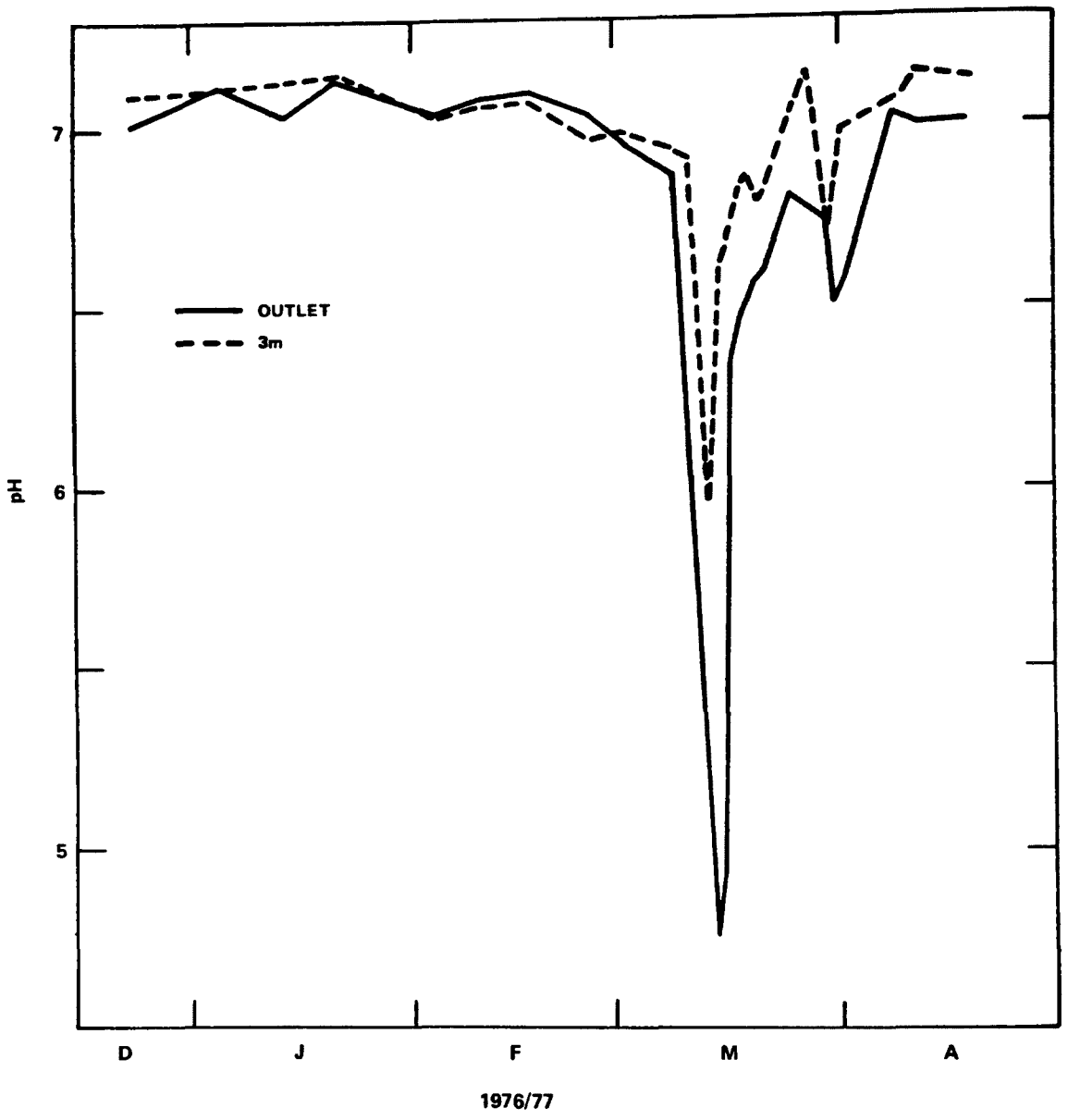


Figure 7-19. pH levels in Little Moose Lake, Adirondack region of New York State, at a depth of 3 meters and at the lake outlet.

Source: Adapted from Schofield and Trojnar (1980).

*
in the microflora is greater than in waters or sediments with neutral or slightly alkaline pH levels. Most aquatic fungi require free oxygen for growth (Rheinheimer, 1971).

Numerous studies have indicated that acidification of surface waters results in a shift in microbial species and a reduction in microbial activity and decomposition rates. It should be noted, however, that microorganisms in general are highly adaptive. Given sufficient time, a given species may adapt to acid conditions or an acid-tolerant species may invade and colonize acidified surface waters. Therefore, some caution is necessary in interpreting short-term experiments on the effects of acidification on microbial activity and decomposition. On the other hand, increased accumulations of dead organic matter (as a result of decreased decomposition rates) are commonly noted in acidic lakes and streams.

Abnormal accumulations of coarse organic matter have been observed on the bottoms of six Swedish lakes. The pH levels in these lakes in July 1973 were approximately 4.4 to 5.4. Over the last three to four decades, pH levels appear to have decreased 1.4 to 1.7 pH units (Grahn et al., 1974). In both Sweden and Canada, acidified lakes have been treated with alkaline substances to raise pH levels. One result of this treatment has been an acceleration of organic decomposition processes and elimination of excess accumulations of detritus (Andersson et al., 1978; Scheider et al., 1975). Litterbags containing coarse particulate detrital matter have been used to monitor decomposition rates in acidified lakes and streams. In general, the rates of weight loss were reduced in acidic waters when compared with more neutral waters (Leivestad et al., 1976; Traaen and Laake, 1980; Petersen, 1980). Traaen and Laake (1980) found that after 12 months of incubation dried birch leaves or aspen sticks showed a weight loss of 50-80 percent in waters with pH levels 6 to 7 as compared to only a 30-50 percent weight loss in waters with pH 4 to 5. Petersen (1980) likewise found reduced weight loss of leaf packs incubated in an acidic stream when compared to leaf packs in either a stream not affected by acidification or a stream neutralized with addition of lime. Petersen, however, found no evidence of differences in microbial respiration between the streams. The acidic stream did show a reduction in the invertebrate functional group that specializes in processing large particles (shredders). Andersson et al. (in press) found no significant differences in oxygen consumption by sediments from acidified and non-acidified lakes. Rates of glucose decomposition were also studied in lake sediment-water systems adapted to pH values from 3 to 9. Glucose transformation increased at pH levels above 6. Lime treatment of acidic Lake Högsjön in Sweden also increased rates of glucose processing. However in a humic lake, the maximum rate of glucose transformation occurred at the in situ value pH 5 (Andersson et al., in press).

Laboratory and field experiments involving decomposition rates have fairly consistently found decreasing microbial activity with increasing acidity. Traaen and Laake (1980) found that litter decomposition at pH level 5.2 was only 50 percent of that at pH 7.0 and at pH 3.5, only 30 percent that at pH 7.0. In addition, increasing acidity (pH 7.0 to 3.5) led to a shift from bacterial to fungal dominance. Incubations of profundal lake sediments at pH 4, 5,

*
and 6 indicated a significant reduction in community respiration with increasing acidity, as well as a possible inhibition of nitrification and a lowering of sediment redox potentials. Bick and Drews (1973) studied the decomposition of peptone in the laboratory. With decreasing pH, total bacterial cell counts and numbers of species of ciliated protozoans decreased, decomposition and nitrification were reduced and oxidation of ammonia ceased below pH 5. At pH 4 and lower, the number of fungi increased.

Disruption of the detrital trophic structure and the resultant interference with nutrient and energy cycling within the aquatic ecosystem may be one of the major consequences of acidification. Investigations into the effects of acidification on decomposition have, apparently, produced somewhat inconsistent results. However, many of these apparent inconsistencies arise only from a lack of complete understanding of the mechanisms relating acidity and rates of decomposition. It is fairly clear that in acidic lakes and streams unusually large accumulations of detritus occur, and these accumulations are related, directly or indirectly, to the low pH level. The processing of organic matter has been reduced. In addition, this accumulation of organic debris plus the development of extensive mats of filamentous algae on lake bottoms (discussed in Section 7.3.1.3) may effectively seal off the mineral sediments from interactions with the overlying water. As a result, regeneration of nutrient supplies to the water column is reduced both by reduced processing and mineralization of dead organic matter and by limiting sediment-water interactions. Primary productivity within the aquatic system may be substantially reduced as a result of this process (Section 7.3.1.3). These ideas have been formulated into the hypothesis of "self-accelerating oligotrophication" by Grahn et al. (1974).

7.3.1.3 Effect on primary producers and primary productivity. Organisms obtain their food (energy) directly or indirectly from solar energy. Sunlight, carbon dioxide, and water are used by primary 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. Each link in the food chain is termed a trophic level. The major trophic levels are the primary producers, herbivores, carnivores, and the decomposers. Energy in an ecosystem moves primarily along two main pathways: the grazing food chain (primary producers-herbivores-carnivores) and the detrital food chain (Smith, 1980; Billings, 1978; Odum, 1971). Interactions between these two food chains are, however, extensive. Green plants convert solar energy to organic matter and, as such, are the base for both food chains. The grazing food chain involves primarily living organic matter; the detrital food chain, dead organic matter. Any changes as a result of acidification in the green plants and primary production within the aquatic ecosystem may therefore have a profound effect on all other organisms in the aquatic food web. As noted in Section 7.3.1.2, a portion of the detrital food chain is supported by dead organic matter imported into the aquatic system from external sources.

*

Extensive surveys of acidic lakes in Norway and Sweden (Leivestad et al., 1976; Almer et al., 1974) have observed changes in species composition and reduced diversity of phytoplankton correlated with decreasing lake pH level (Figure 7-20). Generally at normal pH values of 6 to 8, lakes in the west coast region of Sweden contain 30 to 80 species of phytoplankton per 100-ml sample in mid-August. Lakes with pH below 5 were found to have only about a dozen species. In some very acid lakes (pH<4), only three species were noted. The greatest changes in species composition occurred in the pH interval 5-6. The most striking change was the disappearance of many diatoms and blue-green algae. The families Chlorophyceae (green algae) and Chrysophyceae (golden-brown algae) also had greatly reduced numbers of species in acidic lakes (Figure 7-21). Dinoflagellates constituted the bulk of the phytoplankton biomass in the most acidic lakes (Almer et al., 1978). Similar phenomena were observed in a regional survey of 55 lakes in southern Norway (Leivestad et al., 1976) and in a study of nine lakes in Ontario (Stokes, 1980). Changes in species composition and reduced diversity have also been noted in communities of attached algae (periphyton) (Leivestad et al., 1976; Almer et al., 1978). Mougeotia, a green algae, often proliferates on substrates in acidic streams and lakes.

Shifts in the types and numbers of species present may or may not affect the total levels of primary productivity and algal biomass in acidic lakes. Species favored by acidic conditions may or may not have comparable photosynthetic efficiencies or desirability as a prey item for herbivores. On the other hand, decreased availability of nutrients in acidic water as a result of reduced rates of decomposition (Section 7.3.1.2) may decrease primary productivity regardless of algal species involved. In field surveys and experiments, relationships between pH level and total algal biomass and/or productivity were not as consistent as the relationship between pH and species diversity.

Kwiatkowski and Roff (1976) identified a significant linear relationship of decreasing chlorophyll a concentrations (indicative of algal biomass) with declining pH level in six lakes near Sudbury, Ontario, with a pH range of 4.05 to 7.15. In addition, primary productivity was reduced in the two most acid lakes (pH 4-4.6). Stokes (1980) also reports a decrease in total phytoplankton biomass with decreasing pH level for nine lakes in the same region of Ontario. Crisman et al. (1980) reported a linear decrease in functional chlorophyll a measurements with declining pH for 11 lakes in northern Florida, pH range 4.5 to 6.9. On the other hand, Almer et al. (1978) note that in 58 nutrient-poor lakes in the Swedish west coast region, the largest mean phytoplankton biomass occurred in the most acid lakes (pH <4.5). Yan and Stokes (1978) concluded that they have no evidence that the phytoplankton biomass in Carlyle Lake, with a summer pH level about 5.1, is below that observed in circumneutral lakes in the same region. In a continuing whole-lake acidification project (Schindler et al., 1980), a lowering of the epilimnion pH level from 6.7-7.0 in 1976 to 5.7-5.9 in 1978 resulted in no significant change in the chlorophyll concentration or primary production. Both in situ and experimental acidification have resulted in large increases in periphyton populations (Muller, 1980; Hendrey, 1976; Hall et al., 1980). Hendrey (1976) and Muller (1980) observed

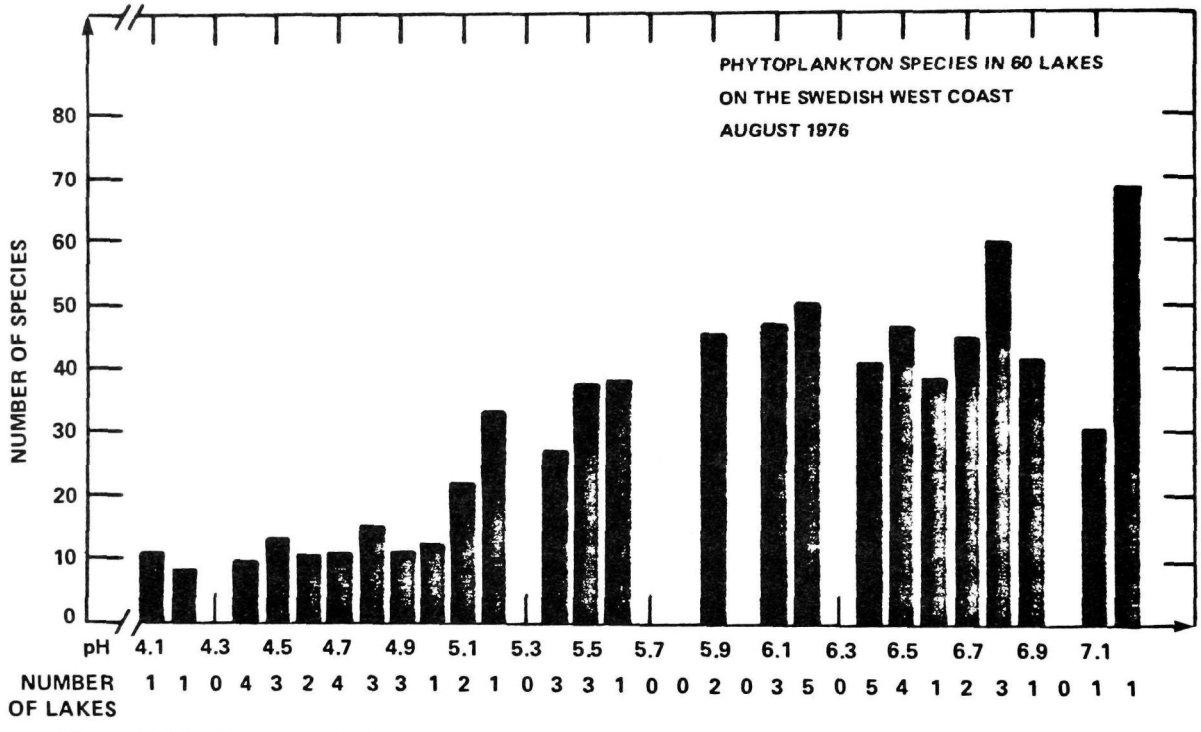


Figure 7-20. Numbers of phytoplankton species in 60 lakes having different pH values on the Swedish West Coast, August 1976.

Source: Adapted from Almer et al. (1978).

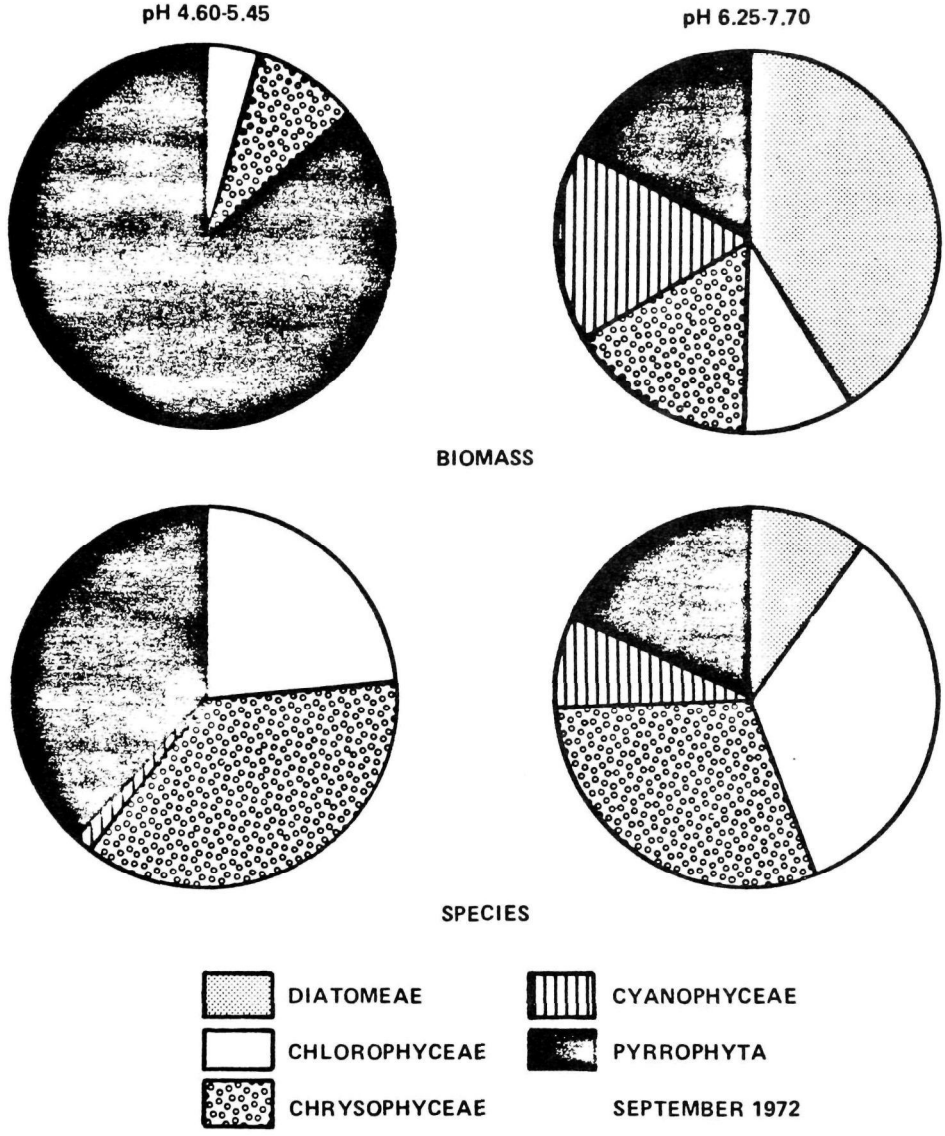


Figure 7-21. Percentage distribution of phytoplankton species and their biomasses. September 1972, west coast of Sweden. Biomass = living weight per unit area.

Source: Adapted from Almer et al. (1978).

*
carbon uptake by periphyton incubated in vitro. They found that, although the total rate of photosynthesis increased with decreasing pH level due to the larger biomass at the lower pH, the photosynthesis per unit biomass decreased with pH.

From the above discussion it is obvious that not only is there no clear correlation between pH level and algal biomass or productivity, but the effects of acidification appear inconsistent between systems. Again, these apparent inconsistencies probably reflect a lack of knowledge about exact mechanisms relating acidification and lake metabolism, and also the complexity of these mechanisms and interactions. Changes in the algal community biomass and productivity probably reflect the balance between a number of potentially opposing factors; those that tend to decrease productivity and biomass versus those that tend to increase productivity and/or biomass when acidity increases. Factors working to decrease productivity and biomass with declining pH levels may include: (1) a shift in pH level below that optimal for algal growth, (2) decreased nutrient availability as a result of decreased decomposition rates and a sealing-off of the mineral sediments from the lake water; and (3) decreased nutrient availability as a result of changes in aquatic chemistry with acidification. For example, despite the fact that the optional pH range for growth of Tabellaria flocculosa is between 5.0 to 5.3 (Cholonsky, 1968) or higher (Källqvist et al., 1975), this species dominated experimentally acidified stream communities at pH level 4 in three out of five replicates (Hendrey et al., 1980). As noted in Section 7.3.1.1, aluminum concentrations increase with decreasing pH level in acidified lakes and streams. Aluminum is also a very effective precipitator of phosphorus, particularly in the pH range 5 to 6 (Dickson, 1978; Stumm and Morgan, 1970). In oligotrophic lakes, phosphorus is most commonly the limiting nutrient for primary productivity (Wetzel, 1975; Schindler, 1975). Therefore, chemical interactions between aluminum and phosphorus may result in a decreasing availability of phosphorus with decreasing pH level, and, as a result, decreased primary production.

Factors working to increase productivity and/or biomass with acidification of a lake or stream may include: (1) decreased loss of algal biomass to herbivores; (2) increased lake transparency; and (3) increased nutrient availability resulting from nutrient enrichment of precipitation. Decreased population of invertebrates (as discussed in Section 7.3.1.4), particularly herbivorous invertebrates, may decrease grazing pressure on algae and result in unusual accumulations of biomass. Hendrey (1976) and Hall et al. (1980) include this mechanism as one hypothesis to explain their observation of increased biomass of periphyton at pH level 4 despite a decreased production rate per unit biomass.

Increases in lake transparency over time have been correlated with lake acidification in Sweden (Almer et al., 1978) and the Adirondack Region of New York (Schofield, 1976c). In addition, after the second year of experimental lake acidification (pH 6.7-7.0 to 5.7-5.9) in northwestern Ontario (Schindler et al., 1980), lake transparency increased by 1-2 m. These increases in transparency have not been correlated with decreases in phytoplankton biomass.

*
Two mechanisms have been proposed. Aluminum acts as a very efficient precipitator for humic substances. Dickson (1978) found that humic substances are readily precipitated in the pH range 4.0 to 5.0. Dickson (1978) and Almer et al. (1978) suggest that increases in aluminum levels with lake acidification (Section 7.3.1.1) have resulted in increased precipitation of humics from the water column and therefore increased lake transparency. Almer at al. (1978) provide data for one lake on the west coast of Sweden. The pH level declined from above 6 to about 4.5 between 1940 and 1975. The secchi disc reading increased from about 3m to about 10m over the same period. Organic matter in the water (as estimated by $KMnO_4$ demand) decreased from 24 to 8 mg/liter from 1958 to 1973. Schindler et al. (1980), on the other hand, found no change in levels of dissolved organic carbon with acidification. Instead, changes in hydrolysis of organic matter with declining pH level may affect the light absorbancy characteristics of the molecules. Levels of particulate organic carbon, and changes with pH level, were not reported by Schindler et al. (1980).

Acidification of precipitation (and dry deposition) has been accompanied by increases in levels of sulfate and nitrate. Both of these are nutrients required by plants. However, as noted above, the primary nutrient limiting primary productivity in most oligotrophic lakes is phosphorus. Almer et al. (1978) report that atmospheric deposition rates of phosphorus have also increased in recent years. The world-wide extent of the correlation between acidic deposition and increased atmospheric phosphorus loading, however, is not known. It is expected that changes in atmospheric phosphorus loading would be much more localized than changes in acidic deposition. It is possible that in some areas increased atmospheric loading of phosphorus has occurred in recent years coincidently with increased acidic deposition. Increased phosphorus nutrient loading into lakes may then increase primary production rates.

The effect of acidification on primary productivity and algal biomass of a particular stream or lake system depends upon the balance of the above forces. Differences in the importance of these factors between systems may account for inconsistencies in the response of different aquatic systems to acidic deposition. Acidification does, however, result in a definite change in the nutrient and energy flux of the aquatic system, and this change may eventually limit the total system biomass and productivity.

Acidification of lakes has also been correlated with changes in the macrophyte community. Documentation for these changes comes mainly from lakes in Sweden. Grahn (1976) reported that in five to six lakes studies in the last three to five decades the macrophyte communities dominated by Lobelia and Isoetes have regressed, whereas communities dominated by Sphagnum mosses have expanded. Acidity levels in these lakes apparently have increased approximately 1.3 to 1.7 pH units since the 1930-40's. In acid lakes where conditions are suitable the Sphagnum peat moss may cover more than 50 percent of the bottom above the 4-m depth, and may also grow at much lower depths (Almer et al., 1978). The Sphagnum invasion may start at lake pH levels just below 6 (Almer et al., 1978). Similar growths of Sphagnum occur in Norwegian lakes (National Research Council, 1978). Increases in Sphagnum as a benthic macrophyte have

*
been documented from one lake in the Adirondack Region of New York (Hendrey and Vertucci, 1980).

Under acid conditions the Sphagnum moss appears to simply outgrow flowering plant aquatic macrophytes. In laboratory tests, the growth and productivity of the rooted macrophyte Lobelia was reduced by 75 percent at a pH of 4, compared with the control (pH 4.3-5.5). The period of flowering was delayed by ten days at the low pH (Laake, 1976). At low pH levels (pH<5), essentially all the available inorganic carbon is in the form of carbon dioxide or carbonic acid (Stumm and Morgan, 1970). As a result, conditions may be more favorable for Sphagnum, an acidophile that is not able to utilize the carbonate ion.

Besides the shift in macrophyte species, the invasion of Sphagnum into acid lakes may have four other impacts on the aquatic ecosystem. Sphagnum has a very high ion-exchange capacity, withdrawing basic cations such as Ca^{++} from solution and releasing H^{+}(Anschütz and Gessner, 1954; Almer et al., 1978). As a result, the presence of Sphagnum may intensify the acidification of the system and decrease the availability of basic cations from other biota. Second, dense growths of Sphagnum form a biotype that is an unsuitable substratum for many benthic invertebrates (Grahn, 1976). Growths of Sphagnum in acidic lakes are also often associated with felts of white mosses (benthic filamentous algae) and accumulations of non-decomposed organic matter. In combination, these organisms and organic matter may form a very effective seal. Interactions between the water column and the mineral sediments, and the potential for recycling of nutrients from the sediments back into the water body, may be reduced (Grahn, 1976; Grahn, et al., 1974). These soft bottoms may also be colonized by other macrophytes. In Sweden, Almer et al. (1978) report that growths of Juncus, Sparaganium, Utricularia, Nuphar, and/or Nymphaea, in addition to Sphagnum, may be extensive in acidic lakes. Thus primary production by macrophytes in lakes with suitable bottoms may be very large. Increased lake transparency may also increase benthic macrophyte and algal primary productivity.

7.3.1.4 Effects on invertebrates. In regional surveys conducted in southern Norway (Hendrey and Wright, 1976), the west coast of Sweden (Almer et al., 1978), the LaCloche Mountain Region of Canada (Sprules, 1975), and near Sudbury, Ontario (Roff and Kwiatkowski, 1977) numbers of species of zooplankton were strongly correlated with pH level (Figure 7-22). Changes in community structure were most noticeable at pH levels below 5. Certain species (e.g., of the genera Bosmina, Cyclops, Diaptomus, and rotiferans, of the genera Polyarthra, Keratella, and Kellicottia) apparently have a high tolerance of acidic conditions and were commonly found in the pH interval 4.4 to 7.9. Others, such as cladocerans of the Daphnia genus, apparently are more sensitive and were only rarely found at pH <6 (Almer et al., 1978).

Similar studies of the relationship between pH level and biomass or productivity of zooplankton are not available. Proposed mechanisms for interactions between lake acidification and zooplankton populations are therefore largely hypothetical.

The species, population size, and productivity of zooplankton are affected both by changes in the quality and quantity of the food supply and shifts in predator populations.

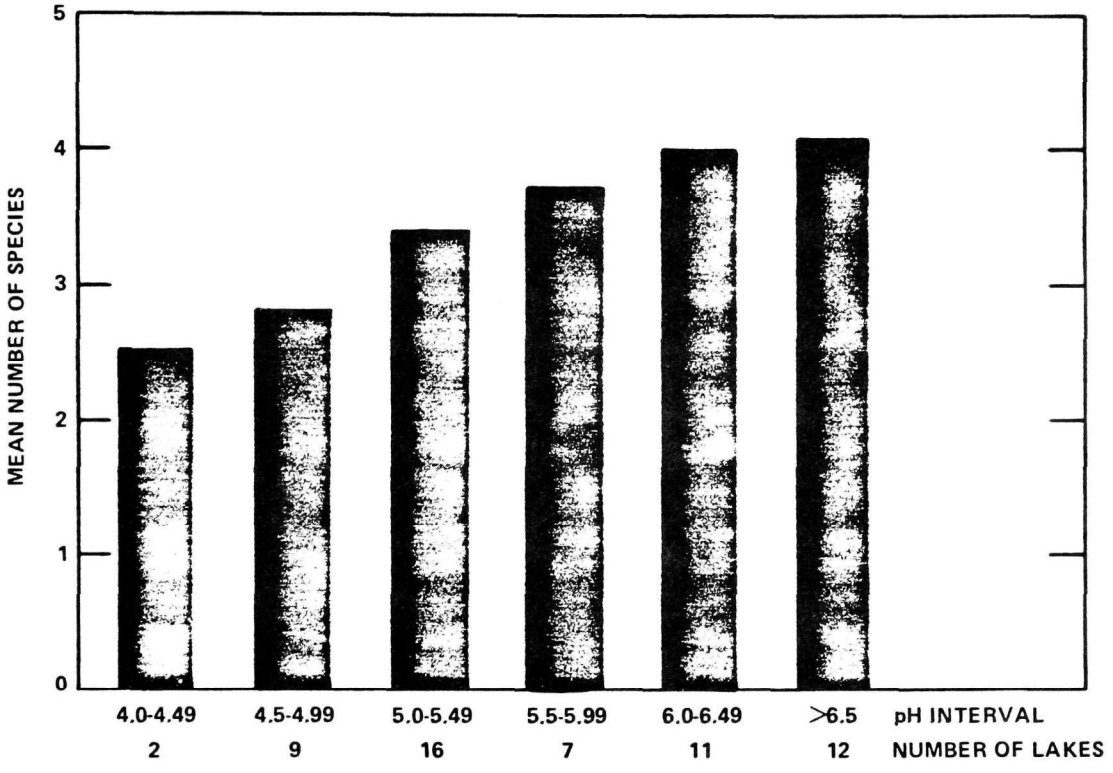


Figure 7-22. The number of species of crustacean zooplankton observed in 57 lakes during a synoptic survey of lakes in southern Norway.

Source: Levestad et al. (1976).

*
Changes in zooplankton species and production in response to changes in fish populations have been clearly demonstrated (Brooks and Dodson, 1965; Walters and Vincent, 1973; Dodson, 1974). Elimination of fish predators often results in dominance of the zooplankton community by large-bodied species. Absence of invertebrate predators (e.g., large-bodied carnivorous zooplankton) as a result of fish predation or other reasons often results in the prevalence of small-bodied species (Lynch, 1979). Surveys of acidic lake waters often have shown the dominance of small-bodied herbivores in the zooplankton community (Hendrey et al, 1980). Fish also often are absent at these pH levels (Section 7.3.1.5). Different zooplankton species may have different physiological tolerances to depressed pH levels (e.g., Potts and Fryer, 1979). Food supplies, feeding habits, and grazing of zooplankton may also be altered with acidification as a consequence of changes in phytoplankton species composition and/or decreases in biomass or productivity of phytoplankton. Zooplankton also rely on bacteria and detrital organic matter for part of their food supply. Thus an inhibition of the microbiota or a reduction in microbial decomposition (Section 7.3.1.2) may also affect zooplankton populations. These alternate mechanisms postulate for changes in community structure and/or production of zooplankton communities probably play an important role in zooplankton responses to acidification.

Synoptic and intensive studies of lakes and streams have also demonstrated that numbers of species of benthic invertebrates are reduced along a gradient of decreasing pH level (Sutcliffe and Carrick, 1973; Leivestad et al., 1976; Conroy et al., 1976; Almer et al., 1978; Roff and Kwiatkowski, 1977). In 1500 freshwater localities in Norway studied from 1953-73, snails were generally present only in lakes with pH levels above 6 (Okland, J., 1980). Likewise Gammarus Lacustris, a freshwater shrimp and an important element in the diet of fish in Scandinavia, was not found at pH levels below 6.0 (Okland, K., 1980). Experimental investigations have shown that adults of this species cannot tolerate two days of exposure to pH 5.0 (Leivestad et al., 1976). Eggs were reared at six different pH levels (4.0 to 6.8). At a pH of 4.5 a majority of the embryos died within 24 hours. Thus the short-term acidification which often occurs during the spring melt of snow could eliminate this species from small lakes (Leivestad et al., 1976). Fiance (1977) concluded that ephemeropterans (mayflies) were particularly sensitive to low pH levels and their populations were reduced in headwater streams of the Hubbard Brook watershed in New Hampshire. In laboratory studies, Bell (1971), Bell and Nebeke (1969), and Raddum (1978) measured the tolerance of some stream macroinvertebrates to low pH levels. Tolerance seems to be in the order caddisflies > stoneflies > mayflies (Hendrey et al., 1980).

Leivestad et al. (1976) reported on decreased standing crops (numbers/m^2 and g/m^2) of benthic invertebrates in two lakes with pH levels near 4.5 as compared to five lakes with pH near 6.0. Chironamids were the dominant group in all lakes. No fish were found in the acid lakes. Lack of predation by fish should favor increases in benthic biomass, the opposite of that observed. Hendrey et al. (1980), on the other hand, from data from eight Ontario lakes (pH 4.3 - < 5.7) reported no reduction in abundance of benthos related to pH level.

*

Air-breathing aquatic insects (e.g., backswimmers, water boatmen, water striders) appear very tolerant of acidic environments. Population densities are often greater in acidic lakes and in the most acid lakes than in circumneutral lakes. Abundance of these large invertebrates may be related to reduced fish predation (Hendrey et al., 1980).

Hall et al. (1980) experimentally acidified a stream to pH 4 and monitored reactions of macroinvertebrate populations. Initially following acidification there was a 13-fold increase in downstream drift of insect larvae. Organisms in the collector and scraper functional groups were affected more than predators. Benthic samples from the acidified zone of Norris Brook contained 75 percent fewer individuals than those for reference areas. There was also a 37 percent reduction in insect emergence; members of the collector group were most affected. Insects seem to be particularly sensitive at emergence (Bell, 1971). Many species of aquatic insects emerge early in the spring through cracks in the ice and snow cover. These early-emerging insects are therefore exposed in many cases to the extremely acidic conditions associated with snowmelt (Hagen and Langeland, 1973).

Low pH also appeared to prevent permanent colonization by a number of invertebrate species, primarily herbivores, in acidified reaches of River Dudden, England (Sutcliffe and Carrick, 1973). Ephemeroptera, trichoptera, Ancylus (Gastropoda) and Gammarus were absent in these reaches.

Damage to invertebrate communities may influence other components of the food chain. Observations that herbivorous invertebrates are especially reduced in acidic streams, as reported in Norris Brook and River Dudden, support the hypothesis (Hendrey, 1976; Hall et al., 1980) that changes in invertebrate populations may be responsible for increased periphytic algal accumulations in acidic streams and benthic regions of acidic lakes (Hendrey et al., 1980). Benthic invertebrates also assist with the essential function of processing dead organic matter. Petersen (1980) noted that decomposition of coarse particulate organic matter in leaf packs was lower in an acidic stream than in two streams with circumneutral pH levels. The invertebrate community also showed a reduction in the invertebrate functional group that specializes in processing large particles (shredders). In unstressed aquatic ecosystems, a continuous emergence of different insect species is available to predators from spring to autumn. In acid-stressed lakes or streams, the variety and numbers of prey may be reduced. Periods may be expected to occur in which the amount of prey available to fish (or other predators) is diminished.

7.3.1.5 Effects on fish. Acidification of surface waters has had its most obvious, and perhaps the most severe, impact on fish populations. Increasing acidity has resulted not just in changes in species composition or decreases in biomass but in many cases in total elimination of populations of fish from a given lake or stream. Extensive depletion of fish stocks has occurred in large regions of Norway, Sweden, and parts of eastern North America. Both commercial and sport fisheries have been affected in these areas. However, precise assessments of losses--in terms of population extinctions, reductions in yields, or economic and

*
social impacts--either have not been attempted or are still in the process of evaluation. Potential damage to fish populations inhabiting other acid-sensitive aquatic ecosystems in New England, the Appalachians, and parts of southeastern, north central, and northwestern United States have not yet been assessed (National Research Council, 1978).

Declines in fish populations have been related to acidification of surface waters in the Adirondack Region of New York State (Schofield 1976), southern Norway (Jensen and Snekyik, 1972; Wright and Snekvik, 1978), southwestern Sweden (Almer et al., 1974), the LaCloche Mountain Region in southern Ontario (Beamish and Harvey, 1972), and southwestern Scotland (Wright et al., 1980a). Schofield (1976) estimated that in 1975 fish populations in 75 percent of Adirondack lakes at high elevation (<610 m) had been adversely affected by acidification. Fifty-one percent of the lakes had pH values less than 5, and 90 percent of these lakes were devoid of fish life (Figure 7-23). Comparable data for the period 1929 to 1937 indicated that during that time only about 4 percent of these lakes had pH values below 5 and were devoid of fish (Figure 7-27). Therefore, entire fish communities consisting of brook trout (Salvelinus fontinalis), lake trout (Salvelinus namaycush), white sucker (Catostomus commersoni), brown bullhead (Icaturus nebulosus) and several cyprinid species were apparently eliminated over a period of 40 years. This decrease in fish populations was associated with a decline in lake pH level. A survey of more than 2000 lakes in southern Norway, begun in 1971, found that about one third of these lakes had lost their fish population (primarily brown trout, Salmo trutta L.) since the 1940's (Wright and Snekvik, 1978). Fish population status was inversely related to lake pH level (Leivestad et al., 1976). Declines in salmon populations in southern Norwegian rivers were reported as early as the 1920's. Catch of Atlantic salmon (Salmo salar, L.) in nine acidified southern Norwegian rivers is now virtually zero (Figure 7-25). In northern and western rivers not affected by acidification, no distinct downward trend in catch has occurred (Leivestad et al., 1976; Wright et al., 1976; Jensen and Snekvik, 1972). Similar changes have been observed in Sweden (Almer et al., 1974) where it is estimated that 10,000 lakes have been acidified to a pH less than 6.0 and 5,000 below a pH of 5.0 (Dickson, 1975). Populations of lake trout, lake herring (Coregonus artedii), white suckers, and other species disappeared rapidly during the 1960's from a group of remote lakes in the LaCloche Mountain Region of Ontario (Beamish et al., 1975).

It is difficult to determine at what pH level fish species disappear from lakes. Disappearance of the fish is usually not due to massive fish kills, but is the result of a gradual depletion of the population following reproductive failures (Leivestad et al., 1976). Field surveys in Scandinavia and eastern North America (Wright and Snekvik, 1978, Almer et al., 1974; Schofield, 1976) suggest that many species do not occur in lakes with pH values below 5.0.

However, large spatial and temporal functions in pH, and the possibility for "refuge areas" from acidic conditions during critical periods make it extremely difficult to generalize about effects of acidification on fish populations based on grab samples or annual mean pH levels.

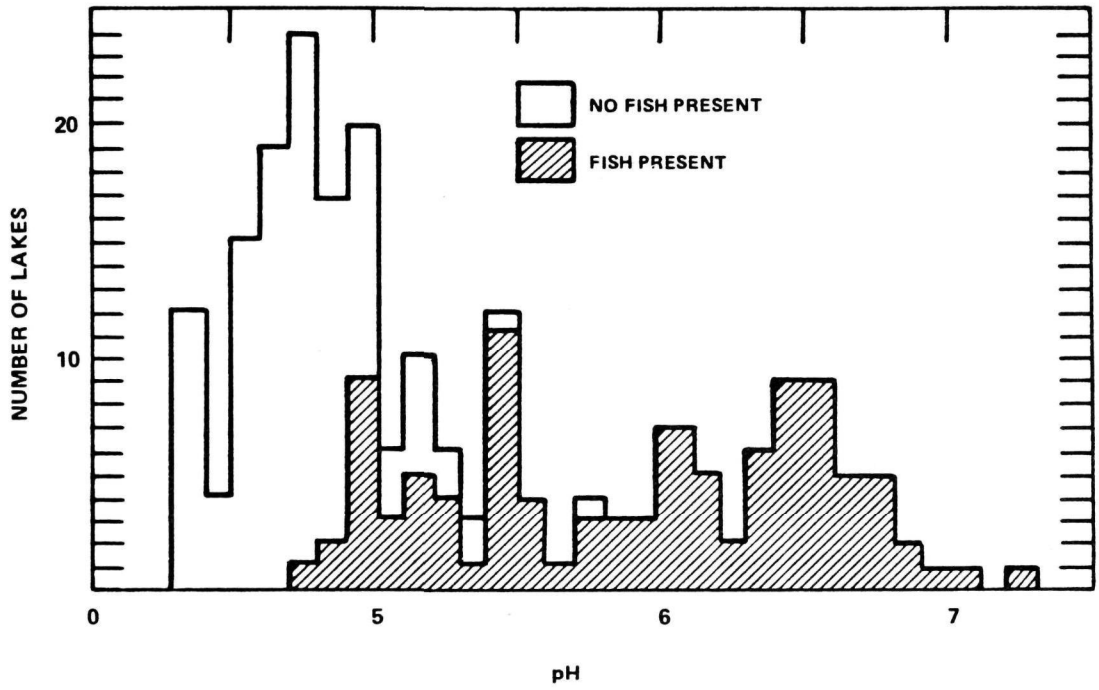


Figure 7-23. Frequency distribution of pH and fish population status in Adirondack Mountain lakes greater than 610 meters elevation. Fish population status determined by survey gill netting during the summer of 1975.

Source: Schofield (1976b).

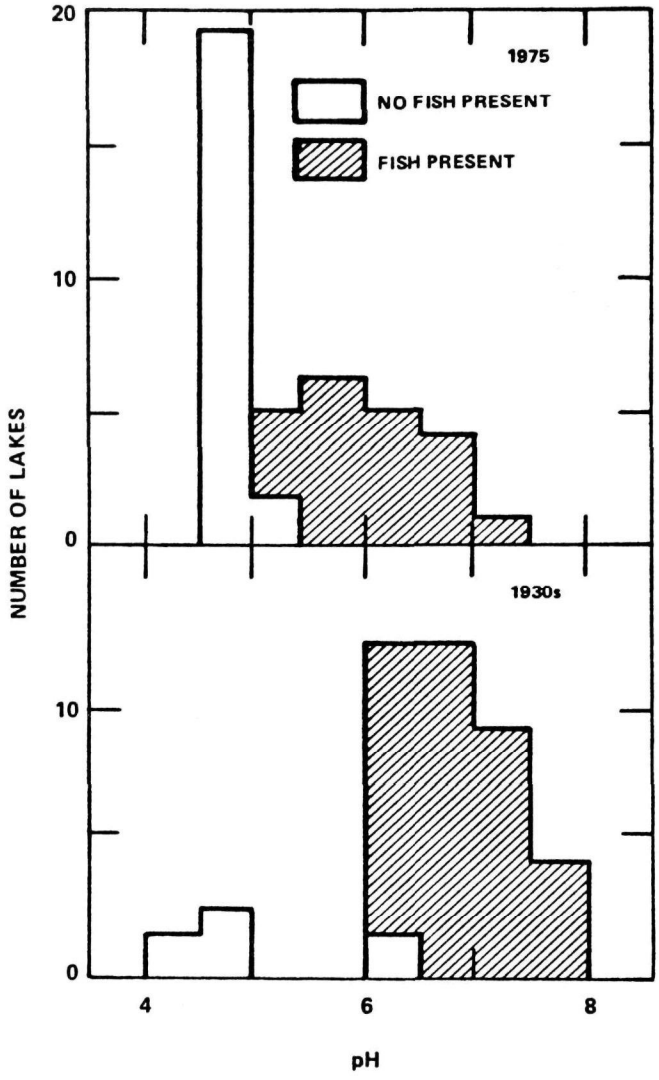


Figure 7-24. Frequency distribution of pH and fish population status in 40 Adirondack lakes greater than 610 meters elevation, surveyed during the period 1929-1937 and again in 1975.

Source: Schofield (1976 b).

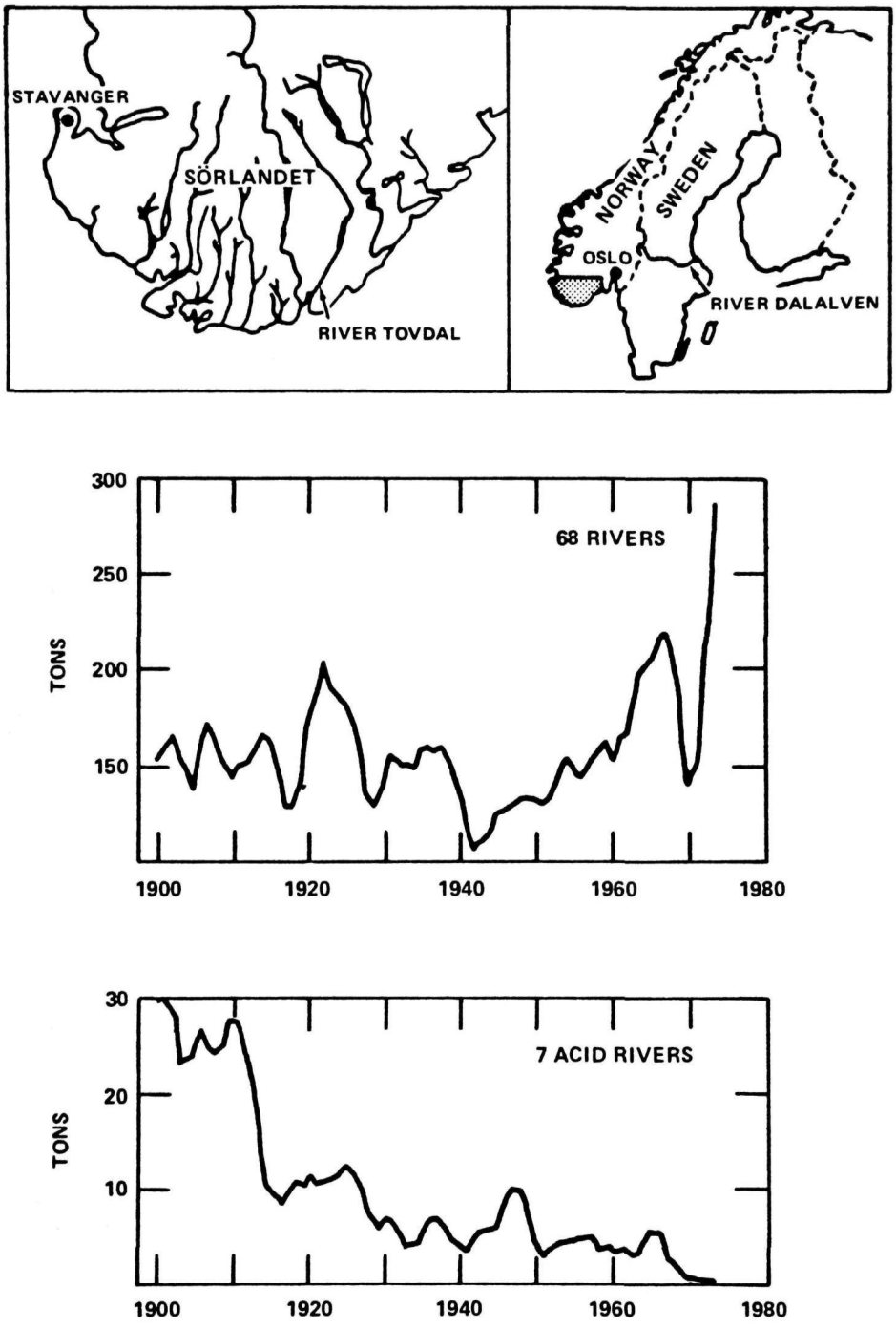


Figure 7-25. Norwegian salmon fishery statistics for 68 unacidified and 7 acidified rivers.

Source: Adapted from Almer et al. (1978).

*
The pH levels identified in the literature as critical for reproduction of a species or correlated with the absence of a species in lake surveys are summarized in Table 7-6. Values range from pH 4.4 to over 6.0, and are highly species dependent.

TABLE 7-6. pH LEVELS IDENTIFIED IN FIELD SURVEYS AS CRITICAL TO LONG-TERM SURVIVAL OF FISH POPULATIONS

Family	Species	Critical pH	Reference
Salmonidae	Brook trout (Salvelinus fontinalis)	5.0	Schofield, 1976c
	Lake trout (Salvelinus namaycush)	5.1	Schofield, 1976c
		5.2-5.5	Beamish, 1976
	Brown trout (Salmo trutta)	5.0	Almer et al., 1978
	Arctic char (Salvelinus alpinus)	5.2	Almer et al., 1978
Percidae	Perch (Perca fluviatilis)	4.4-4.9	Almer et al., 1978
	Yellow perch (Perca flavescens)	4.5-4.7	Beamish, 1976
	Walleye (Stigostedion vitreum)	5.5-6.0+	Beamish, 1976
Catostomidae	White sucker (Catostomus commersoni)	4.7-5.2	Beamish, 1976
		5.1	Schofield, 1976c
Ictaluridae	Brown bullhead (Icaturus nebulosus)	4.7-5.2	Beamish, 1976
		5.0	Schofield, 1976c
Cyprinidae	Minnow (Phoxinus phoxinus)	5.5	Almer et al., 1978
	Roach (Rutilus rutilus)	5.5	Almer et al., 1978
	Lake chub (Couesius plumbeus)	4.5-4.7	Beamish, 1976
	Creekchub (Semotilus atromaculatus)	5.0	Schofield, 1976c
	Commonshiner (Notropis cornutas)	5.5	Schofield, 1976c
	Goldenshiner (Notemigonus crysoleucas)	4.9	Schofield, 1976c
Centrarchidae	Smallmouth bass (Micropterus dolomieui)	5.5-6.0+	Beamish, 1976
	Rock bass (Ambloplites rupestris)	4.7-5.2	Beamish, 1976
Esocidae	Pike (Esox lucius)	4.4-4.9	Almer et al., 1978

Recent field and laboratory studies (Schofield and Trojnar, 1980; Dickson, 1978; Driscoll et al., 1979; Baker and Schofield, 1980; Muniz and Leivestad, 1980) have indicated that aluminum levels in acidic surface waters (Section 7.3.1.1, Figure 7-18) may be highly toxic to fish (and perhaps other biota). Schofield and Trojnar (1980) analyzed survival of brook trout stocked into 53 Adirondack lakes as a function of 12 water quality parameters. Levels of pH, calcium, magnesium, and aluminum were significantly different between the two groups of lakes, with and without trout survival. However, after accounting for the effects of aluminum

*
concentrations on differences between the two groups of lakes, differences in calcium, magnesium, and pH levels were no longer significant. Aluminum, therefore, appears to be the primary chemical factor controlling survival of trout in these lakes. Likewise, in laboratory experiments with natural Adirondack waters and synthetic acidified aluminum solutions, levels of aluminum, and not the pH level per se, determined survival and growth of fry of brook trout and white suckers (Baker and Schofield, 1980). In addition, speciation of aluminum had a substantial effect on aluminum toxicity. Complexation of aluminum with organic chelates eliminated aluminum toxicity to fry (Baker and Schofield, in press; Driscoll et al., 1979). As a result, waters high in organic carbon, e.g., acidic bog lakes, may be less toxic to fish than surface waters at similar pH levels but with lower levels of dissolved organic carbon.

Inorganic aluminum levels, and not low pH levels, may therefore be a primary factor leading to declining fish populations in acidified lakes and streams. However, many laboratory or in situ field experiments have been conducted on the effects of pH on fish without taking into account aluminum or other metal concentrations in naturally acidic waters. As a result, many of the conclusions based on these experiments regarding pH levels critical for fish survival are suspect. Therefore these experiments will not be reviewed here.

Sensitivity of fish and other biota to low pH levels has also been shown to depend on aqueous calcium levels (Wright and Snekvik, 1978; Trojnar, 1977; Bua and Snekvik, 1972). In southern Norway, the mean calcium level in lakes studied was approximately 1.1 mg/liter, as compared to about 3 mg/liter in the LaCloche Mountain Region (Table 7-5) or 2.1 mg/liter in the Adirondack Region (Schofield, 1976b). In Norwegian lakes, Wright and Snekvik (1978) identified pH and calcium levels as the two most important chemical parameters related to fish status.

Decreased recruitment of young fish has been cited as the primary factor leading to the gradual extinction of fish populations (Leivestad et al., 1976; Rosseland et al., 1980; Wright and Snekvik, 1978). Field observations (Jensen and Snekvik, 1972; Beamish, 1974; Schofield, 1976; Almer et al., 1974) indicate changes in population structure over time with acidification. Declining fish populations consist primarily of older and larger fish with a decrease in total population density. Recruitment failure may result from inhibition of adult fish spawning and/or increased mortality of eggs and larvae. Effects on spawning and decreased egg deposition may be associated with disrupted spawning behavior and/or effects of acidification on reproductive physiology in maturing adults (Lockhart and Lutz, 1976). Field observations by Beamish et al. (1975) related reproductive failure in white suckers to an inability of females to release their eggs. On the other hand, Amundsen and Lunder (1974) observed total mortality of naturally spawned trout eggs in an acid brook a few weeks after spawning. A summary of Norwegian studies (Leivestad et al., 1976) concluded that egg and fry mortality is the main cause of fish reproduction failure. Spawning periods and occurrence of early life history stages for many fish species coincide with periods of extreme acidity, particularly during and immediately after snowmelt in the spring.

*

In some lakes, fish population decreases are associated with a lack of older fish (Rosseland et al., 1980). In Lake Tveitvatn on the Tovdal River in southern Norway, brown trout mortality apparently occurs primarily after the first spawning. Since 1976, no fish past spawning age have been found and population density has decreased steadily (Rosseland et al., 1980). Fish kills of adult salmon in rivers in southern Norway have been recorded as early as 1911 (Leivestad et al., 1976).

When evaluating the potential effects of acidification on fish, or other biotic, populations, it is very important to keep in mind the highly diversified nature of aquatic systems spatially, seasonally, and year-to-year. As a result of this diversity, it is necessary to evaluate each system independently in assessing the reaction of the population to acidification. Survival of a fish population may depend more on the availability of refuge areas from acid conditions during spring melt or of one tributary predominantly fed by baseflow and supplying an adequate area for spawning than on mean annual pH, calcium, or inorganic aluminum levels.

7.3.1.6 Effects on vertebrates other than fish. Certain species of amphibians may be the vertebrate animals, other than fish, most immediately and directly affected by acidic deposition (Pough and Wilson, 1976). Their vulnerability is due to their reproductive habits. In temperate regions, most species of frogs and toads, and approximately half of the terrestrial salamanders, lay eggs in ponds. Many of these species breed in temporary pools formed each year by accumulation of rain and melted snow. Approximately 50 percent of the species of toads and frogs in the United States regularly breed in ephemeral pools; about one-third of the salamander species that have aquatic eggs and larvae and terrestrial adults breed in temporary pools. Most of these pools are small and collect drainage from a limited area. As a result, the acidity of the eater in these pools is strongly influenced by the pH of the precipitation that fills them. Ephemeral pools are usually more acidic than adjacent permanent bodies of water. Pough and Wilson (1976) report that in 1975, in the vicinity of Ithaca, N.Y., the average pH of 12 temporary ponds was 4.5 (range 3.5 to 7.0), while the average pH of six permanent ponds was 6.1 (range 5.5 to 7.0). Amphibian eggs and larvae in temporary pools are exposed to these acidic conditions.

Pough and Wilson (1976) and Pough (1976) studied the effect of pH level on embryonic development of two common species of salamanders: the spotted salamander (Ambystoma maculatum) and the Jefferson salamander (A. jeffersonianum). In laboratory experiments, embryos of the spotted salamander tolerated pH levels from 6 to 10 but had greatest hatching success at pH 7 to 9. The Jefferson salamander tolerated pH levels 4 to 8 and was most successful at 5 to 6. Mortality of embryos rose abruptly beyond the tolerance limits. In a four-year study of a large breeding pond (pH 5.0-6.5) 938 adult spotted salamanders produced 486 metamorphosed juveniles (0.52 juveniles/adult), while 686 adult Jefferson salamanders produced 2157 juvenile (3.14 juveniles/adult). Based on these findings, Pough and Wilson (1976) predict that continued acidic deposition may result in substantial shift in salamander and other amphibian populations.

*

Gosner and Black (1957) report that only acid-tolerant species of amphibians can breed in the acid (pH 3.6 to 5.2) sphagnoceous bogs in the New Jersey Pine Barrens.

Frog populations in Tranevatten, a lake near Gothenberg, Sweden, acidified by acidic precipitation, have also been investigated (Hagström, 1977; Hendrey, 1978). The lake has pH levels 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 eight to ten years old were found. Many egg masses of Rana temporaria were observed in 1974, but few were found in 1977, and the few larvae (tadpoles) observed at that time died.

Frogs and salamanders are important predators on invertebrates, such as mosquitoes and other pest species, in pools, puddles, and lakes. They also are themselves important prey for higher tropic levels in an ecosystem. In many habitats salamanders are the most abundant vertebrates. In a New Hampshire forest, for example, salamanders were found to exceed birds and mammals in both numbers and biomass (Hanken et al., 1980).

The elimination of fish and vegetation from lakes by acidification may have an indirect effect on a variety of vertebrates: species of fish-eating birds (e.g., the bald eagle, loon, and osprey), fish-eating mammals (e.g., mink and otter), and dabbling ducks which feed on aquatic vegetation. In fact, any animal that depends on aquatic organisms (plant or animal) for a portion of its food may be affected.

Increasing acidity in freshwater habitats results in shifts in species, populations, and communities. Virtually all trophic levels are affected. Summaries of the changes which are likely to occur in aquatic biota with decreasing pH are listed in Tables 7-7 and 7-8.

TABLE 7-7. CHANGES IN AQUATIC BIOTA LIKELY TO OCCUR WITH INCREASING ACIDITY

1. Fish populations are reduced or eliminated.
2. Bacterial decomposition is reduced and fungi may dominate saprotrophic communities. Organic debris accumulates rapidly, tying up nutrients and limiting nutrient mineralization and cycling.
3. Species diversity and total numbers of species of aquatic plants and animals are reduced. Acid-tolerant species dominate.
4. Phytoplankton productivity may be reduced due to changes in nutrient cycling and nutrient limitations.
5. Biomass and total productivity of benthic macrophytes and algae may increase due partially to increased lake transparency.
6. Numbers and biomass of herbivorous invertebrates decline. Tolerant invertebrate species, e.g., air-breathing bugs (water-boatmen, back-swimmers, water striders) may become abundant primarily due to reduced fish predation.
7. Changes in community structure occur at all trophic levels.

*

TABLE 7-8. SUMMARY OF EFFECTS ON AQUATIC ORGANISMS ASSOCIATED WITH A RANGE IN 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.	Almer et al., 1974; Leivestad et al., 1976; Almer et al., 1978
	• 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.	Almer et al., 1974; Leivestad et al., 1976; Conroy et al., 1976; Almer et al., 1978
	• Phytoplankton plentiful and well distributed but numbers of species begin to decrease as pH decreases.	Almer et al., 1974; Kwiatkowski and Roff, 1976; Almer et al., 1978
6.0-5.5	• Decreasing pH from 6.0 to 5.5 will cause a reduction in species numbers and, among remaining species, alterations in ability to withstand stress, and change in species dominance. Reproduction of some salamander species is impaired.	Almer et al., 1974; Leivestad, 1976; Kwaitkowski and Roff, 1976; Almer et al., 1978 Pough and Wilson, 1976
5.5-5.0	• Below pH 5.5, numbers and diversity of species will be reduced. Many species will be eliminated. Crustacean 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 (i.e., Sialis lutaria), and some forms which live within the sediments (Oligochaeta, Chiromomidae, and Tubificidae). Overall, invertebrate biomass may be reduced.	Almer et al., 1974; Leivestad et al., 1976; Hendrey et al., 1976; Grahn et al., 1974; Grahn, 1976; Kwiatkowski and Roff, 1976; Hagen and Langeland, 1973; Henriksen and Wright, 1977 Hultberg, 1976; Almer et al., 1978
5.0-4.5	• Below pH 5.0, decomposition of organic detritus will be severely impaired. Organic matter accumulates rapidly. Some fungal species increase (Hyphomycetes, basidomycetes). Many fish species are eliminated. (see Table 7-7.)	Leivestad et al., 1976; Schofield, 1976b; Almer et al., 1978 Hall et al., 1980.

	• Macrophytes, such as Lobelia, are replaced by Sphagnum moss.	Leivestad et al., 1976 Hendrey et al., 1976; Grahn, 1974; Almer et al., 1978
	• Number of algal species decreases. Acid-tolerant forms remain.	Leivestad et al., 1976; Hendrey et al., 1976; Grahn et al., 1974; Almer et al., 1978
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.	Almer et al., 1974 Leivestad et al., 1976; Schofield, 1976b; Wright et al., 1976 Beamish et al., 1975; Menedex, 1976; Trojnar, 1977; Trojnar, 1977; Schofield, 1975; Schofield, 1979

Modified from Hendrey (1978).

*

7.3.2 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 changes in pH that occur in acidified waters and then observe the response of organisms living in aquatic ecosystems to the shifts in pH. In the case of terrestrial ecosystems the situation is more complicated since no component of terrestrial ecosystems appears to be as sensitive to acidic precipitation as organisms living in poorly buffered aquatic ecosystems. Nonetheless, soils and vegetation may be affected, directly or indirectly, by acidic precipitation, albeit in complex ways.

7.3.2.1 Effects on soils--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. As water containing hydrogen cations (usually from weak acids) moves through the soil, some of the hydrogen ions replace adsorbed exchangeable cations, such as Ca^{++}, Mg^{++}, K^{+}, and Na^{+} (see Figure 7-26). The removed cations are then carried deep into the soil profile or into the ground water. In native soils hydrogen ions are derived from the following sources (Wiklander, 1979):

1. nutrient uptake by plants--the roots 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 B horizons;
5. atmospheric deposition of H_2SO_4 and some HNO_3, NO_x, HCl and NH_4^{+} (after nitrification to HNO_3).

In addition to the acidifying factors listed above, the use of ammonium fertilizers on cultivated lands increases the hydrogen cations in the water solution. Ammonium fertilizers are oxidized by bacteria to form nitrate (NO_3^{-}) and hydrogen ions (H^{+}) (Donahue et al., 1977). Increased leaching causes soils to become lower in basic Ca^{++}, Mg^{++}, Na^{+}, and K^{+} cations (Donahue et al., 1977). Sensitivity to leaching is according to the following sequence: $Na^{+} >> K^{+} > Mg^{2+} > Ca^{2+}$ (Wiklander, 1979).

Norton (1977) cited the potential effects of acidic deposition on soils that are listed in Table 7-9. Of those listed, only the increased mobility of cations and their accelerated loss has been observed in field experiments. Overrein (1972) observed an increase in calcium leaching under simulated acid rain conditions and increased loss by leaching of Ca^{++}, Mg^{++}, and Al^{+3} were observed by Cronan (1980) when he treated New Hampshire soils with simulated acid rain at a pH 4.4.

Wiklander (1979) 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

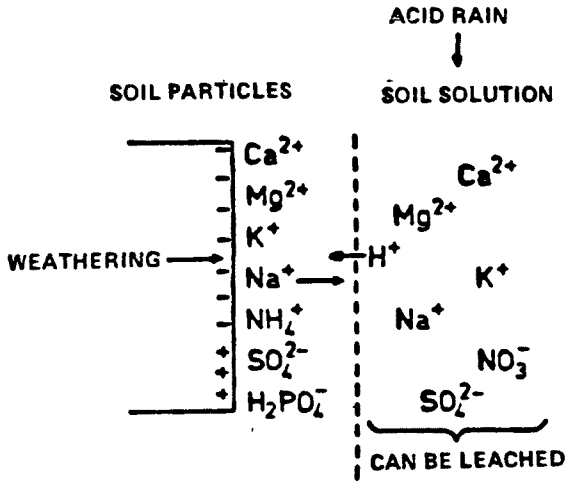


Figure 7-26. Showing the exchangeable ions of a soil with pH 7, the soil solution composition, and the replacement of Na^+ by H^+ from acid rain.

Source: Wiklander (1979).

*

TABLE 7-9. 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: Norton (1977).

*
the buffering capacity of the soil and the amount and composition of precipitation (pH and salt content). Leaching sooner or later leads to soil acidification 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.

Acidic 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 in the soil for both plants and soil microorganisms, it is rapidly taken up and retained within the soil-plant system (Gjessing et al., 1976; Abrahamsen et al., 1976; Abrahamsen and Dollard, 1979). The fate of sulfate is determined by its mobility. 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. Insignificant amounts of the hydrated oxides of iron (Fe) and aluminum (Al) are found in organic soils; therefore, sulfate retention is low (Abrahamsen and Dollard, 1979). The presence of hydrated oxides of iron and aluminum, however, is only one of the factors associated with the capability of a soil to retain sulfur. The capacity of soils to adsorb and retain anions increases as the pH decreases and with the salt concentration. Polyvalent anions of soluble salts added experimentally to soils increases adsorption and decreases leaching of salt cations. The effectiveness of the anions studied in preventing leaching was in the following order: $Cl^- \sim NO_3^- < SO_4^{2} < H_2PO_4^-$ (Wiklander, 1980). Additions of sulfuric acid to a soil will have no effect on cation leaching unless the sulfate is mobile, as cations cannot leach without associated anions (Johnson et al. 1980; Johnson, 1980; Johnson and Cole, 1980).

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 (Abrahamsen and Dollard, 1979).

In lysimeter experiments in Norway, plots with vegetation cover were used. One plot had a dense layer of the grass, Deschampsia flexuosa (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 in the lysimeters covered with grass; the relative retention increased with increasing additions of sulfate (Abrahamsen and Dollard, 1979). 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 there 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 (Abrahamsen and Dollard, 1979).

The Scandinavian lysimeter experiments appear to demonstrate that the relative rate of adsorption of sulphate increases as the amounts applied are increased. In the 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 (Gjessing et al., 1976; Abrahamsen and Dollard, 1979). 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 sulfate 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 (Abrahamsen and Dollard, 1979). Shriner and Henderson (1978), however, in their study of sulfur distribution and cycling in the Walker Branch Watershed in eastern Tennessee noted the additions of sulfate sulfur by precipitation were greater than the amount lost in stream flow. Analysis of the biomass and soil concentrations of sulfur indicated that sulfur was being retained in the mineral soil horizon. It is suggested that leaching from organic soil horizons may be the mechanism by which sulfur is transferred to the mineral horizon. Indirect evidence suggests that vegetation scavenging of atmospheric sulfate plays an important role by adding to the amounts of sulfur entering the forest system over wet and dry deposition.

Studies of the nutrient cycling of sulfur in a number of forest ecosystems indicate that some ecosystem accumulate (Johnson et al. 1980; Heinricks and Mayer, 1977, Shriner and Henderson 1978) while other ecosystems maintain a balance between the additions and losses of sulfur or show a net loss (Cole & Johnson, 1977). Sulfur accumulation appears to be associated with sulfate adsorption in subsoil horizons. Sulfate adsorption is strongly dependent on pH. Little adsorption occurs above pH 6-7 (Harward and Reisenaur, 1966). The amount of sulfate in a soil is a function of a soil's adsorption properties and the amount of sulfate that has been added to the soil, integrated over time. Soil properties may favor the adsorption of sulfate; however, the net annual accumulation of sulfate at any specific time will be influenced by the degree of soil saturation (Johnson et al. 1980).

The effects of acidic precipitation on soils potentially could be long-lasting. Oden (1971) 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 as well as base saturation. McFee et al. (1976) 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 A-1 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 and 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 (1975) reported that aluminum released by acidified soils could be phytotoxic if acid 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 (Malmer, 1976). Baker et al. (1976) 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 (Tamm et al., 1977). Highly acidic rainfall, frequently with a pH less than 3.0, in combination with heavy metal particulate fallout from smelters, has caused soils to become toxic to seedling survival and establishment according to observations by Hutchinson and Whitby (1976). 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 (Tyler, 1972). The heavy metals when bound may interfere with litter decay and nutrient cycling, and in this manner interfere with ecosystem functioning (Tyler, 1972). 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 in soil and litter (Tyler, 1972, 1977).

Biological processes in the soil necessary for plant growth can be affected by soil acidification. Nitrogen fixation, decomposition of organic material, and mineralization, especially of nitrogen, phosphorus and sulfur, might be affected (Abrahamsen and Dollard, 1979; Tamm et al., 1977; Malmer, 1976; Alexander, 1980). 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 (Alexander, 1980). It is principally through the activity of heterotrophic microorganisms that nitrogen, phosphorus, and sulfur are made available to the autotrophic 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 (Alexander, 1978).

Many, and probably most, microbial transformations in soil may be brought about by several species. Therefore, the reduction or elimination of one population is not necessarily detrimental since a second population, not affected by the stress, may fill the partially or totally vacated niche. For example, the conversion of organic nitrogen compounds to inorganic forms is characteristically catalyzed 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, there are a few processes that are in fact carried out, so far as it is now known, by only a single species, 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 (Alexander, 1980).

The nitrification process 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 acidity (Dancer et al., 1973). 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. (Connell and Patrick, 1968) and studies of the presumably responsible organisms in culture attest to the inhibition linked with the acid conditions (Alexander, 1978).

Blue-green algae have been found to be absent from acid soils even though there is both adequate moisture and exposure to sunlight. Studies by Wodzinki et al. (1977) attest to the sensitivity of these organisms to acidity. Inhibition of the rates of both CO_2 fixation and nitrogen fixation was 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 (Alexander, 1980). 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 (Dancer et al., 1973). The pH of soil not only influences the microbial community at large but also those specialized populations that colonize the root surfaces (Alexander, 1980).

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 (Alexander, 1980). 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 (Alexander, 1980). The consequences of increased acidity in the subterranean ecosystem are totally unclear.

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 (Fredricksen, 1972) to 4.9 kg N/ha/yr in the eastern United States (Likens et al., 1970; Henderson and Harris, 1975). 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 (1958) 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 (National Research Council, 1978).

In comparison, rates of annual uptake by plants range from 11 to 125 kg N/ha/yr in ecosystems selected from several bioclimatic zones (National Research Council, 1978). 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 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 comparisons 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 acidic precipitation, nitrogen additions from atmospheric depositions are certainly important to biological productivity. 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 (National Research Council, 1978).

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 (Donahue et al., 1977). Another major source is the wet and dry deposition of atmospheric sulfur (Donahue et al., 1977; Brady, 1974; Jones, 1975).

*

In agricultural soils crop residues, manure, irrigation water, and fertilizers and soil amendments are important sources of sulfur. 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 (Halsteand and Rennie, 1977). Near fossil-fueled power plants and industrial installations the amount of sulfur in precipitation may be as much as 150 pounds per acre (168 kg/ha) or more (Jones, 1975). By contrast, in rural areas, based on the equal distribution of sulfur oxide emissions over the coterminous states, the amount of sulfur in precipitation is generally well below the average 15 pounds per acre (17 kg/ha). Approximately 5 to 7 pounds per acre (7 to 8 kg/ha) per year were reported for Oregon in 1966 (Jones, 1975). Shinn and Lynn (1979) 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 (Brady, 1974). Hoeft et al. (1972) estimated the overall average sulfur as sulfate deposition at 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/yr). Approximately 40 to 50 percent of the sulfur additions occurred from November to February. Tabatabai and Laflin (1976) 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 for Ames in 1976 as were reported for 1923, approximately 15 lbs/acre. The average annual additions of sulfur by precipitation were similar to that reported for rural Wisconsin by Hoeft et al. (1972)

Experimental data have shown that even though plants are supplied with adequate soil sulfate they can absorb 25 to 35 percent of their sulfur from the atmosphere (Brady, 1974). Particularly if the soil sulfur is low and atmosphere sulfur high, most of the sulfur required by the plant can come from the atmosphere (Brady, 1974). Atmospheric sulfur would be of benefit chiefly to plants growing on lands with a low sulfur content (Brezonik, 1975).

Tree species vary in their ability to utilize sulfur. Nitrogen and sulfur are biochemically associated in plant proteins, therefore, a close relationship exists between the two in plants. Apparently, nitrogen is only taken up at the rate at which sulfur is available. Protein formation is, therefore, limited by the amount of sulfur available (Turner and Lambert, 1980). Conifers accumulate as sulfate any sulfur beyond the amount required to balance the available nitrogen. Protein formation proceeds at the rate at which nitrogen becomes available. Trees are not injured when sulfur is applied as sulfate rather than SO_2 (Turner and Lambert, 1980).

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. On managed soils more than adequate amounts of lime are used to counteract the acidifying effects of fertilizers in agricultural soils. Ammonium fertilizers, usually as ammonium sulfate

* $[(NH_4)_2SO_4]$ or ammonium nitrate, (NH_4NO_3) are oxidized by bacteria to form sulfate (SO_4^{2-}) and/or nitrate (NO_3^-) and hydrogen ions (H^+) (Donahue et al. 1977; Brady, 1974). The release of hydrogen ions into the soil causes the soil to become acidified. Hydrogen ions are also released into the soil when plants take up mineral nutrients. Hence, substances (notably various complexes of ammonium and sulfate ions), although of neutral pH, or nearly so, are acidifying in their effects when they are taken up by plants or animals. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation."

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 acidic soils (Donahue et al., 1977; Likens et al., 1977). Costs of liming all natural soils would be prohibitive as well as extremely difficult to carry out.

Precipitation may add many chemicals to terrestrial, aquatic, and agricultural ecosystems. In addition to sulfur and nitrogen, phosphorus and potassium are biologically most important because they often are in limited supply in the soil (Likens et al., 1977). Other chemicals of varying biological importance and varying concentration found in precipitation over North America are the following: chlorine, sodium, calcium, magnesium, iron, nickel, copper, zinc, cadmium, lead, manganese (Beamish, 1976; Hutchinson and Whitby, 1976; Brezonik, 1975), mercury (Brezonik, 1975), and cobalt (Hutchinson and Whitby, 1976). Rain over Britain and the Netherlands, according to Gorham (1976), contained the following elements in addition to those reported for North American precipitation: aluminum, arsenic, beryllium, cerium, chromium, cesium, antimony, scandium, selenium, 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. Of chemical elements found in precipitation, magnesium, iron, copper, zinc, and manganese are essential in small amounts for the growth of plants; 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 microorganisms that may ingest or decompose these plants.

Wiklander (1979) 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 acidic precipitation depends on the soil buffer capacity and on the soil pH. Noncalcareous sandy soils with pH > 5 are the most sensitive to acidification; however, acidic soils would be most likely to release aluminum.

Very acid soils are less sensitive to further acidification 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 which limits productivity in these soils. Even a slight decrease in nutrient status by leaching may have a detrimental effect on plant yield (Wiklander, 1979). 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 (Wiklander, 1979).

7.3.2.2 Effects 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. Nitrates and sulfates are not the only components of precipitation falling onto the plant surface. Other chemical elements (cadmium, lead, zinc, manganese), 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 raindrop deposited on trees in a typical forest washes over three tiers of foliage 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 (Galloway and Cowling, 1978). Substances accumulated on the leaf surfaces strongly influence the chemical composition of precipitation not only at the leaf surface, but also when it reaches the forest floor. The chemistry of precipitation reaching the forest floor is considerably different from that collected above the forest canopy or a ground level where the canopy has no influence. (Lindberg et al. 1979). Except for the hydrogen ion (H^{+}) the mean concentrations of all elements (lead, manganese, zinc and cadmium) studied in the Walker Branch Watershed in Tennessee found by Lindberg et al. (1979) to be present in greater amounts in the throughfall than in incident rain. The presence of trace elements was more variable than that of the sulfate and hydrogen ions. Throughfall with a pH 4.5 appeared to be a more dilute solution of sulfuric acid than rain not influenced by the forest canopy. The solution was found to contain a relatively higher concentration of alkaline earth salts of sulfate and nitrate as well as a somewhat higher concentration of trace elements (Lindberg et al. 1979).

Lee and Weber (1980) studied the effects of sulfuric acid rain on two model hardwood forests. The experiment, conducted under controlled field conditions, consisted of the

*
application of simulated sulfuric acid rain (pH values of 3.0, 3.5, and 4.0), and a control rain of pH 5.6 to the two model forest ecosystems for a duration of 3 and 1/2 years. Rainfall applications approximated the annual amounts of areas in which sugar maple and red alder communities normally occur.

In evaluating the results of the study, the authors conclude that a well developed forest canopy and litter layer can increase the pH and concentration of bases (i.e., calcium and magnesium) in rainwater. Such conditions would tend to decrease the acidification rate of forest soils by acid rain. However, as bases are continually leached from the soil column these cations could eventually be lost from the ecosystem and unavailable to influence the acidification reactions. Changes in the ionic and pH balance of forest systems may impact the productivity of forests through acidity-induced changes in the nutrient cycling process, decomposition, reproduction, tree growth, and the structure of forest systems.

The additions of hydrogen, sulfate and nitrate ions to soil and plant systems have both positive and negative effects. 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 (Jacobson, 1980). 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 United States (Jacobson, 1980) and Canada (Linzon personal communication).

7.3.2.2.2.1 Direct effects on vegetation. Hydrogen ion concentrations equivalent to that measured in more acidic rain events ($\leq$ pH 3.0) have been observed experimentally to cause tissue injury in the form of necrotic lesions to a wide variety of plant species under greenhouse and laboratory conditions. This visible injury has been reported as occurring between pH 3.0 and 3.6 (Shriner, 1980). The various types of direct effects which have been reported are shown in Table 7-10. Such effects must be interpreted with caution because the growth and morphology of leaves on plants grown in greenhouses frequently are atypical of field conditions (Shriner, 1980).

Small necrotic lesions, the most common form of direct injury, appear to be the result of the collection and retention of water on plant surfaces and the subsequent evaporation of these water droplets once a lesion occurs. The depression formed by the lesion further enhances the collection of water. A large percentage of the leaf area may exhibit lesions after repeated exposures to simulated acid rain at pH concentrations of 3.1, 2.7, 2.5 and 2.3 (Evans et al. 1977a, 1977b). 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 (Evans et al., 1977b). Evans et al. (1978) using six clones of Populus spp. hybrids found that leaves that had just reached full expansion were more sensitive to simulated acid rain at pH 3.4, 3.1, 2.9, and 2.7 than were unexpanded or those which were fully expanded. On two of the clones, gall formation due to abnormal cell proliferation and enlargement occurred. Other effects attributed to simulated

TABLE 7-10. TYPES OF DIRECT, VISIBLE INJURY REPORTED IN RESPONSE TO ACIDIC WET DISPOSITION

Injury Type	Species	pH Range	Reference	Remarks
Pitting, curl shortening, death	Yellow birch	2.3-4.7	Wood and Bormann (1974)	
1-mm necrotic lesions, premature abscission	Kidney bean, soybean, loblolly pine, E. white pine, willow oak	3.2	Shriner et al. (1974)	
Cuticular erosion	Willow oak	3.2	Shriner (1978a), Lang et al. (1978)	
Chlorosis	Sunflower, bean	2.3-5.7	Evans et al. (1977)	
(A) small, shallow circular depressions: slight chlorosis	Sunflower, bean	2.7	Evans et al. (1977)	More frequent near veins. (A) - (D) represent sequential stages of lesion development, through time, up to 72 h (one 6-min rain event daily for 3 d)
(B) larger lesions, chlorosis always present palisade collapse	Sunflower, bean	2.7	Evans et al. (1977)	
(C) 1-mm necrotic lesions general distortion	Sunflower, bean	2.7	Evans et al. (1977)	
(D) 2-mm bifacial necrosis sue to coalescence of smaller lesions, total tissue collapse.	Sunflower, bean	2.7	Evans et al. (1977)	
Wrinkled leaves, excessive adventitious budding, premature abscission	Bean	1.5-3.0	Ferenbaugh (1976)	

TABLE 7-10 (Continued).

Injury Type	Species	pH Range	Reference	Remarks
Incipient bronzed spot	Bean	2.0-3.0	Hindawi et al. (1980)	After first few hours
Bifacial necrotic pitting	Bean	2.0-3.0	Hindawi et al. (1980)	After 24 h (reported pooling of drops = more injury)
Necrotic lesions, premature abscission	E. white pine, scotch pine, spinach, sunflower, bean	2.6-3.4	Jacobson and van Leuken (1977)	Injury associated with droplet location within 24-48 h.
Marginal and tip necrosis	Bean, poplar, soybean, ash birch, corn, wheat	Submicron H_2SO_4 aerosol	Lang et al. 1978	
Galls, hypertrophy, hyperplasia	Hybrid poplar	2.7-3.4	Evans et al. (1978)	
Dead leaf cells	Soybean	3.1	Irving (1979)	
Necrotic lesions	Citrus	0.5-2.0	Heagle et al. (1978)	

Shriner, 1980

*
acid rain include the modification of the leaf surface, e.g. epicuticular waxes, and alteration of physiological processes such as carbon fixation and allocation.

Lee et al. (1980) studied the effects of simulated acidic precipitation on crops. Depending on the crop studied, they reported positive, negative or no effects on crop yield when exposed to sulfuric acid rain at pH volumes of 3.0, 3.5 and 4.0 when compared to crops exposed to a control rain of pH 5.6. The yield of tomatoes, green peppers, strawberries, alfalfa, orchard grass and timothy were stimulated. Yields of radishes, carrots, mustard greens and broccoli were inhibited. Potatoes were ambiguously affected except at pH 3.0 where their yield as well as that of beets was inhibited. Visible injury of tomatoes could possibly have decreased their market value. In sweet corn, stem and leaf production was stimulated, but no statistically significant effects on yield were observed for 15 other crops. Results suggest that the possibility of yield's being affected by acid rain depends on the portion of the plant being utilized as well as the species. Plants were regularly examined for foliar injury associated with acid rain. Of the 35 cultivars examined, the foliage of 31 was injured at pH 3.0; 28 at pH 3.5; and 5 at pH 4.0. Foliar injury was not generally related to effects on yield. However, foliar injury of swiss chard, mustard greens, and spinach was severe enough to adversely affect marketability. These results are from a single growing season and therefore considered to be preliminary.

Studies indicate that wet deposition of acidic or acidifying substances may result in a range of direct or indirect effects on vegetation. Environmental conditions before, during and after a precipitation event affect the responses of vegetation. Nutrient status of the soil, plant nutrient requirements, plant sensitivity and growth stage and the total loading or deposition of critical ions e.g. H^+, NO_3^- and SO_4^- all play a role in determining vegetational response to acidic precipitation.

Wettability of leaves appears to be an important factor in the response of plants to acid deposition. This has been demonstrated in the work of Evans et al. (1977), Jacobson and Van Leuken (1977), and Shriner (1978a), who variously report a threshold of between pH 3.1 and 3.5 for development of foliar lesions on beans. The cultivars of Phaseolus vulgaris L. used in the above studies are all relatively non-waxy and therefore fairly easily wettable. By comparison, studies with the very waxy leaves of citrus (Heagle et al., 1978) reported a threshold for visible symptoms to be near pH 2.0. Waxy leaves apparently minimize the contact time for the acid solutions, thus accounting for the <400X increase in H^+ ion concentration required to induce visible injury. Table 7-11 summarizes the thresholds, including range, species sensitivity, concentration, and time, for visible injury associated with experimental studies of wet deposition of acidic substances.

Leaching of chemical elements from exposed plant surfaces is an important effect 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

TABLE 7-11. THRESHOLDS FOR VISIBLE INJURY AND GROWTH EFFECTS ASSOCIATED WITH EXPERIMENTAL STUDIES OF WET DEPOSITION OF ACIDIC SUBSTANCES (AFTER JACOBSON, 1980a,b)

Effect	Species	Threshold[1]	Reference	Remarks
Foliar lesions, decrease in growth	Yellow birch	pH 3.1	Wood and Bromann (1974)	greenhouse
Foliar aberrations, decrease in growth	Bean	pH 2.5	Ferenbaugh (1976)	greenhouse
Foliar lesions	Bean, sunflower	pH 3.1	Evans et al. (1977a)	greenhouse
Foliar lesions	Bean	pH 3.2	Shriner (1978a)	greenhouse
Foliar lesions	Hybrid poplar	pH 3.4	Evans et al. (1978)	greenhouse
Foliar lesions	Sunflower	pH 3.4	Jacobson and van Leuken (1977)	greenhouse
Foliar symptons, no reduced growth	Soybean	pH 3.0	Jacobson (1980b)	greenhouse
Increased growth, increased/decreased nutrient content	Lettuce	pH 3.0, 3.2	Jacobson (1980b)	greenhouse (varied with $SO_4^=$ & NO_3^-)
Reduced growth	Pinto bean	pH 3.1	Jacobson (1980b)	greenhouse
Reduced yield	Pinto bean	pH 2.7		
Reduced growth	Soybean	pH 3.1		
Reduced yield	Soybean	pH 2.5		

TABLE 7-11 (Continued).

Effect	Species	Threshold[1]	Reference	Remarks
Increased yield	Soybean	pH 3.1		
Foliar symptoms	Tomato	pH 3.0	Jacobson (1980b)	greenhouse
Reduced growth	Tomato	pH 3.0		
Reduced yield	Tomato	pH 3.0		
Reduced quality	Tomato	pH 3.0		
No foliar symptoms, or effects on growth	Soybean	pH 3.1	Irving (1979)	field
No foliar symptoms, but	Soybean	pH 2.8	Jacobson (1980b)	field, low ozone
a) decreased growth, yield	Soybean	pH 2.8		field, high ozone
b) increased yield	Soybean	pH 2.8		field, low ozone
No effect on growth, yield	Tomato	pH 3.0	Jacobson (1980b)	field
Reduced quality	Tomato	pH 3.0		field

[1]Highest pH to elicit a negative response, or lowest pH to elicit a positive response

Shriner, 1980.

*
among the materials which have been detected in plant leachates (Tukey, 1970). 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 rainwater falling on foliage 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 (Nihlgard, 1970).

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 (Comerford and White, 1977; Eaton et al., 1973). 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, and susceptibility or immunity of plants to soil pests and plant-chemical interactions (Tukey, 1970).

It has been demonstrated under experimental conditions that precipitation of increased acidity can increase the leaching of various cations and organic carbon from the tree canopy (Abrahamsen et al., 1976; Wood and Bormann, 1975). 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 pH 3.3 and 4.0 with no observable tissue damage (Wood and Bormann, 1975). Hindawi et al. (1980) 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 (1979), in experiments using Norway spruce (Picea abies L. Karst), observed that despite increased leaching under the most acid treatment, there was no evidence of change in the foliar cation content. Wood and Bormann (1977), using Eastern white pine (Pinus strobus L.), also noted no significant changes in calcium, magnesium or potassium content of needles. Tukey (1970) states that increased leaching of nutrients from foliage 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; however, injury could occur if nutrients are in short supply. To date, the effects, if any, of the increased leaching of substances from vegetation by acidic precipitation remain unclear.

Some experimental evidence suggests that acidic solutions affect the chlorophyll content of leaves and the rate of photosynthesis. Sheridan and Rosenstreter (1973) reported marked reduction of photosynthesis in a moss exposed to increasing H^+ ion concentrations. Sheridan

*
and Rosenstreter (1973), Ferengaugh (1976), and Hindawi et al. (1980) reported reduced chlorophyll content as a result of tissue exposure to acid solutions. In the case of Ferenbaugh (1976), however, the significant reductions in chlorophyll in the leaves of Phaseolus vulgaris at pH 2.0 were associated with large areas of necrosis. A significant aspect of this study was the loss of capacity by the plant to produce carbohydrates. The rate of respiration in these plants showed only a slight but significant increase while the rate of photosynthesis at pH 2.0 increased nearly fourfold as determined by oxygen evolution. Ferenbaugh concluded that due to a reduction in biomass accumulation and sugar and starch concentrations, photophosphorylation in the treated plants was in some way being uncoupled by the acidic solutions.

Irving (1979) reported a higher chlorophyll content and an increase in the rate of photosynthesis in field-grown soybeans exposed to simulated rain at pH 3.1. She attributed the increases to improved nutrition due to the sulfur and nitrogen components of the simulated acid rain overcoming any negative effects.

Vegetation is commonly exposed to gaseous phytotoxicants such as ozone and sulfur dioxide at the same time as acidic precipitation. Little information is available upon which to evaluate the potential for determining the effects of the interaction of wet-and dry-deposited pollutants on vegetation. Preliminary studies by Shriner (1978b), Irving (1979), and Jacobson et al. (1980) suggest that interactions may occur. Irving (1979) found that simulated acid precipitation at pH of 3.1 tended to limit the decrease in photosynthesis observed when field-grown soybeans were exposed 17 times during the growing season to 0.19 ppm of SO_2. Shriner (1978b), however, reported no significant interaction between multiple exposure to simulated rain at p 4.0 and four SO_2 exposures (3 ppm peak for 1 hr.) upon the growth of bush beans. Shriner (1978b) also exposed plants to 0.15 ppm ozone (4 3-hour exposures) in between 4 weekly exposures to rainfall of pH 4.0, and observed a significant growth reduction at the time of harvest. Jacobson et al. (1980), using open-top exposure chambers with field-grown soybeans, compared growth and yield between three pH levels of simulated rain (pH 2.8, 3.4, and 4.0) and two levels of ozone (<0.03 and ≤ 0.12 ppm). Results demonstrated that ozone depressed both growth and yield of soybeans with all three rain treatments, but that the depression was greatest with the most acidic rain. Ozone concentrations equal to or greater than those used in the studies are common in most areas of the northeastern United States where acidic deposition is a problem (Jacobson et al., 1980); therefore, the potential for ozone-acidic deposition interaction is great.

Shriner (1978a) 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 Cronartium fusiforme. 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 acid rain was applied. The effects which inhibited disease development could

*
result in a net benefit to plant health. Shriner (1976, 1980) also observed that root nodulation by Rhizobium on common beans and soybeans was inhibited by the simulated acid rain, suggesting a potential for reduced nitrogen fixation by legumes so effected.

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 (Denison et al., 1977; Sheridan and Rosenstreter, 1973). Gorham (1976) and Giddings and Galloway (1976) 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. (1977), 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 (Abrahamsen and Dollard, 1979).

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 (1977), using buffered solutions to simulate acidic precipitation, observed that flagellar movement of sperm was reduced at pH levels below 5.8. 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 mM) decreased fertilization at least 50 percent at all pH values observed. In another study, Evans and Bozzone (1978) observed that both sperm motility and fertilization in gametophytes of Pteridium aquilinum were reduced when anions of sulfate, nitrate, and chloride were added to buffered solutions.

Sulfur and nitrogen in precipitation have been shown to play an important role in vegetational response to acidic deposition. Jacobson et al. (1980) investigated the impact of simulated acidic rain on the growth of lettuce at acidities of pH 5.7 and 3.2. At pH 3.2, solutions were compared with NO_3:SO_4 mass ratios of 20:1, 2:1, and 1:7.5. The high nitrate at pH 3.2 showed no difference from the treatments controls at pH 5.7 for those growth parameters (root dry weight, apical leaf dry weight) that responded to treatment; however, the results were significantly less than those from the low nitrogen, high sulfur, treatment. These observations suggest that sulfur was possibly a limiting factor in the nutrition of these plants, with the result that the plant response to sulfur overwhelmed the hydrogen ion effect. Other studies also have cited the beneficial effects of simulated acidic precipitation. Irving and Miller (1978) observed that an acidic simulant had a positive effect on productivity of field-grown soybeans as reflected by seed weight. Increased growth was attributed to a fertilizing effect from sulfur and nitrogen delaying senescence. Irving and Miller (1978), 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 additive when compared to the effects of each taken singly. Wood and Bormann (1977) 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. Abrahamson and Dollard (1979) also presented data suggesting positive growth responses in forest tree species resulting from nitrogen and sulfur in simulated rain. Simulated acidic precipitation was observed to increase the growth of Scots pine saplings in experiments conducted in Norway. 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 mineralization and uptake. Turner and Lambert (1980) reported evidence indicating a positive growth response in Monterey pine from the deposition of sulfur in ambient precipitation in Australia.

Acidifying forest soils that are already acid 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, Tamm et al. (1977) 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 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.

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 possibly short-lived as depletion of nutrient cations through accelerated leaching could eventually retard growth (Wood, 1975). Laboratory investigations by Overrein (1972) 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 (Oden, 1972).

Major uncertainty in estimating effects of acid rain on forest productivity is the capacity of forest soils to buffer against leaching by hydrogen ions. 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 (Eaton et al., 1973). As a result, solutions reaching the forest floor are less acidic (pH 5.0). Mayer and Ulrich (1977), however, point out that their studies

*
suggest 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.

Forest ecosystems are complicated biological organizations. Acidic precipitation will cause some components within the ecosystem to respond even though it is not possible at present to evaluate the changes that occur. The impact of the changes on the ecosystem can only be determined with certainty after the passage of a long period of time.

7.3.2.3 Effects on Human Health--One effect of acidification that is potentially of concern to human health is the possible contamination by toxic metals of edible fish and of water supplies. Studies in Sweden (Landner and Larsson, 1975; Turk and Peters, 1977), Canada (Tomlinson, 1979; Brouzes et al., 1977), and the United States (Tomlinson, 1979) 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 (Fagerström and Jernelöv, 1972). 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 (1979) 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 (Schofield, 1976b). The ingestion of fish contaminated by these metals is a distinct possibility.

Another human health aspect is the possibility that, as drinking-water reservoirs acidify, owing to acidic 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, more important, 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." (Turk and Peters, 1977) 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 7-12 (see following page).

7.3.2.4 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 manmade ecosystems. At present in most areas, the dominant factor in the formation of acidic precipitation is sulfur, usually as sulfur dioxide (Likens, 1976; Cowling and Dochinger, 1978). Because of this fact, it is difficult to isolate the effect of acidic precipitation

*

TABLE 7-12. LEAD AND COPPER CONCENTRATION AND pH OF WATER FROM PIPES CARRYING OUTFLOW FROM HINCKLEY BASIN AND HANNS AND STEELE CREEK BASIN, NEAR AMSTERDAM, NEW YORK

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 Turk and Peters (1979)

from changes induced by sulfur pollution in general. (The effects of sulfur oxides on materials are 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 (Nriagu, 1978). 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 (Kucera, 1976). 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 (Kucera, 1976). The corrosion effect, particularly of certain metals, in areas where the pH of precipitation is very low may be greatly enhanced by that precipitation (Kucera, 1976). In a Swedish study the sulfur content of precipitation,

*
expressed as meq/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 (Kucera, 1976).

Materials reported to be affected by acidic precipitation, in addition to steel, are: copper materials, linseed oil, alkyd paints on wood, antirust paints on steel, limestone, sandstone, concrete, and both cement-lime and lime plaster (Cowling and Dochinger, 1978).

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 pyramids, which have survived since antiquity, are made of stone. What is usually forgotten is that the structures built with stone that was not durable have long since disappeared (Sereda, 1977).

Atmospheric sulphur compounds (mainly sulfur dioxide, with subsidiary amounts of sulfur trioxide and ammonium sulfate) react with the carbonates in limestone and dolomites, calcareous sandstone and mortars to form calcium sulfate (gypsum). The results of these reactions are blistering, scaling, and loss of surface cohesion, which in turn induces similar effects in neighboring materials not in themselves susceptible to direct attack (Sereda, 1977).

Sulfates have been implicated by Winkler (1966) as very important in the disintegration of stone. The surface flaking on the Egyptian granite obelisk (Cleopatra's Needle) in Central Park, New York is cited as an example. The deterioration occurred within two years of its erection in 1880.

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 Recklinghausen, 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 Madonna--eyes, nose, mouth and hair--are readily discernable. In pictures taken in 1969 after 267 years, no features are visible (Cowling and Dochinger, 1978).

It is not certain in what form sulfur is absorbed into stone, as a gas (SO_2) forming sulfurous or sulfuric acid or whether it is deposited in rain. Rain and hoarfrost both contain sulfur compounds. Schaffer (1932) compared the sulfate ion in both rain and hoarfrost at Heachingley, Leeds, England in 1932 (Table 7-13) and showed that the content of hoarfrost was approximately 7 times greater than rain. Wet stone surfaces unquestionably increase the condensation or absorption of sulfates. 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 (Sereda, 1977).

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 sulfur pollution to specific compounds.

*

TABLE 7-13. 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

Schaffer (1932)

Microbial action can also contribute to the deterioration of stone surfaces. Tiano et al. (1975) isolated large numbers (250 to 20,000 cells per gram) of sulfate-reducing bacteria from the stones of two historical buildings of Florence, Italy. The majority of the bacteria belonged to the genus Thiobacillus. This genus of chemosynthetic aerobic microorganisms oxidizes sulfide, elemental sulfur, and thiosulphate to sulfate to obtain energy (Anderson, 1978). Limestone buildings and particularly mortar used in the construction of brick and stone buildings are particularly susceptible to when Thiobacillus can convert reduced forms of sulfur to sulfuric acid. Sulfate in acidic precipitation as well as other sulfur compounds deposited in dry deposition could permit the formation of sulfur compounds utilizable by microorganisms. (For more information concerning the effects of sulfur oxides on materials, please consult Chapter 10).

7.4 ASSESSMENT OF SENSITIVE AREAS

7.4.1 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 deposition (precipitation) and dry deposition, (2) the hydrology of the lake, (3) the soil system, geology, and canopy effects, (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. 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. 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 (Wetzel, 1975; Wright and Gjessing, 1976; Wright and Henriksen, 1978). The cation exchange capacity and weathering rate of the watershed and the alkalinity of the surface water determine the ability of the system 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 (Wright and Gjessing, 1976; Galloway and Cowling, 1978; Wright and Henriksen, 1978). 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 low and, therefore, its buffering capacity is low (Schofield, 1979; Wright and Henriksen, 1978).

Wright and Henriksen (1978) 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 these lakes was low in most major ions and had low electrical conductivity. [The fewer the minerals in water the lower its conductivity (Wetzel, 1975)]. The waters in the lakes surveyed were "among the softest waters in the world." (Wright and Henriksen, 1978) Sedimentary rocks generally weather readily, whereas igneous rocks are highly resistant. The Adirondacks, as pointed out by Schofield (1975; 1979) have granite bedrock with much of the area covered with a mantle of mixed gneisses. Shallow soils predominate in the area. Thus, areas are susceptible to acidification.

Limestone terrains, on the other hand, are capable of buffering intense concentrations of acids. Glacially derived sediment has been found to be more important than bedrock in assimilating acidic precipitation in the Canadian Shield area (Kramer, 1976). Generally, however, bedrock geology is the best predictor of the sensitivity of aquatic ecosystems to acidic precipitation (Hendrey et al., 1980).

Areas with aquatic ecosystems that have the potential for being sensitive to acidic precipitation are shown in Figure 7-27. In Figure 7-27, 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 (Galloway and Cowling, 1978)]. Galloway and Cowling verified this

Figure 7-27. Regions in North America with lakes that are sensitive to acidification by acid precipitation by virtue of their underlying bedrock characteristics.

Source: Galloway and Cowling (1978).

*
hypothesis by compiling alkalinity data. The lakes having low alkalinity existed in regions having igneous and metamorphic rock (Galloway and Cowling, 1978). Hendry et al. (1980) have developed new bedrock geology maps of the eastern United States for predicting areas which might be impacted by acidic precipitation. The new maps permit much greater resolution for detecting sensitivity than has been previously available for the region.

Henriksen (1979) has developed a lake acidification "indicator model" using pH-calcium and calcium-alkalinity relationships as an indicator for determining decreased surface water acidification. The indicator is based on the observation that in pristine lake environments (e.g., Northwest Norway or the Experimental Lakes Area in Northwest Ontario, 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., Southeast Norway and the Adirondack region) will exhibit lower pH or lower alkalinity than the reference lakes, at comparable calcium levels, due to the replacement of bicarbonate by strong acid anions.

Schofield (1979) has illustrated the use of Henriksen's model with 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 7-28 and 7-29) and is derived primarily from precipitation. 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 (1979) 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/l. 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 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 to 10 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. The amount of precipitation must also be considered since it affects total sulfate additions.

The report by Hendrey et al. (1980) compared pre-1970 data with post-1975 data. A marked decline in both alkalinity and pH of sensitive waters of North Carolina and New Hampshire were tested. In the former, pH and alkalinity have decreased in 80 percent of the streams and in the latter pH has decreased 90 percent since 1949. These areas are predicted to be sensitive by the geological map on the basis of their earlier alkalinity values. Detailed county by county maps of other states in the eastern United States suggest the sensitivity of these regions to acidic precipitation.

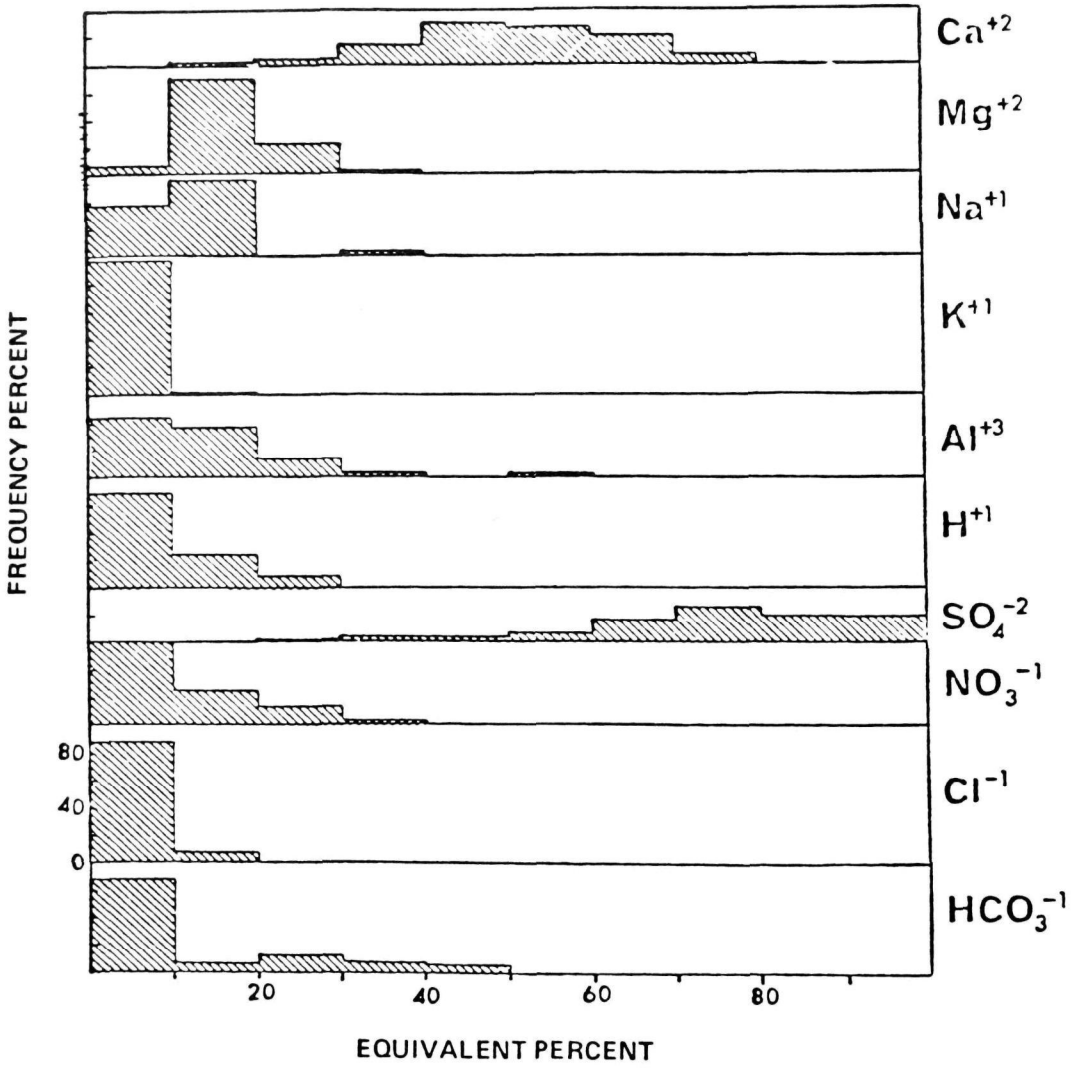


Figure 7-28. Equivalent percent composition of major ions in Adirondack lake surface waters (215 lakes) sampled in June 1975.

Source: Schofield (1979).

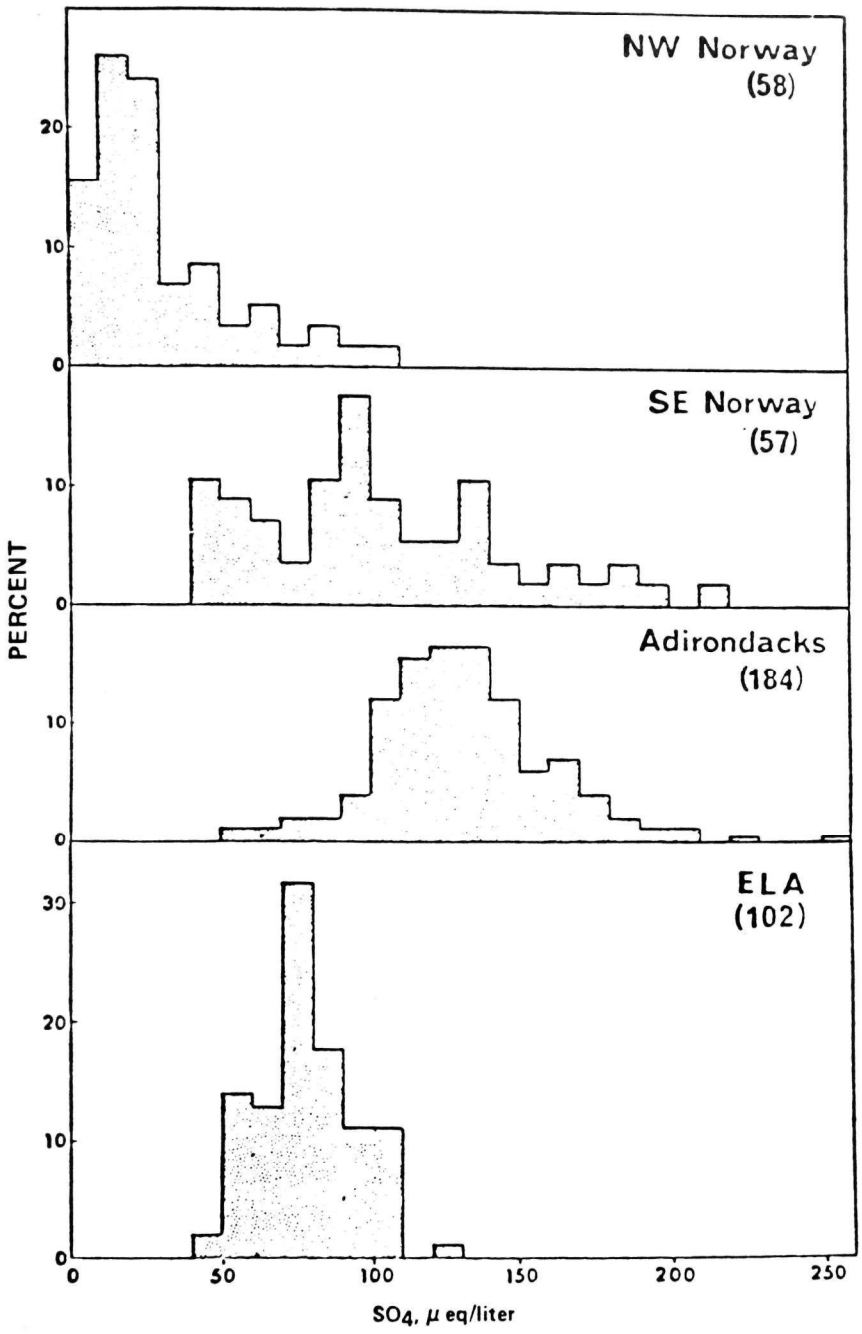


Figure 7-29. Percent frequency distribution of sulfate concentrations in surface water from lakes in sensitive regions. (ELA refers to Experimental Lake Area of Ontario.)

Source: Schofield (1979).

*

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 (Hendrey, 1980). 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 (Davis et al., 1978). 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 (Davis et al., 1978). The occurrence of limestone outcroppings in the Adirondack Mountains of New York state are highly correlated with lake pH levels. The occurrence of limestone apparently counteracts any effects of acidic precipitation. 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. Local variations in bedrock and soils are very important in explaining variations in acidification between lakes within an area.

7.4.2 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 ones 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 link the two ecosystems, i.e., data on 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 acidic 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 (McFee, 1980).

*

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 (Gorham, 1958). Soil buffering capacity varies widely in different regions of the country (Figure 7-30). 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 (Donahue et al., 1977). 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 runoff water (Donahue et al., 1977). The sensitivity of different soils based on pH, texture, and calcite content is summarized in Table 7-14.

TABLE 7-14. 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

Reference: Wiklander (1979).

Soils are the most stable component of a terrestrial ecosystem. Any changes which occur in this component would probably have far-reaching effects. McFee (1980) 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 or lime or renewed by flooding or by other additions?
4. The presence or absence of carbonates in the soil profile.

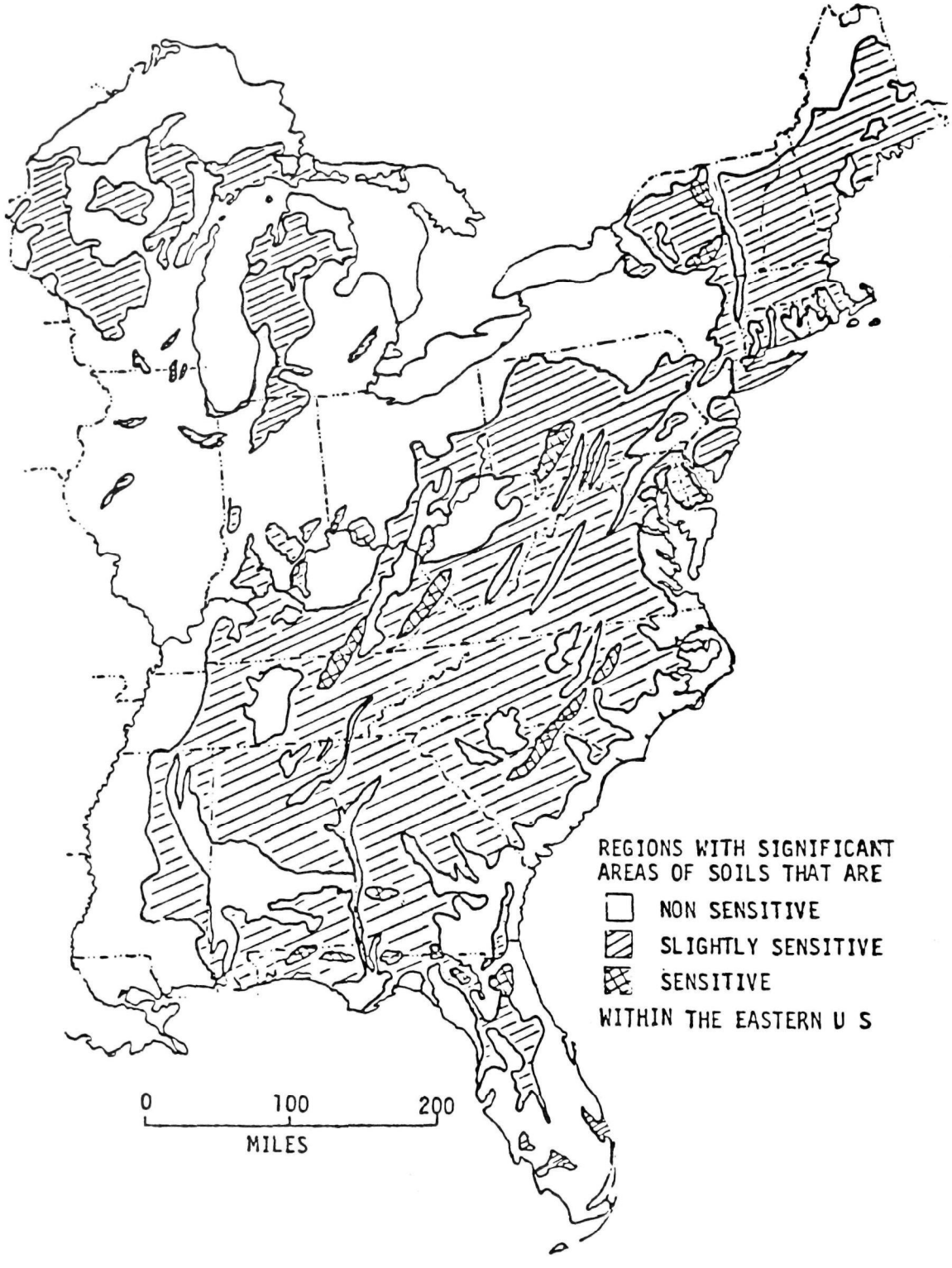


Figure 7-30. Soils of the Eastern United States sensitive to acid rainfall.

Source: McFee (1980).

*

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 by 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. Acidic 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 (McFee, 1980). Soils having a low CEC are usually low in plant nutrients; therefore, significant changes in their productivity could occur with only a slight loss of nutrients (McFee, 1980).

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?" (McFee, 1980)

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 meq/100 g (assuming 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 meq/100 g, the soils are considered sensitive.

Based on the above concepts, the soils of the eastern United States including effects of cultivation were mapped (Figure 7-31) by McFee. The areas containing most of the soils potentially sensitive to acidic precipitation are in the upper Coastal Plain 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 (McFee, 1980). 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.

The capacity of soils to absorb and retain anions also important in determining whether soils will become acidified was not discussed by McFee (1980). The capacity for anion absorption is great in soils rich in hydrated oxides of aluminum (Al) and iron (Fe). Reduced leaching of salt cations is of great significance not only in helping to prevent soil

*
acidification but in geochemical circulation of nutrients, fertilization in agriculture and preventing water pollution (Wilklander, 1980, Johnson et al. 1980, Johnson, 1980). (See Section 7.3.2.1) This parameter, as well as those listed by Mc Fee (1980) should be used in determining the sensitivity of soils to acidification by both wet and dry deposition.

7.5 SUMMARY

Occurrence of acidic precipitation (rain and snow) in many regions of the United States, Canada, and Scandanavia has been implicated in the disappearance or reduction of fish, other animals, and plant life in ponds, lakes, and streams. In addition, acidic precipitation possesses the potential for impoverishing sensitive soils, degrading natural areas, injuring forests, and damaging monuments and buildings made of stone.

Sulfur and nitrogen oxides, emitted through the combustion of fossil fuels are the chief contributors to the acidification of precipitation. The fate of sulfur and nitrogen oxides, as well as other pollutants emitted into the atmosphere, depends on their dispersion, transport, transformation and deposition. Emissions from automobiles occur at ground level, those from electric power generators from smoke stacks 1000 feet or more in height. Transport and transformation of the sulfur and nitrogen oxides are in part associated with the height at which they are emitted. The greater the height, the greater the likelihood of a longer residence time in the atmosphere and a greater opportunity for chemical transformation of the oxides to sulfates, nitrates or other compounds. Ozone and other photochemical oxidants are believed to be involved in the chemical transformations. Because of long range transport, acidic precipitation in a particular state or region can be the result of emissions from sources in states or regions hundreds of miles away rather than local sources. To date the complex nature of the chemical transformation processes has not made the demonstration of a direct cause and effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation possible.

Natural emissions of sulfur and nitrogen compounds are also involved in the formation of acidic precipitation; however, in industrialized regions anthropogenic emissions exceed natural emissions.

Precipitation is arbitrarily defined as being acidic if its pH is less than 5.6. Currently the acidity of precipitation in the northeastern United States, the region most severely impacted, ranges from pH 3.0 to 5.0. Precipitation episodes with a pH as low as 3.0 have been reported for other regions of the United States. The pH precipitation can vary from event to event, from season to season and from geographical area to geographical area.

The impact of acidic precipitation on aquatic and terristrial ecosystems is not the result of a single or several precipitation events, but the result of continued additions of acids or acidifying substances over time. Wet deposition of acidic substances on freshwater lakes, streams, and natural land areas is only part of the problem. Acidic substances exist in gases, aerosols, and particulate matter transferred into the lakes, streams, and

*
land areas by dry deposition. Therefore all the observed biological effects should not be attributed to acidic precipitation alone.

Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition, the soil system of the drainage basin, canopy effects of ground cover and the composition of the watershed bedrock.

Ecosystems can respond to environmental changes or perturbations only through the response of the populations of organisms of which they are composed. Species of organisms sensitive to environmental changes are removed. Therefore, the capacity of an ecosystem to maintain internal stability is determined by the ability of individual organisms to adjust their physiology or behavior. The success with which an organism copes with environmental changes is determined by its ability to yield reproducing offspring. The size and success of a population depends upon the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that adjust best contribute most to future generations because they have the greatest number of progeny in the population.

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition or polluted air follows the principle of limiting factors. According to this principle, for each physical factor in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and in extreme cases a species. When one limiting factor is removed another takes its place. The range of tolerance of an organism may be broad for one factor, narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth or growth form of an organism. Limiting factors are, therefore, factors which, when scarce or overabundant, limit the growth, reproduction and/or distribution of an organism. The increasing acidity of water in lakes and streams appears to be such a factor. Significant changes that have occurred in aquatic ecosystems with increasing acidity include the following:

1. Fish populations are reduced or eliminated.

2. Bacterial decomposition is reduced and fungi may dominate saprotrophic communities. Organic debris accumulates rapidly, tying up nutrients, and limiting nutrient mineralization and cycling.

3. Species diversity and total numbers of species of aquatic plants and animals are reduced. Acid-tolerant species dominate.

4. Phytoplankton productivity may be reduced due to changes in nutrient cycling and nutrient limitations.

5. Biomass and total productivity of benthic macrophytes and algae may increase due partially to increased lake transparency.

*

6. Numbers and biomass of herbivorous invertebrates decline. Tolerant invertebrate species, e.g., air-breathing bugs (water-boatmen, back-swimmers, water striders) may become abundant primarily due to reduced fish predation.

7. Changes in community structure occur at all trophic levels.

Studies indicate that pH concentrations between 6.0 and 5.0 inhibit reproduction of many species of aquatic organisms. Fish populations become seriously affected at a pH lower than 5.0.

Disappearance of fish from lakes and streams follows two general patterns. One results from sudden short-term shifts in pH, the other arises from a long-term decrease in the pH of the water. A major injection of acids and other soluble substances occurs when polluted snow melts during warm periods in winter or early spring. Fish kills are a dramatic consequence of such episodic injections.

Long-term increases in acidity interfere with reproduction and spawning, producing a decrease in population density and a shift in size and age of the population to one consisting primarily of larger and older fish. Effects on yield often are not recognizable until the population is close to extinction; this is particularly true for late-maturing species with long lives. Even relatively small increases (5 to 50 percent) in mortality of fish eggs and fry can decrease yield and bring about extinction.

Aluminum is mobilized at low pH values. Concentrations of aluminum may be as or more important than pH levels as factors leading to declining fish populations in acidified lakes. Certain aluminum compounds in the water upset the osmoregulatory function of the blood in fish. Aluminum toxicity to aquatic biota other than fish has not been assessed.

An indirect effect of acidification potentially of concern to human health is possible heavy metal contamination of edible fish and of water supplies. Studies in Canada and Sweden reveal high mercury concentrations in fish from acidified regions. Lead and copper have been found in plumbing systems with acidified water, and persons drinking the water could suffer from lead or copper poisoning.

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

At present there are no documented observations or measurements of changes in natural terrestrial ecosystems that can be directly attributed to acidic precipitation. This does not necessarily indicate that none are occurring. The information available on vegetational effects is an accumulation of the results of a wide variety of controlled research

*
approaches largely in the laboratory, using in most instances some form of "simulated" acidic rain, frequently dilute sulfuric acid. The simulated "acid rains" have deposited hydrogen (H^+), sulfate ($SO_4^=$) and nitrate (NO_3^-) ions on vegetation and have caused necrotic lesions in a wide variety of plants species under greenhouse and laboratory conditions. Such results must be interpreted with caution, however, because the growth and morphology of leaves under greenhouse conditions are often atypical of field conditions. Based on laboratory studies, sensitivity of plants to acidic depositions seems to be associated with the wettability of leaf surfaces. The shorter the time of contact, the lower the resulting dose, and the less likelihood of injury.

Erosion of monuments and buildings made of stone and corrosion of metals can result from acidic precipitation. Because sulfur compounds are a dominant component of acidic precipitation and are deposited during dry deposition also, the effects resulting from the two processes cannot be distinguished. In addition, the deposition of sulfur compounds on stone surfaces provides a medium for microbial growth that can result in deterioration.

7.6 REFERENCES

Abrahamsen, G., K. Bjor, R. Horntvedt, and B. Tveite. Effects of acid precipitation on coniferous forest. In: F. H. Braekke, ed., Research Report FR-6. SNSF Project, NISK, Aas, Norway, 1976. pp 37-63.

Abrahamsen, G., Horntvedt, R., and Tveite, B. Impacts of acid precipitation on coniferous forest ecosystems, Water, Air and Soil Pollution, 8:57-73, 1977.

Abrahamsen, G., and G. J. Dollard. Effects of Acid Deposition on Forest Vegetation. In: Wood, M. J. (ed.). Ecological Effects of Acid Precipitation. Report of workshop held at Calley Hotel, Gatehouse-of-Fleet, Galloway, U.K., 4-7 Sept. 1978. EPRI SOA77-403, Electric Power Res. Institute, 3412 Hillview Ave., Palo Alto, California 94303, 1979.

Alexander, M. Effects on acidity on microorganisms and microbial processes in the soil. p. 341-362. In: Effects of Acid Precipitation on Terrestrial Ecosystems. T. C. Hutchinson and M. Havas (eds.) Plenum Press, NY, 1978.

Alexander, M. Effects of Acidity on Microorganisms and Microbial Porcesses in a Soil. In: Effects of Acid Precipitation on Terrestrial Ecosystems. T. C. Hutchinson and M. Havas, eds., 1980. pp. 363-374.

Almer, B. W., C. Dickson, C. Ekström, and E. Hornström. Chapter 7. Sulfur Pollution and the Aquatic Ecosystem. In: Sulfur in the Environment, Part II: Ecological Impacts. J. Nriagu, ed. John Wiley and Sons, NY, 1978. pp. 271-311.

Almer, B., W. Dickson, C. Ekström, E. Hörnström, and U. Miller. Effects of acidification on Swedish lakes. Ambio 3:30-36, 1974.

Altshuller, A. P., and G. A. McBean, Co-Chairman, 1979. The LRTAP Problem in North America: a preliminary overview. Prepared the United States-Canada Research Consultation Group on the Long-Range transport of Air Pollutants, 1979. pp. 48.

Amundsen, T., and K. Lunder. Report on fishery-biological surveys in Tjagevatn and Sonstevatn in Grandsherod, Notodden in Telemark. Fiskerikonsulenten i Ost-Norge, Direktoratet for vitt og ferskvannsfisk, Oslo, 1974. 13 pp.

Andersson, I., O. $_{o}$Grahn, H. Hultberg, and L. Landner. Jämförande undersökning av olika tekniker för aterställande av försurade sjöar. STU Report 73-3651. Stockholm: Institute for Water and Air Research, 1975. Cited in: National Research Council, Sulfur Oxides, National Academy of Sciences, Washington, DC, 1978. 118 pp.

Anschütz, J., and F. Gessner. Der Ioneraustausch bei torfmoosen (Sphagnum). Flora 141:178-236, 1954. Cited in: Almer et al., 1978.

Armstrong, F. A. J., and D. W. Schindler. Preliminary Chemical Characterization of Waters in the Experimental Lakes Area, Northwestern Ontario. Jour. Fish. Research Board, Canada 28:171-, 1971.

Arnold, D. E., R. W. Light, and V. J. Dymond. Probable Effects of Acid Precipitation on Pennsylvania Waters. EPA 600/3-80-D12. January 1980. EPA Corvallis, OR. 19 p.

Baker, J., D. Hocking, and M. Nyborg. Acidity of open and intercepted precipitation in forests and effects on forest soils in Alberta, Canada. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976.pp. 779-790.

Baker, J., and C. Schofield. Aluminum toxicity to fish as related to acid precipitation and Adirondack surface water quality. In: Proc. International Conference on the Ecological Impact of Acid Precipitation, March 1980, SNSF-project report, Oslo, Norway. (in press).

Beamish, R. J., and H. H. Harvey. Acidification of the La Cloche Mountain Lakes, Ontario and resulting fish mortalities. Jour. Fisheries Res. Board Canada. 29:1131-1143, 1972.

Beamish, R. J. Growth and survival of white suckers (Catostomus commersoni) in an acidified lake. J. Fish Res. Board Can. 31:49-54, 1974.

Beamish, R. J., W. L. Lockhart, J. C. Van Loon, and H. H. Harvey. Long-term acidification of a lake and resulting effects on fishes. Ambio 4:98-102, 1975.

Beamish, R. J. Acidification of lakes in Canada by acid precipitation and the resulting effects on fishes, pp. 479-498. In: L. S. Dochinger and T. A. Seliga, eds. Proc. First International Symposium on Acid Precipitation and the Forest Ecosystem, 12-15 May 1975, USDA Forest Service General Technical Report NE-23, Upper Darby, Pennsylvania, 1976.

Beamish, R. J. Acidification of Lakes in Canada By Acid Precipitation and the Resulting Effects of Fish. Water, Air and Soil Poll. 6:501-514, 1976.

Bell, H. L., and A. V. Nebecker. Preliminary studies on the tolerance of aquatic insects to low pH. J. Kansas Entomological Soc. 42:230-236, 1969.

Bell, H. L. Effect of low pH on the survival and emergence of aquatic insects. Water Res. 5:313-319, 1971.

Bick, H., and E. F. Drews. Selbstreiningung und ciliatenbesiedlung in saurem milieu (modellversuche). Hydrobiologia 42:393-402, 1973, Cited in Leivestad et al., 1976.

Billings, W. D. Plants and the Ecosystem. 3rd ed. pp. 1-62. Wadsworth Publishing Company, Inc. Belmont, PA., 1978. 177 p.

Bolin, B., et al. Sweden's Case Study for the United Nations Conference on the Human Environment: Air Pollution Across National Boundaries. In: The Impact on the Environment of Sulfur in Air and Precipitation. Norstadt and Sons, Stockholm, 1972. 97 pp.

Boling, R. H., Jr., E. D. Goodman, J. A. VanSickle, J. O. Zimmer, K. W. Cummins, R. C. Petersen, and S. R. Reice. Toward a model of detritus processing in a woodland stream. Ecology 56:141-151, 1975.

Borgström, R., J. Brittain, and A. Lillehammer. Evertebrater og surt vann: Oversikt over innsamlingslokaliteter. Research Report IR 21/76. 1432 Aas-NLH, Norway: SNSF Project Secretariat, 1976. Cited in: National Research Council, Sulfur Oxides, National Academy of Sciences, Washington, DC, 1978. 33 pp.

Boughey, A. S. Fundamental Ecology. Scranton, Pa., Intex Educational Publishers, 1971. p. 11-50.

Brady, N. C. The Nature and Property of Soils. McMillan Publishing Co., New York. p. 464-472, 1974.

Braekke, F. H., ed. Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. SNSF Project, Research Report FR 6/76, Oslo, Norway, 1976.

Brezonik, P. L. Nutrients and Other Biologically Active Substances in Atmospheric Precipitation. Proc. First Specialty Symposium on Atmospheric Contribution to the Chemistry of Lake Waters. Internat. Assoc. Great Lakes Res. Sept. 28-Oct. 1, 1975. p. 166-186.

Brock, Thomas D. Lower pH Limit for the Existence of Blue-Green Algae: Evolutionary and Ecological Implications. Science 179:480-483, 1973.

Brooks, J. L., and S. I. Dodson. Predation, body size and composition of plankton. Science 150:28-35, 1965.

Brosset, C. Air-borne acid. Ambio 2:2-8, 1973.

Brouzes, R. J. P., R. A. N. McLean, and G. H. Tomlinson. Mercury - the Link Between pH of Natural Waters and the Mercury Content of Fish. Paper presented at a meeting of the Panel on Mercury of the Coordinating Committee for Scientific and Technical Assessments of Environmental Pollutants, National Academy of Sciences, National Research Council, Washington, DC, May 3, 1977. Montreal, Quebec: Domtar Research Center, 1977.

Bua, B., and E. Snekvik. Hatching experiments with roe of salmonid fish 1966-1971. Effects of acidity and salt content of hatchery water. Van 7: 86-93. Cited in Wright and Snekvik, 1978, 1972.

Chamberlain, A. C. Dry deposition of sulfur dioxide. In: Atmospheric Sulfur Deposition, Environmental Impact and Health Effects. Proceedings of the Second Life Sciences Symposium, Potential Environmental and Health Consequences of Atmospheric Deposition. D. E. Shriner, C. R. Richmond, and S. E. Lindberg, eds., Ann Arbor Science, 1980. pp. 185-197.

Cholonky, B. J. Die Ökologie der diatomeen in Binnengewässer. Cramer, Weinheim, 1968. 699 pp. Cited in Hendrey et al., 1980.

Cogbill, C. V. The effect of acid precipitation on tree growth in eastern North America, Water, Air and Soil Pollution, 8:89-93, 1977.

Cogbill, C. V., and G. E. Likens. Acid precipitation in the northeastern United States. Water Resour. Res. 10:1133-1137.

Cole, D. W., and D. W. Johnson. Atmospheric sulfate additions and cation leaching in a Douglas fir ecosystem. Water Resour. Res. 13:313-317, 1977.

Comerford, N. b. and White, E. H., 1977, Nutrient content of throughfall in paper birch and red pine stands in northern Minnesota, Can. J. For. Res., 7, (4), pp. 556-551.

Connell, W. E., and W. H. Patrick, Jr., Science 159, 86, 1968.

Conroy, N., K. Hawley, W. Keller, and C. Lafrance. Influences of the atmosphere on lakes in the Sudbury area. J. Great Lakes Res. 2(Suppl.1):146-165, 1976.

Cowling, E. B., and L. S. Dochinger. The Changing Chemistry of Precipitation and Its Effects on Vegetation and Materials. AICHE Symposium Series. Control and Dispersion of Air Pollutants: Emphasis on NO_x and Particulte Emissions. 7:134-142, 1978.

Crisman, T. L., R. L. Schulze, P. L. Brenzonik, C. D. Hendrey, and S. A. Bloom. The biotic response in Florida lakes. In: Proc. International Conf. on the Ecological Impact of Acid Precipitation, March 1980, SNSF-project report, Oslo, Norway. (in press).

Cronan, C. S. Consequences of Sulfuric Acid Inputs to a Forested Soil. In: Atmospheric Sulfur Deposition, Environmental Impact and Health Effects. D. S. Shriner, C. R. Richmond, and S. E. Lindberg, eds., Ann Arbor Science, 1980. pp. 325-343.

Cronan, C. S. Solution chemistry of a New Hampshire subalpine ecosystem: biochemical patterns and processes. Ph.D. Thesis, Dartmouth College, Hanover, NH, 1978. 248 pp.

Cronan, C. S., and C. L. Schofield. Aluminum Leeching Response to Acid Precipitation: Effects on High-Elevation Watersheds in the Northeast. Science 204:304-305, 1979.

Dancer, W. S., L. A. Peterson, and G. Chesters. Ammonification and nitrification of N as influenced by soil pH and previous N treatments. Soil Sci. Soc. Am. Proc. 37:67-69, 1973.

Dannevig, A. Influence of precipitation on the acidity of water courses and on fish stocks. Jeger og Fisker. 3:116-118, 1959. Cited in Leivestad et al., 1976.

Davis, R. B., M. O. Smith, J. H. Baily, and S. A. Norton. Acidification of Maine (U.S.A.) Lakes By Acidic Precipitation. Verh. Internat. Verein Limnol. 20:532-537, 1978.

Denison, R., Caldwell B.,, Bormann, B., Eldred, L., Swanberg, C., and Anderson, S. The effects of acid rain on nitrogen fixation in western Washington coniferous forests. Water, Air and Soil Pollution 8:(1), 1977. pp. 21-34.

Dickson, W. The acidification of Swedish lakes. In: Fishery Board of Sweden, Institute of Freshwater Research, Drottningholm, Sweden. Report No. 54, Lund, Sweden: Carl Bloms Boktryckeri A.-B, 1975. pp. 8-20.

Dickson, W. Some effects of the acidification of Swedish lakes. Verh. Internat. Verein. Limnol. 20:851-856, 1978.

Dillon, P. J., D. S. Jefferies, W. Snyder, R. Reid, N. D. Yan, D. Evans, J. Moss, and W. A. Scheider. Acidic precipitation in south-central Ontario: recent observations. J. Fish. Res. Board Can. 35:809-815, 1978.

Dodson, S. I. Zooplankton competition and predation: an experimental test of the size-efficiency hypothesis. Ecology 55:605-613, 1974.

Donahue, R. L., R. W. Miller, and J. C. Shickluna. Soils. An introduction to soils and plant growth. 4th ed. p. 244-248. Prentice-Hall, Inc. Englewood Cliffs, NJ 07632, 1977.

Donnevig, A. Influence of precipitation on the acidity of water courses and on fish stocks. Jeger og Fisker. 3:116-118, 1959 (in Norwegian cited in Wright #12).

Drabløs, D., and T. Sevaldrud. Lake acidification, fish damage, and utilization of outfields. A comparative survey of six highland areas, southeastern Norway. In: Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, March 1980. D. Drabløs and A. Tollan, eds., SNSF Project Report, Oslo, Norway, 1980. pp. 354-357.

Driscoll, C. T., Jr., J. P. Baker, J. I. Bisogin, Jr., and C. Schofield. Aluminum Speciation in Dilute Acidified Waters and Its Effects on Fish. Nature 284:161-163, 1979.

Driscoll, C. T. Chemical characterization of some dilute acidified lakes and streams in the Adirondack region of New York state. Ph.D. Thesis, Cornell University, Ithaca, New York, 1980. 309 pp.

Eaton, J. S., G. E. Likens, and F. H. Bormann. Throughfall and Stemflow Chemistry in a Northern Hardwood Forest. J. Ecol. 61:495-508, 1973.

Eliassen, A., and J. Saltbones. Decay and transformation rates of SO_2 as estimated from emission data, trajectories and measured air concentrations. Atmos Environ. 9:425-429, 1975.

European Inland Fisheries Advisory Committee (EIFAC). Water quality criteria for European freshwater fish. Report on extreme pH values and inland fisheries. Water Res. 3:593-611, 1969.

Evans, K. S., N. F. Gmur, and J. J. Kelsch. Perturbations of upper leaf surface structures by simulated acid rain. Environ and Exptl. Bot. 17:145-149, 1977.

Evans, L. S., and D. M. Bozzone. Effect of buffered solutions and sulfate on vegetative and sexual development in gametophytes of Pteridium aquilinum. Amer. J. Bot. 64:897-902, 1977.

Evans, L. S., N. F. Gmur, and F. DaCosta. Leaf surface and histological perturbations of leaves of Phaseolus vulgaris and Helianthus annuus after exposure to simulated acid rain. Amer. J. Bot. 64:903-913, 1977.

Evans, L. S., and D. M. Bozzone. Effect of buffered solutions and various anions on vegetative and sexual development in gameophytes of Pteridium aquilinum. Canadian Jour. Bot. 56:779-785, 1978.

Evans, L. S., N. F. Gmur, and F. DaCosta. Foliar response of six clones of hybrid poplar to simulated acid rain. Phytopathology 68:847-856, 1978.

Evans, L. S., and T. M. Curry. Differential responses of plant foilage to simulated acid rain. Amer. J. Bot. 66:953-962, 1979.

Fageström, T., and A. Jernelöv. Some Aspects of the Quantitative Ecology of Mercury. Water Res. 6:1193-1202, 1972.

Ferenbaugh, R. W. Effects of simulated acid rain on Phaseolus vulgaris L. (Fabaceae). Amer. J. Bot. 63:283-288, 1976.

Fiance, S. B. Distribution and biology of mayflies and stoneflies of Hubbard Brook, New Hampshire, MS. Thesis, Cornell University, Ithaca, NY, 1977.

Fisher, B. E. A. Long-range transport and deposition of sulfur oxides. In: Sulfur in the Environment, Part I: The Atmospheric Cycle. J. O. Nriagu, ed., John Wiley and Sons, New York, NY, 1978. pp. 243-295.

Foster, R. J. Geology. Charles E. Merrill Publishing Co., Columbus, Ohio, 1971. 162 pp.

Fredricksen, R. L. Nutrient budget of a Douglas-fir forest on an experimental watershed in western Oregon. Pages 115-131, Research on Coniferous and R. H. Waring. Portland, Oreg.: Pacific Northwest Forest and Range Experiment Station, 1972.

Galloway, J. N., and E. B. Cowling. The effects of precipitation on aquatic and terrestrial ecosystems: A proposed precipitation network. JAPCA 28:229-235, 1978.

Galloway, J. N., and D. M. Whelpdale. An Atmospheric Sulfur Budget for Eastern North America. Atmos. Environ. 14:409-417, 1980.

Galmström, G., G. Andersson, and S. Fleischer. Decomposition and exchange processes in acidified lake sediment. In: Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, March 11-14, 1980, D. Drablos and A. Tollan, eds., SNSF Project Report, Oslo, Norway, 1980. pp. 306-308.

Galvin, P. J., P. J. Samson, P. E. Coffey, and D. Romeno. Transport of sulfate to New York State. Environ. Sci. and Tech. 12:580-584, 1973.

Galvin, P. J., and J. A. Cline. Measurement of anions in the snow cover of the Adirondack Mountains. Atmos. Environ. 12:1163-1167, 1978.

Garrett, A. Compositional changes of ecosystem during chronic gamma irradiation. In: Symposium on Radioecology. Proc. Second National Symposium, Ann Arbor, Mich., May 15-17, 1967.

Gatz, D. F. Comment on 'Acid precipitation in the northeastern United States' by Charles V. Cogbill and Gene E. Likens. Water Resour. Res. 12:569-570, 1976.

Giddings, J., and J. N. Galloway. The Effects of Acid Precipitation on Aquatic and Terrestrial Ecosystems. Literature Reviews on Acid Precipitation, EEP-2. Cornell University, Ithaca, NY, 1976.

Gjessing, E. T., A. Henriksen, M. Johannessen, and R. F. Wright. Changes in the Chemical Composition of Lakes. In: Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway. F. H. Braekke, ed., Research Report FR 6/76, 1432 Aas-NLH, Norway, SNSF Project Secretariat, 1976. pp. 65-85.

Glass, G. E., and O. L. Loucks (eds). Impacts of Air Pollutants on Wilderness Areas of Northern Minnesota. pp. 188. Environmental Research Laboratory-Duluth, ORD, U.S. Environmental Protection Agency, Duluth, Minnesota, October 1979.

Glass, N. R., G. E. Glass, and P. J. Rennie. Effects of acid precipitation. Environ. Sci. Tech. 13:1350-1355, 1979.

Glover, G. M., and A. H. Webb. Weak and Strong Acids in The Surface Waters of The Tovdal Region in S. Norway. Water Res. 13:781-783, 1979.

Gorham, E. On the acidity and salinity of rain. Geochim. Cosmochim. Acta. 7:231-239, 1955.

Gorham, E. The influence and importance of daily weather conditions in the supply of chloride, sulfate and other ions to fresh waters from atmospheric precipitation. Phil. Trans. R. Soc. London, Ser. B 241:147-178, 1958.

Gorham, E. Acid precipitation and its influence upon aquatic ecosystems--an overview. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Selinga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. pp. 425-458.

Gosner, K. L., and I. H. Black. The effects of acidity on the development and hatching of New Jersey frogs. Ecology 38:256-262, 1957.

Grahn, O. Macrophyte succession in Swedish lakes caused by deposition of airborne acid substances, pp. 519-530. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, L. S. Dochinger and T. A. Seliga, eds., Ohio State University, May 12-15, 1975. U.S.D.A. Forest Service General Technical Report NE-23. Upper Darby, Pennsylvania. Forest Service, U.S. Department of Agriculture, Northeastern Forest Experiment Station, 1976.

Grahn, O., H. Hultberg, and L. Landner. Oligotrophication--a self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio 3:93-94, 1974.

Granat, L. On the relationship between pH and the chemical composition in atmospheric precipitation. Tellus 24:550-560, 1972.

Grennard, A., and F. Ross. Progress report on sulfur dioxide. Combustion 45:4-9, 1974.

Hagen, A., and A. Langeland. Polluted snow in southern Norway and the effect of the meltwater on freshwater and aquatic organisms. Environ. Pollut. 5:45-57, 1973.

Hagström, T. 1977. Grodornas försvinnande i an försurad sjö. Sveriges Natur 11/77:367-369. Cited in Hendrey, 1978.

Haines, E. B. Nitrogen content and acidity of rain on the Georgia coast. Water Resour. Bull. 12:1223-1231, 1976.

Hall, R. J., G. E. Likens, S. B. Fiance, and G. R. Hendrey. Experimental acidification of a stream in the Hubbard Brook Experimental Forest, New Hampshire. Ecology 61:976-989, 1980.

Halstead, R. L., and P. J. Rennie. Effects of Sulphur on Soils in Canada. 181-220. In: Sulphur and its Inorganic Derivatives in the Canadian Environment. Nat. Res. Council of Canada. NRC Assoicate Committee on Scientific Criteria for Environmental Quality. Ottawa, Canada, 1977.

Hamilton, W. C. Estimate by the National Coal Association. Personal communication. Jan. 1980.

Hanken, I., J. F. Lynch, and D. B. Wake. Salamander invasion of the tropies. Natural Hist. 89:47-53, 1980.

Harr, T. E., and P. E. Coffey. Acid Precipitation in New York State. Technical Paper No. 43. New York State Department of Environmental Conservation, Albany, NY. pp. 21-29, 1975.

Harward, M. E., and H. H. Reisenaur. Movement and reactions of inorganic soil sulfur. Soil Sci. 101:326-335, 1966.

Heagle, A. S., W. W. Heck, W. M. Knott, J. W. Johnston, E. P. Stahel, and E. B. Cowling. Responses of Citrus to Acidic Rain from Simulated SRM Fuel Exhaust Mixtures and Exhaust Components, Internal report, 1978. 11 pp.

Heinrichs, H., and R. Mayer. Distribution and cycling of major and trace elements in two central forest ecosystems. J. Environ. Qual. 6:402-407, 1977.

Henderson, G. S., and W. F. Harris. An ecosystem approach to characterization of the nitrogen cycle in a deciduous forest watershed. Pages 179-193, Forest Soils and Forest Soils Conference, edited by B. Bernier and C. H. Winget. Quebec, Canada: Les Presses de l'Universite Laval, 1975.

Hendrey, C. D., and P. L. Brezonik. Chemistry of precipitation at Gainesville, Florida. Environ. Sci. and Tech. 14:843-849, 1980.

Hendrey, G. R., K. Baalstrud, T. S. Traaen, M. Laake, and G. Raddum. Acid precipitation: Some hydrobiological changes. Ambio 5:224-227, 1976.

Hendrey, G. R., and R. F. Wright. Acid precipitation in Norway: Effects on aquatic fauna. J. Great Lakes Res. 2(Suppl 1):192-207, 1976.

Hendrey, G. R. Effects of low pH on the growth of periphytic algae in artificial stream channels. SNSF Project, 1432 Aas-NLH, Norway, 1976.

Hendry, C. Chemical composition of rainfall at Gainesville, Florida. M.S. Thesis. Department of Environmental Engineering Sciences, University of Florida, Gainesville, 1977.

Hendrey, G. R. Aquatics Task Force on Environmental Assessment of the Atikokan Power Plant: Effects on Aquatic Organisms. Land and Fresh Water Environmental Sciences Group, Department of Energy and Environment. Brookhaven National Laboratory Associated Universities, Inc. Lipton, NY BNL 50932. November 1978. 16 p.

Hendrey, G., and F. W. Barvenik. Impact of Acid Precipitation on Decomposition and Plant Communities in Lakes. In: Scientific Papers from the Public Meeting on Acid Precipitation, May 4-5, 1978, Lake Placid, New York, published by Science and Technology Staff, New York State Assembly, Albany, NY March, 1979. p. 92-103.

Hendrey, G. R., J. N. Galloway, S. A. Norton, C. L. Schofield, P. W. Shaffer and D. A. Burns. Geological and Hydrochemical Sensitivity of the Eastern United Stated to Acid Precipitation. Report prepared for Ecological Effects Division, Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency under EPA-DOE Interagency Agreement 79-D-X0672. EPA-600/3-80-024. January 1980.

Hendrey, G. R., N. D. Yan, and K. J. Baumgartner. Responses of freshwater plants and invertebrates to acidification. EPA/OECD International Symposium for Inland Waters and Lake Restoration, September 1980, Portland, Maine, 1980.

Hendrey, G. R., and F. Vertucci. Benthic plant communities in acidic Lake Colden, New York: Sphagnum and the algal mat. In: Proc. Internat. Conf. on the Ecological Impact of Acid Precipitation. March 1980, SNSF-project report, Oslo, Norway. (in press).

Henriksen, A., and R. F. Wright, Effects of acid precipitation on a small acid lake in southern Norway. Nord. Hydrol. 8:1-10, 1977.

Henriksen, A. Acidification of Freshwaters: A Simple Approach for Identification and Quantification. Nature 278:542-545, 1979.

Hicks, B. B., and M. L. Wesely. Turbulent transfer processes to a surface and interaction with vegetation. In: Atmospheric Sulfur Deposition, Environmental Impact and Health Effects. D. E. Shriner, C. R. Richmond, and S. E. Lindberg, eds., Proceedings of the Second Life Sciences Symposium, Potential Environmental and Health Consequences of Atmospheric Deposition, Ann Arbor Science, 1980. pp. 199-207.

Hindawi, I. J., and H. C. Ratsch. Growth Abnormalities of Christmas Trees attributed to Sulfur Dioxide and Particulate Aerosol. Presented at the 67th Annual Meeting of the Air Poll. Control Assoc. Abstract Number 74-252, 1974.

Hindawi, I. J., J. A. Rea, and W. L. Griffis. Response of bush bean exposed to acid mist. J. Bot. 67:168-172, 1980.

Hörnström, E., C. Ekström, U. Miller, W. Dickson, Försurnings inverkan på västkustsjöar (Effects of the Acidification on Lakes in the Swedish West Coast Region) Statens Naturvårdsverk, Slona, Sweden, Publikationer 1973: 7 (in Swedish, summary in English). Cited in: Wright, R. F., and Engil. T. Gjessing. Changes in the chemical composition of lakes. Ambio. 5: 219-223, 1976.

Hoeft, R. G., D. R. Kieney, and L. M. Walsh. Nitrogen and Sulphur in Precipitation and Sulfur Dioxide in the Atmosphere in Wisconsin. J. Environ. Quality 1:203-208, 1972.

Holling, C. C. Resilience and stability of ecological systems. Ann. Rev. Ecol. Syst. 4:1-23, 1973.

Hornbeck, J. W., G. E. Likens, and J. S. Eaton. Seasonal patterns in acidity of precipitation and their implications for forest stream ecosystems. In: Proceedings of the First International Conference on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio. L. S. Dochinger and T. A. Seliga, eds. U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experimental Station, Upper Darby, PA, 1976. pp.

Hubbert, M. K. Outlook for fuel reserves. In: McGraw-Hill Encyclopedia of Energy, D. N. Lapedes, ed., McGraw-Hill Inc., New York, NY, 1976. pp 11-23.

Hultberg, H. Thermally stratified acid water in late winter - A key factor inducing self-accelerating processes which increase acidification p. 503-517. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, Upper Darby, Pennsylvania, Forest Service, U.S. DOA, Northeastern Forest Experiment Station, 1976.

Hutchinson, T. C., and L. M. Whitby. The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. pp.

Hutchinson, T. C., W. Gizym, M. Havas, and V. Zoberns. Effects of long-term lignite burns on Arctic ecosystems at the Smoking Hills, N.W.T., pp. 317-332. In: D. D. Hemphill, ed., Trace Substances in Environmental Health-XII, University of Missouri, Columbia, Missouri, 1978.

Irving, P. Rainfall Acidity at Argonne. RER Division Annual Report, Argonne National Laboratory, Argonne, IL, ANL-78-65-III, 1978.

Irving, P. M. Induction of Visible Injury in Chamber-Grown Soybeans Exposed to Acid Precipitation. RER Division Annual Report, ANL-78-65-III, Argonne, IL, 1978.

Irving, P., and J. E. Miller. The Effects of Acid Precipitation Alone and in Combination with Sulfur Dioxide on Field-Grown Soybeans. RER Division Annual Report, ANL-78-65-III, Argonne, IL, 1978.

Irving, P. M. Response of Field-Grown Soybeans to Acid Precipitation Alone and in Combination with Sulfur Dioxide. PhD. Thesis, University of Wisconsin, Milwaukee, WI, 1979.

Jacobson, J. S., L. J. Heller, and P. Van Leuken. Acidic precipitation at a site within the northeastern concentration. Water, Air and Soil Poll. 6:339-349, 1976.

Jacobson, J. S., and P. van Leuken. Effects of acidic precipitation on vegetation. Proc. Fourth Intern. Clean Air Congress, pp. 124-127. 1977.

Jacobson, J. S. J. Trojano, L. J. Colavito, L. I. Heller, and D. C. McCune. Polluted Rain and Plant Growth. In: Polluted Rain, 12th Rochester International Conference on Environmental Toxicity. Plenum Publishing Co., New York, NY, 1980.

Jacobson, J. S. Experimental Studies on the Phytotoxicity of Acidic Precipitation: The United States Experience. In: Effects of Acid Precipitation on Terrestrial Ecosystems. T. C. Hutchinson and M. Havas, eds., Plenum Press, New York, NY, 1980a. pp. 151-160.

Jacobson, J. S. The influence of rainfall composition on the yield and quality of agricultural crops. In: Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 11-14, 1980. SNSF project report Oslo, Norway, D. Drabløs and A. Tollan, eds., 1980b. pp. 41-46.

Jensen, K. W., and E. Snekvik. Low pH Levels Wipe Out Salmon and Trout Populations in Southernmost Norway. Ambio 1:223-225, 1972.

Johannessen, M., and A. Henriksen. Chemistry of snow meltwater: changes in concentration during melting. Water Resources Res. 14:615-619, 1978.

Johannessen, M., R. F. Wright, and A. Skartvect. Streamwater chemistry before, during and after snowmelt. In: Proc. International Conference on the Zoological Impact of Acid Precipitation, SNSF-project, Oslo, Norway. (in press).

Johnson, N. M., G. E. Likens, F. H. Bormann, D. W. Fisher, and R. S. Pierce. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Res. 5: 1353-1363, 1969.

Johnson, D. W. Site Susceptibility to Leaching by H_2SO_4 in Acid Rainfall. In: Effect of Acid Precipitation on Terrestrial Ecosystems. T. C. Hutchinson and M. Havas, eds., Plenum Press, New York, NY, 1980. pp. 525-535.

Johnson, D. W., and D. W. Cole. Anion mobility in sols: Relevance to nutrient transport from forest ecosystems. Environ. International 3:79-90, 1980.

Johnson, D. W., J. W. Hornbeck, J. M. Kelly, W. T. Swank, and D. E. Todd. Regional patterns of soil sulfate accumulation: Relevance to ecosystem sulfur budgets. In: Atmospheric Sulfur Deposition, Environmental Impact and Health Effects. D. E. Shriner, S. R. Richmond, and S. E. Lindberg, eds., Proceedings of the Second Life Science Symposium, Potential Environmental Health Consequences of Atmospheric Deposition, Ann Arbor Science, 1980. pp. 507-520.

Jones. M. B. Sulfur in Agricultural Lands. p. 146-158. In: Sulfur in the Environment. Missouri Botanical Garden in cooperation with Union Electric Company, St. Louis, Mo., July, 1975.

Jonsson, B., and R. Sundberg. Has the acidification by atmospheric pollution cause a growth reduction in Swedish forests? Rep. Notes No. 20. Stockholm, Sweden: Royal College of Forestry, 1972.

Junge, C. E. The distribution of ammonia and nitrate in rainwater over the United States. Trans. Amer. Geophys. Union 39:241-248, 1958.

Källqvist, T., R. Romstad, and J. Kotai. Orienterende undersøkelse av pH-effekter pa algesamfunn i forsøksrenner. (Preliminary study of pH-effects on algal communities in experimental channels.) SNSF-Project IR 7/75 (in Norwegian), 1975. Cited in Hendry et al., 1980.

Kramer, J. R., Geochemical and Lithological Factors in Acid Precipitation. p. 611-618. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, Upper Darby, Pennsylvania, Forest Service, U.S. Department of Agriculture, Northeastern Forest Experiment Station, 1976.

Krupa, Sagar. Acidic Rain: Its Chemistry and Effects on Terrestrial Vegetation. Proc. 3rd International Congress of Plant Pathology, Munich, West Germany, August 1978. p. 345 (Abstract).

Kucera, V. Effects of Sulfur Dioxide and Acid Precipitation on Metals and Anti-Rust Painted Steel. Ambio 5:243-248, 1976.

Kwiatkowski, R. E., and J. C. Roff. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. Can. J. Bot. 54:2546-2561, 1976.

Laake, M. Effekter av lav pH på produksjon, nedbryting og stoffkret sløp i littoralsonen. Research Project IR 29/76, 1432 Aas-NLH, Norway. SNSF-project, 1976. 75 pp. Cited in National Research Council, 1978.

Landner, L., and P. O. Larsson. Biological Effects of Mercury Fall-Out Into Lakes from the Atmosphere, IUL Report B115. Stockholm: Institute for Water and Air Research, 1972. 18 pp. (in Swedish, translated by H. Altosaar, Domtar Research Centre, December 23, 1975)

Lang, D. S., D. S. Shriner, and S. V. Krupa. Injury to vegetation incited by sulfuric acid aerosols and acidic rain. Paper 78-7.3, 71st Annual Meeting, Air Pollution Control Association, Houston, Texas, 1978.

Larson, T. V., R. J. Charlson, E. J. Knudson, G. D. Christian, and H. Harrison. The influence of a sulfur dioxide point source on the rain chemistry of a single storm in the Puget Sound region. Water Air Soil Pollut. 4:319-328, 1975.

Lee, J. J., and D. E. Weber. Effects of Sulfuric Acid Rain on Two Model Hardwood Forests: Throughfall, Litter Leachate, and Soil Solution. EPA-600/3-80-014, U.S. Environmental Protection Agency, Corvallis, OR, January 1980.

Lee, J. J., G. E. Neely, and S. C. Perrigan. Sulfuric Acid Rain Effects on Crop Yield and Foliar Injury. January EPA-600/3-80-016, U.S. Environmental Protection Agency, Corvallis, OR, January 1980.

Leivestad, H., and I. P. Muniz. Fish Kill at Low pH in a Norwegian River. Nature 259:391-392, 1976.

Leivestad, H., G. Hendrey, I. P. Muniz, and E. Snekvik. Effects of acid precipitation on freshwater organisms. In: Impact of Acid Precipitation of Forest and Freshwater Ecosystems in Norway. F. J. Braekke, ed., SNSF Project Report FR 6/76, 1432 Aas-NLH, Norway, 1976. pp. 87-111.

Lewis, W. M., Jr., and M. C. Grant. Acid Precipitation in the Western U.S. Science 207:176-177, 1980.

Likens, G. E., G. H. Bormann, N. M. Johnson, D. W. Fisher, and R. S. Pierce. Effects of cutting and herbicide treatment on nutrient budgets in the Hubbard Brook Watershed - ecosystem. Ecol. Monogr. 40:23-47, 1970.

Likens, G. W., F. H. Bormann, and N. M. Johnson. Acid rain. Environment 14:33-40, 1972.

Likens, G. E. The Chemistry of Precipitation in the Central Finger Lakes Region. Technical Report No. 50. Water Resources and Marine Science Center, Cornell University. Ithaca, NY, 1972.

Likens, G. E., and F. H. Bormann. Acid rain: A serious regional environmental problem. Science 184:1176-1179, 1974.

Likens, G. E., and F. H. Bormann. Linkages Between Terrestrial and Aquatic Ecosystems. BioScience 24:447-456, 1974.

Likens, G. E. Acid precipitation. Chem. Eng. News 54:(48)29-44, 1976.

Likens, G. E., F. H. Bormann, J. S. Eaton, R. S. Pierce, and N. M. Johnson. Hydrogen ion input to the Hubbard Brook Experimental Forest, New Hampshire, during the last decade. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio. L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23. U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. pp. 397-407.

Likens, G. E., J. S. Eaton, and J. N. Galloway. Precipitation as a Source of Nutrients for Terrestrial and Aquatic Ecosystems. Precipitation Seevenging (1974). Proc. of a Symposium held at Champaign, Ill. Oct. 14-18, 1974. Illinois State Water Survey. Publ. Tech. Information Center, ERA. CONF-741003, 1977. p. 552-570.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler. Acid Rain. Scientific American. 241:43-51, 1979.

Liljestrand, H., and J. J. Morgan. Chemical composition of acid precipitation in Pasadena, California. Environ. Sci. Tech. 12:1271-1273, 1978.

Lindberg, S. E., R. C. Harriss, R. R. Turner, D. S. Shriner, and D. D. Huff. Mechanisms and rates of atmospheric deposition of selected trace elements and sulfate to a deciduous forest watershed. ORNL/TM 6674, Environmental Sciences Division Pub. No. 1299, 1979. pp. 514.

Lipske, M. Sour Rain, Deadly Rain. Defenders. 55:2-5, 1980.

Livingstone, D. A. Chemical composition of rivers and lakes. U. S. Geological Survey Professional Paper 440-6, Washington, DC, 1963.

Lockhart, W. L., and A. Lutz. Preliminary biochemical observations of fishes inhabiting an acidified lake in Ontario, Canada, pp. 545-569. In: L. S. Dochinger and T. A. Seliga, eds., Proc. First International Symposium on Acid Precipitation and the Forest Ecosystem, USDA Forest Service General Technical Report NE-23, Upper Darby, Pennsylvania, 1976.

Lynch, H. Predation, competition and zooplankton community structure: an experimental study. Limnol. Oceanogr. 24:253-272, 1979.

Malmer, N. Acid precipitation: Chemical changes in the soil. Ambio 5:231-234, 1976.

Marenco, A, and J. Fontan. Influence of drt deposition on the residence time of particulate pollutants in the troposphere. In: Proceedings, Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants-1974 Energy Reasearch and Development Administration Symposium Series, CONF-740921, National Technical Information Service, U.S. Department of Commerce. Springfield, VA. pp. 54-61.

Mayer, R., and B. Ulrich. Acidity of Precipitation as Influenced by the Filtering of Atmospheric Sulphur and Nitrogen Compounds-Its Role in the Element Balance and Effect on Soil. Water, Air, and Soil Poll. 7:409-416, 1977.

McColl, J. G., and D. S. Bush. Precipitation and throughfall chemistry in the San Francisco Bay Area. J. Environ. Qual 7:352-357, 1978.

McFee, W. W., J. M. Kelly, and R. H. Beck. Acid precipitation: Effects on soil base pH and base saturation of exchange sites. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. pp. 725-735.

McFee, W. W. Sensitivity of Soil Regions To Long Term Acid Precipitation. p. 131. Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, OR. EPA-600/3-80-013, January 1980.

Menendex, R. Chronic effects of reduced pH on brook trout (Salvelinus fontinalis). J. Fish. Res. Board Can. 33:118-123, 1976.

Miller, J. M., J. N. Galloway, G. E. Likens. Origin of air masses producing acid precipitation at Ithaca, NY, A preliminary report. Geophysical Research Letters 5:757-769, 1978.

Minshall, G. W. Role of Allochtronous detritus in the trophic structure of a woodland spring-brook community. Ecology 48:139-149, 1967.

Moran, J. M., M. D. Morgan, and J. H. Wiersma. Introduction to Environmental Science. W. H. Freeman and Co., San Francisco, CA, 1980. pp. 7-75.

Müller, P. Effects of artificial acidification on the growth of periphyton. Can. J. Fish. Aquat. Sci. 37:355-363, 1980.

Muniz, I. P., and H. Leivestad. Toxic effects of aluminum on brown trout (Salmo trutta, L.). In: Proc. International Conference on the Ecological Impact of Acid Precipitation, 11-14 March 1980, SNSF-project, Oslo, Norway. (in press).

National Research Council. Scientific and Technical Assessments of Environmental Pollutants. Nitrates: An Environmental Assessment. National Academy of Sciences, 1978. p. 275-317.

National Research Council. Sulfur Oxides. National Academy of Sciences. Washington, D. C. Chapter 5. Effects of Sulfur Oxides on Aquatic Ecosystems, 1978.

National Research Council. Sulfur Oxides. Chapter 4. National Academy of Sciences. Washington, D.C. 1978.

Nihlgard, B. Precipitation, its chemical composition and effect on soil water in a beech and a spruce forest in south Sweden, Oikos, 21:208-217, 1970.

Nisbit, I. C. T. Sulfates and acidity in precipitation: Their relationship to emissions and regional transport of sulfur oxides. In: Air Quality and Stationary Source Emission Control. A report prepared by the Commission on Natural Resources, National Academy of Sciences for the Committee on Public Works, U.S. Senate, 94th Congress, 1st Session. Committee Serial No. 94-4, U.S. Government Printing Office, Washington, D.C., 1975. pp. 276-312.

Norton, S. A. Changes in Chemical Processes in Soils Caused by Acid Precipitation. Water, Air and Soil Poll. 7:389-400, 1977.

Nriagu, J. Deteriorative Effects of Sulfur Pollution on Materials. In: Sulfur in the Environment Part II: Ecological Impacts, Nriagu, J. ed. John Wiley and Sons, New York, 1978. pp. 2-59.

Øakland, J. Distribution and ecology of the freshwater snails Gastropoda) of Norway. Malacologia 9:143-151, 1969.

Øakland, K. A. On the distribution and ecology of Gammarus lacustris, G. O. Sars in Norway, with notes on its morphology and biology. Norw. J. Zool. 17:111-152, 1969.

Økland, J. A group of fish-food organisms (snails, Gastropoda) and environmental parameters in 1000 lakes in Norway, with emphasis on low pH habitats. In: Proc. Internat. Conf. The Ecological Impact of Acid Precipitation, March 1980, Oslo Norway. (in press).

Økland, K. Some fish-food organisms in Norway, Asellus aquaticus, Gammarus lacustris (Crustacea) and small mussels (Sphaeriidae): ecology and distribution. In: Proc. Internat. Conf. on the Ecological Impact of Acid Precipitation, March 1980, Oslo Norway. (in press).

Odén, S. The acidification of air and precipitation and its consequences on the natural environment. Swedish Nat. Sci. Res. Council, Ecology Committee Bull. 1, 1968. 68 pp.

Odén, S. Acidification by Atmospheric Precipitation--A General Threat to the Ecosystem. In: Acidification of the Biological Environment. I. Mysterus, ed., Translation Series No. 2564, Fisheries Research Board of Canada, Ottawa, Canada, 1971.

Odén, S., R. Andersson, and M. Barting. The long-term changes in the chemistry of soils in Scandanavia due to acid precipitation. In: Supporting Studies to air Pollution Across National Boundaries. The impact on the environment of sulfur in air and precipitation, B. Bolin, ed., Sweden's case study for the United Nations conference on the human environment, Royal Ministry of Foreign Affairs., Royal Ministry of Agriculture, Stockholm, Sweden, 1972. p. 20.

Odén, S. Acid precipitation: A world concern. In: Proceedings of the Conference on Emerging Environmental Problems, Acid Precipitation, May 19-20, 1975, The Institute on Man and Science, Rensselaerville, N.Y. U.S. Environmental Protection Agency, Region II. Water Resources and Marine Sciences Center, Cornell Univeristy and Center for Environmental Quality Management, Cornell University, EPA-902/9-75-001, November 1975. pp. 5-44.

Odén, S. The acidity problem--An outline of concepts. In: Proceedings of the First International Conference on Acid Precipitation and the Forest Ecosystem. May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service, General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, August 1976. pp. 1-36.

Odum, E. P. Summary. In: Ecological Effects of Nuclear War. G. M. Woodwell (ed.). Brookhaven National Lab. 917 (C-43), 1965.

Odum, E. P. Fundamental of Ecology 3 ed. W. B. Saunders Co. Philadelphia, 1971. p. 5, 8-139.

Oliver, D. R. Life history of the Chironomidae. Ann. Rev. Entomol. 16:211-230, 1971.

Overrein, L. N. Sulphur pollution patterns observed; leaching of calcium in forest soil determined. Ambio. 1:145-147, 1972.

Pack, D. H., G. J. Ferber, J. L. Heffter, K. Telegadas, J. K. Angell, W. H. Hoecker, and L. Machta. Meterology of Long-Range Transport. Atmos. Environ. 12:425-444, 1978.

Pack, D. W. Sulfate behavior in eastern U.S. precipitation. Geophysical Res. Letters. 5:673-674, 1978.

Peterson, R. C. Dynamics of coarse particulate organic material processing in diversified pH regimes. In: Internat. Conf. The Ecological Impact of Acid Precipitation, March 1980, SNSF-project, Oslo, Norway. (in press).

Pfeiffer, M. List and Summary of Acidified Adirondack Waters Based on Data Available as of April 1979. New York State Department of Environmental conservation. Albany, New York, May 1979.

Pfeiffer, M., and P. Festa. Acidity status of lakes in the Adirondack region of New York in relation to fish resources. New York State Department of Environmental Conservation Publication FW-P168, 1980. 36 pp.

Potts, D. T. W., and C. Fryer. The effect of pH and salt content on sodium balance in Daphnia magna and Acantholeberis curvirostris (Crustacea; Cladocera). J. Comp. Physiol. Series B 129:289-294, 1979.

Potts, W. T. W., and D. J. A. Brown. Study Group 5 Discussions. D.5.1-D.5.5. In: Wood, M. J. (ed). Ecological Effects of Acid Precipitation. Report of workshop held at Cally Hotel, Gatehouse-of-Fleet, Galloway, U.K. 4-7 Sept. 1978. EPRI SOA77-403, Electric Power Res. Institute, 3412 Hillview Ave., Palo Alto, California 94303, 1979.

Pough, F. H. Acid precipitation and embryonic mortality of spotted salamanders, Ambystoma maculatum. Science 192:68-70, 1976.

Pough, F. H., and R. E. Wilson. Acid precipitation and reproductive success of Ambystoma salamanders, pp. 531-544. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State University, May 12-15, 1975. U.S. For. Serv. Gen. Tech. Rep. NE-23, 1976.

Prahm, L. R., U. Trop, and R. M. Stern. Deposition and transformation rates of sulfur oxides during atmospheric transport over the Atlantic. Tellus 18:355-372, 1976.

Raddum, G. Invertebrates: quality and quantity as fish food In: Hendrey, G. R., ed., Limnological Aspects of Acid Precipitation, Rep. Internat. Workshop. Brookhaven National Laboratory Report No. 51074, 1978.

Reid, G. K., and R. D. Wood. Ecology of Inland Waters and Estuaries. 2nd ed. D. Von Nostrand Co. New York, 1976. p. 261-319.

Rheinheimer, G. Aquatic Microbiology. John Wiley & Sons, New York, 1971. 184 pp.

Roff, J. R., and R. E. Kwiatkowski. Zooplankton and zoobenthos communities of selected northern Ontario lakes of different acidities. Can. J. Zool. 55:899-911, 1977.

Rosenqvist, I. T. A contributor towards analysis of buffer properties of geological materials against strong acids in precipitation water, report written for the Council for Research in Natural Sciences, Norwegian General Research Council, 1976.

Rosseland, B. O., I. Sevaldrun, D. Svalastog, and I. P. Muniz. Studies on freshwater fish populations - effects of acidification or reproduction, population structure, growth and food selection. In: Proc. International Conference on the Ecological Impact of Acid Precipitation, 11-14 March 1980, SNSF-project. (in press).

Schaffer, R. J. The weathering of natural building stones. Spec. Ref. No. 18, London, HMSO. 149 pp. Cited in: Sereda, P. J. Effects of Sulphur on Building Materials.

Scheider, W., J. Adamski, and M. Paylor. Reclamation of Acidified Lakes Near Sudbury, Ontario. Rexdale, Ontario, Canada: Ontario Ministry of the Environment, 1975. 129 pp.

Scheider, W., J. Adamski, and M. Paylor. Reclamation of Acidified Lakes Near Sudbury, Ontario (Ontario Ministry of the Environment, Rexdale, Ontario, Canada, 1975. Cited in: Wright, R. F., and Egil. T. Gjessing. Changes in the chemical composition of lakes. Ambio. 5:219-223, 1976.

Scheider, W., J. Adamski, and M. Paylor. Reclamation of Acidified Lakes Near Sudbury, Ontario (Ontario Ministry of the Environment, Rexdale, Ontario, Canada, 1975. Cited in: Wright, R. F., and Egil. T. Gjessing. Changes in the chemical composition of lakes. Ambio. 5:219-223, 1976.

Schindler, D. W. Whole lake eutrophication experiments with phosphorus, nitrogen and carbon. Verh. Internat. Verein. Limnol. 19:577-582, 1975.

Schindler, D. W., R. Wagemann, R. B. Cook, T. Ruszczynski, and J. Prokopowich. Experimental acidification of Lake 223, experimental lakes area: background data and the first three years of acidification. Can. J. Fish. Aquat. Sci. 37:342-354, 1980.

Schlesinger, W. H., and M. M. Hasey. The Nutrient Content of Precipitation, Dry Fallout, and Intercepted Aerosols in the Chaparral of Southern California. Am. Midland Naturalist 103:114-122, 1980.

Schmel, G. A. Particle and gas dry deposition: a review. Atmos. Environ. 14:983-1011, 1980.

Schofield, C. L. Acid precipitation: Effects on fish. Ambio. 5:228-230, 1976.

Schofield, C. L. Lake acidification in the Adirondack Mountains of New York: Causes and consequences. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. p. 477. (Abstract)

Schofield, C. L. Acidification of Adirondack lakes by atmospheric precipitation: extent and magnitude of the problem. Final Rep. D. J. Project F-28-R, NYS Dept. Env. Cons., 1976b. 11 pp.

Schofield, C. L. Dynamics and management of Adirondack fish populations: acidification of Adirondack lakes by atmospheric precipitation - long-term and seasonal trends and effects of lake acidification on fish populations. Research Report F-28-R-4, N.Y.S. Dept. of Env. Cons., 1976c.

Schofield, C. L. Acid precipitation's destructive effects on fish in the Adirondacks. N.Y. Food Life Sci. Q. 10(3):12-15, 1977.

Schofield, C. L. The Acid Precipitation Phenomenon and Its Impact in the Adirondack Mountains of New York State. In: Scientific Paper from the Public Meeting on Acid Precipitation, May 4-5, 1978, Lake Placid, New York, published by Science and Technology Staff, New York State Assembly, Albany, NY, March, 1979. p. 86-91.

Schofield, C. Effects of Acid Rain on Lakes. Presented at the American Society of Civil Eng. Convention, Boston. April 2, 1979. 13 pp.

Schofield, C., and J. R. Trojnar. Aluminum toxicity to brook trout (Salvelinus fontinalis) in acidified waters, pp. 341-365. In: T. Y. Toribara, M. W. Miller and P. E. Morrow, eds., Polluted Rain. Plenum Press, New York, 1980.

Seip, H. M. Acidification of freshwater-sources and mechanisms. In: Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, D. Drabløs and A. Tollan, eds., SNSF Project Report, Oslo, Norway, 1980.

Sereda, P. J. Chapter 8. Effects of Sulphur on Building Materials. p. 359-426. In: Sulphur and its Organic Derivatives in the Canadian Environment. Nat. Res. Council of Canada. NRC Associate Committee on Scientific Criteria For Environmental Quality. Ottawa, Canada, 1977.

Sheridan, R. P., and R. Rosenstreter. The effect of hydrogen ion concentration in simulated rain on the moss Tortula ruralis (Hedw) Sm. Bryologist 76:168-173, 1973.

Shinn, J. H., and S. Lynn. Do man-made sources affect the sulfur cycle of northeastern states? Environ. Sci. and Tech. 13:1062-1067, 1979.

Shriner, D. S., M. DeCot, and E. B. Cowling. Simulated acid rain caused direct injury to vegetation. Proc. Am. Phytopath. Soc. 1:112, 1974.

Shriner, D. S. Effects of simulated rain acidified with sulfuric acid on host-parasite interactions. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, May 12-15, 1975, Columbus, Ohio, L. S. Dochinger and T. A. Seliga, eds., U.S. Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station, Upper Darby, PA, 1976. pp. 919-925.

Shriner, D. S., and G. S. Henderson. Sulfur distribution and cycling in a deciduous forest watershed. J. Environ. Qual. 7:392-397, 1978.

Shriner, D. S. Effects of simulated acidic rain on host-parasite interactions in plant diseases. Phytopathology 68:213-218, 1978a.

Shriner, D. S. Interactions between acidic precipitation and SO_2 or O_3: Effects on plant response. Phytopathol. News, 12:153, 1978b.

Shriner, D. S. Chapter 11. Atmospheric deposition: monitoring the phenomenon; studying the effects. In: Handbook of Methodology for the Assessment of Air Pollutant Effects on Vegetation. W. W. Heck, S. V. Krupa, and S. N. Linzon, Editors. Air Pollution Control Association, Pittsburgh, Pennsylvania, 1979.

Shriner, D. S. Terrestrial vegetation - air pollutant interactions: Nongaseous pollutants, wet deposition. Paper presented at the International Conference on Air Pollutants and Their Effects on Terrestrial Ecosystems, Banff, Alberta, Canada, May 10-17, 1980.

Sinclair, W. A. Polluted air: Potent new selective force in forest. J. Forestry. 67:305-309, 1969.

Smith, F. B., and G. H. Jeffrey. Airborne transport of sulfur dioxide from the United Kingdom. Atmos. Environ. 9:643-659, 1975.

Smith, R. A. Air and Rain: The Beginnings of Chemical Climatology. Longmans, Green, London, 1872. 600 pp.

Smith, R. L. Ecology and Field Biology, 3rd ed., p. 170. New York, Harper and Row, 1980. pp. 11-199.

SNSF Project. Acid precipitation and some alternative sources as the cause of the acidifying water courses. Norway's Agrarian Science Research Board, Norway's Technical Nature Science Research Board, Dept. of Environmental Protection, ed., A. Tollan, 1977.

Sprules, G. W. Midsummer crustacean zooplankton communities in acid-stressed lakes. J. Fish Res Board Can. 32:389-395, 1975.

Stensland, G. J. A Comparison of Precipitation Chemistry Data At A Central Illinois Site in 1954 and In 1977. Presented at 71st Annual Meeting of the Air Poll. Control. Assoc., Houston, TX. June 25-26, 1978.

Stensland, G. J., Precipitation chemistry trends in the northeastern United States. In: Proceedings Twelfth Annual Rochester International Conference on Environmental Toxicity: Polluted Rain, May 21-23, 1979, Rochester, N. Y. T. Y. Toribara, M. W. Miller, P. E. Morrow, eds. Plenum Press, NY, 1980. pp. 87-103.

Stokes, P. Phytoplankton of acidic lakes in Killarney Ontario: community structure related to water chemistry. In: Proc. International Conference on the Ecological Impact of Acid Precipitation, March 1980, SNSF-project report, Oslo, Norway. (in press).

Stumm, W., and J. J. Morgan. Aquatic Chemistry, Wiley-Interscience, New York, NY, 1970. 583 pp.

Sutcliffe, D. W., and T. R. Carrick. Studies on mountain streams in the English Lake District I. pH, calcium, and the distribution of invertebrates in the River Duddon. Freshwater Biol. 3:437-462, 1973.

Tabatabai, M. A., and J. M. Laflen. Nitrogen and Sulfur Content and pH of Precipitation in Iowa. J. Environ. Quality. 5:108-112, 1976.

Tamm, Co. O., Wiklander, G., and Popovie, B. Effects of application of acid to poor pine forests, Water, Air and Soil Pollution, 8:75-87, 1977.

Tomlinson, G. H. Acidic Precipitation and Mercury In Canadian Lakes and Fish. Scientific Paper From the Public Meeting on Acid Precipitation, May 4-5, 1978. Lake Placid, N.Y. Sponsored by The Committee on Environmental Conservation, New York State Assembly. Pub. by Science and Technology Staff, New York State Assembly. p. 104-118. March 1979.

Traaen, T., and M. Laake. Microbial decomposition and community structure as related to acidity of fresh waters - an experimental approach. In: Proc. Internat. Conf. on Ecological Impact of Acid Precipitation, March 1980, SNSF-project report, Oslo, Norway. (in press).

Trojnar, J. R. Egg and larval survival of white suckers (Catostomus commersoni) at low pH. J. Fish. Res. Board Can. 34:262-266, 1977.

Trojnar, J. R. Egg hatchability and tolerance of brook trout (Salvelinus fontinalis) fry at low pH. J. Fish. Res. Board Can. 34:574-579, 1977.

Tukey, H. B., Jr. The leaching of substances from plants. Ann. Review of Plant Physiology. 21:305-324, 1970.

Turk, J. T., and N. E. Peters. Acid-rain weathering of a metasedimentary rock basin, Herkimer County, New York. U.S. Geol. Surv. Open file Report 77-538, 1977. 14 pp.

Turk, J. T., and N. Peters. Acid-rain Weathering of a Metasedimentary Rock Basin, Herkimer County, New York. Scientific Paper From the Public Meeting on Acid Precipitation, May 4-5, 1978. Lake Placid, N.Y. Sponsored by The Committee on Environmental Conservation, New York State Assembly. Pub. by Science and Technology Staff, New York State Assembly. p 136-145. March 1979.

Turner, J., and M. Lambert. Sulfur nutrition of forests. In: Atmospheric Sulfur Deposition Environmental Impact and Health Effects. Proceedings of the Second Life Science Symposium, Potential Environmental Health Consequences of Atmospheric Deposition, D. E. Shriner, S. R. Richmond, and S. E. Lindberg, eds., Ann Arbor Science, 1980. pp. 321-333.

Tyler, G. Heavy metals pollute nature, may reduce productivity, Ambio, 1, (2), pp. 52-59, 1972.

Tyler, G. Leaching rates of heavy metal ions in forest soil, Water, Air and Soil Pollution, 9, pp. 137-148, 1977.

U.S. Bureau of Mines. Minerals Yearbook 1952. Volume II. Area Reports: Domestic. U.S. Department of the Interior, Washington, DC, 1954. p. 117.

U.S. Bureau of Mines. Minerals Yearbook 1974. Volume II. Area Reports: Domestic. U.S. Department of the Interior, Washington, DC, 1976. p. 392.

U.S. Department of Commerce. Climatic Atlas of the United States. National Climatic Center, Asheville, NC, June 1968.

U.S. Department of the Interior, Fish and Wildlife Service. Impacts of Cool-Fired Power Plants on Fish, Wildlife, and their Habitats. FWS/OBS-78/29, March, 1978. p. 64-70.

U.S. Environmental Protection Agency. National Air Quality, Monitoring, and Emissions Trends Report, 1977. EPA-450/2-78-052, Office of Air Quality, Standards, and Planning. U.S. Environmental Protection Agency, Research Triangle Park, NC, December, 1978.

Ulrich, B. Die Umweltbeeinflussung des Nährstoffhaushaltes eines bodensauren Buchenwalds. Forstwiss. Centralbl. 94:280-287, 1975.

Walters, C. J., and R. E. Vincent. Potential productivity of an alpine lake as indicated by removal and reintroduction of fish. Trans. Amer. Fish Soc. 102:675-697, 1973.

Wetzel, R. G. Limnology, p. 287-621, W. B. Saunders Co., Philadelphia, PA, 1975. 743 pp.

Whelpdale, D. M. Acidic Deposition. Sect. 4.1. Precipitation Chemistry and Deposition. In: Ecological Effects of Acid Precipitation. M. J. Wood, ed., report of workshop held at Calley Hotel, Gatehouse-of-Fleet, Galloway, U.K., September 4-7, 1978. EPRI SOA77-403, Electric Power Res. Institute, Palo Alto, CA, 1979. pp. 2-12.

Wiklander, L. Interaction between cations and anions influencing adsorption and leaching. In: Effects of Acid Precipitation on Terrestrial Ecosystems. T. C. Hutchinson and H. Havas, eds. Plenum Press, New York, NY, 1980.

Wiklander, L. Leaching and Acidification of Soils. In: Wood, M. J. (ed.). Ecological Effects of Acid Precipitation. Report of workshop held at Cally Hotel, Gatehouse-of-Fleet, Galloway, U.K. 4-7 Sept. 1978. EPRI SOA77-403, Electric Power Res. Institute, 3412 Hillview Ave., Palo Alto, California 94303, 1979.

Williams, Wayne T. Acid Rain: The California Context. Citizens for Better Environment. Environmental Review, May 1978. p. 6-8, 10.

Winkler, E. M. Important Agents of Weathering For Building and Monumental Stone. Eng. Geol. 1:381-400, 1966.

Wodzinski, R. S., D. P. Labeda, and M. Alexander. Toxicity of SO_2 and NO_x: Selective inhibition of blue green algae by bisulfite and nitrite. J. Air Poll. Control Assoc. 27: 891-893, 1977.

Wolff, G. T., P. J. Lioy, H. Golub, and J. S. Hawkins. Acid precipitation in the New York Metropolitan Area: Its relationship to meteorological factors. Env. Sci. and Tech. 13:209-212, 1979.

Wood, T. Acid Precipitation. In: Sulfur in the Environment. Missouri Botanical Garden in cooperation with Union Electric Company, St. Louis, MO, 1975. pp. 39-50.

Wood, T., and F. Bormann. Increases in foliar leaching by acidification of an artificial mist. Ambio 4:169-171, 1975.

Wood, T., and F. H. Bormann. Short-term effects of a simulated acid rain upon the growth and nutrient relations of Pinus strobus L. Water, Air Soil Pollut. 7:479-488, 1977.

Wood, T., and F. H. Bormann. The effects of an artificial acid mist upon the growth of Betula alleghaniensis. Brit. Environ. Pollut. 7:259-268, 1974.

Woodwell, G. M. Effects of ionizing radiation on terrestrial ecosystems. Science. 138:572-577, 1962.

Woodwell, G. M. Effects of pollution on the structure and physiology of ecosystems. Science. 168:429-433, 1970.

Woodwell, G. M. The ecological effects of radiation. Scientific American. 208:40-49, 1963.

Wright, R. F., A. Henriksen, R. Harriman, B. Norrison, and L. A. Caines. Acid lakes and streams in the Galloway area, southwestern Scotland. In: Proc. International Conference on the Ecological Imapct of Acid Precipitation, 11-14 March 1980, SNSF-project, 1980a. (in press).

Wright, R. F., and A. Henriksen. Chemistry of small Norwegian lakes with special reference to acid precipitation. Limnol. Oceanog. 23:487-498, 1978.

Wright, R. F., and E. Snekvik. Acid precipitation: Chemistry and fish populations in 700 lakes in southernmost Norway. Verh. Int. Ver. Theor. Angew. Limnol. 20:765-775, 1978.

Wright, R. F., and E. T. Gjessing. Changes in the chemical composition of lakes. Ambio. 5:219-223, 1976.

Wright, R. F., N. Conroy, W. T. Dickson, R. Harriman, A. Henriksen, and C. L. Schofield. Acidified lake districts of the world: a comparison of water chemistry in southern Norway, southern Sweden, southwestern Scotland, the Adirondack Mountains of New York, and southeastern Ontario. In: Proc. International Conference on the Ecological Impact of Acid Precipitation, 11-14 March 1980, SNSF-project, Oslo, Norway, 1980b. (in press).

Wright, R. F., T. Dale, E. T. Gjessing, G. R. Hendry, A. Henriksen, M. Johannessen, and I. P. Muniz. Impact of Acid Precipitation on Freshwater Ecosystems in Norway. Water, Air and Soil Poll. 6:483-499, 1976.

Yan, N. D., and P. Stokes. Phy to plankton of an Acidic Lake, and Its Responses to Experimental Alterations of pH. Environ. Conservation 5:93-100, 1978.

*

8. EFFECTS ON VEGETATION

8.1 GENERAL INTRODUCTION AND APPROACH

The objective of this chapter is to review available data relating atmospheric concentrations of SO_2 and particulates to effects on terrestrial vegetation. Many reviews of the general effects of SO_2 (Daines, 1968; Guderian, 1977; Jacobson and Hill, 1970; Linzon, 1978; Mudd, 1975; NAS, 1978; Treshow, 1970; U.S. Environmental Protection Agency, 1973, 1978; Van Haut and Stratmann, 1970) and, to a lesser extent, of particulate matter (Guderian, 1981) exist in the literature. Additional reports of SO_2 effects on plants for use in diagnostic situations have also been prepared (Davis, 1972a,b; Lacasse and Moroz, 1969; U.S. Environmental Protection Agency, 1976).

This chapter has a more specific purpose. It addresses factors which influence our ability to quantify relationships between exposure dose and plant response. Principal focus is placed on quantifying specific concentrations of SO_2 and particulates associated with vegetation responses at levels ranging from biochemical to that of plant populations. In this process, information of historical interest has been kept to a minimum and emphasis has been placed rather on more recent studies that have employed modern monitoring, experimental, and statistical techniques. Since air quality standards are formulated around effects of single pollutants, only studies in which SO_2 or particulates were determined to be the major cause of measured effects have been included.

As a backdrop against which to consider pollutant effects on plants, it is important to recognize that the many factors which play a major role in determining the likelihood that a given quantity of pollutant will produce a known level of effect vary tremendously in nature. These factors include the type of exposure (acute or chronic), influences of stress from other biotic (plants, disease) or abiotic (edaphic or climatic) factors, the type of response measured, and the species or population under study. These factors and associated terminology have been addressed in Sections 8.2 and 8.4 for SO_2, and Sections 8.6 and 8.7 for particulate matter.

While a broad variety of responses measured following exposure of vegetation to SO_2 or particulates are discussed, it should be noted that not all responses are negative, and that all short-term negative responses do not ultimately result in negative effects on plant growth and development. These concepts are developed more fully in Sections 8.2.7 and 8.3.

The end-point of this presentation of concepts, components, and modifiers of pollutant dose and plant response can be found in attempts to generalize dose-response relationships. This is done in Sections 8.3 and 8.8 for SO_2 and particulates, respectively. With SO_2 dose-response, mathematical models are presented for visible injury to foliage of plants, for numbers of species in a plant population, and for degree of effects on plant growth and yield. The latter effort attempts to synthesize both average and "upper limit" conditions from a broad variety of species, sites, and exposure conditions.

*

The concluding section on ecosystem responses (Section 8.10) derives information from a much more limited number of studies in this area. Here reliance on the broadly based concepts of ecosystem analyses, in many cases, form the basis for strong inference rather than proof of effects on a more subtle scale. In this area definitive data to evaluate the degree or extent of ecosystem changes over broad regions do not at present exist.

8.2 REACTION OF PLANTS TO SO_2 EXPOSURES

8.2.1 Introduction to Terminology

As with all plant stress-inducing agents, SO_2 may initiate changes within plant metabolic systems that may substantially lead to extensive physiological dysfunctions; and if sufficient physiological modification occurs, visible symptoms may be manifested. In some instances, the addition of low SO_2 concentrations to a plant's environment may induce a fertilizer-like response, but only relatively few studies of this phenomenon in agronomic crops have been completed to date; none have shown beneficial effects on natural ecosystems.

The following definitions as relevant to this document have generally been acceptable to plant scientists working on air pollutant induced effects to plants (American Phytopath. Soc., 1974).

Chronic Injury (effects) - injury which develops only after long-term or repeated exposure to an air pollutant and is expressed as chlorosis, bronzing, premature senescence, reduced growth, etc., can include necrosis.

Acute Injury (effects) - injury, usually involving necrosis, which develops within several hours to a few days after short-time exposure to a pollutant, and is expressed as fleck, scorch, bifacial necrosis, etc.

Injury - a change in the appearance and/or function of a plant that is deleterious to the plant.

Damage - a measure of decrease in economic or aesthetic value resulting from plant injury by pollutants.

Plant death may result from continual exposure to low or high pollutant doses and, if such is the case, other mitigating factors may also be involved, i.e., abiotic or biotic disease-inducing agents or insect attack. 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.

Injury does not necessarily imply damage, i.e., economic loss. Timing of pollutant exposure in relation to the stage of crop development often determines the relationship of foliar injury to subsequent yield losses.

The influence of SO_2 as affecting plant health is a complex process that involves not only pollutant concentration and duration of exposure but also environmental factors and

*
then influence on the overall response of the plant itself as a biological entity under stress. In simplistic overview, this process involves pollutant ingress through gas phase interaction at leaf and stomatal surfaces, contact with wet cellular membranes and subsequent liquid phase reactions, induced perturbations of metabolic and/or physiological systems, plant responses through homeostasis (repair) mechanisms, and some resultant disposition of plant health. Figure 8-1 has been modified from a similar description as prepared by Tingey and Taylor (1980) for plant response to ozone.

There are several possible plant responses to SO_2 and related sulfur compounds: (1) fertilizer effects appearing as increased growth and yields, (2) no detectable responses, (3) injury manifested as growth and yield reductions without visible symptom expressions on the foliage or with very mild foliar symptoms that would be difficult to perceive as air pollution incited without the presence of a control set of plants grown in pollution-free conditions, (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reductions in growth and yield, and (5) death of plants and plant communities (Figure 8-1).

8.2.2 Wet and Dry Deposition of Sulfur Compounds on Leaf Surfaces

Deposition processes limit the lifetime of sulfur compounds in the atmosphere, control the distance traveled before deposition, and limit the atmospheric pollutant concentrations (Garland, 1978).

There have been several studies of the deposition of particulate material to natural surfaces (Chamberlain, 1975; Little and Wiffen, 1977; Sehmel and Hodgson, 1974). Very large particles are chiefly deposited by sedimentation. Particles in the range of 1 to 100 μm are also borne towards the surface by turbulence where sedimentation is supplemental to impaction on rough surfaces. Submicron-sized particles (e.g., sulfuric acid aerosols) diffuse by Brownian motion through the thin laminar layers close to the plant surface. This may be followed by active uptake by plants. The mean SO_2 deposition velocities are surprisingly similar for a wide range of plant leaf surfaces (Garland, 1978).

Dry deposition results in the removal of significant amounts of the larger particles from the atmosphere within 2 or 3 days following emission, but several weeks are required to remove the submicrometer fraction.

8.2.3 Routes and Methods of Entry Into the Plant

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 (Guderian, 1977; Katz, 1949; Thomas and Hendricks, 1951, 1956; U.S. Environmental Protection Agency, 1973), there is still controversy as to the importance of stomatal movement relative to plant biochemistry in determining plant sensitivity. Many factors that govern the mechanism of stomatal opening and closing have been determined to be independent of SO_2 exposure concentrations. Physical factors such as light, leaf surface moisture, relative humidity, and soil moisture availability influence stomatal opening and

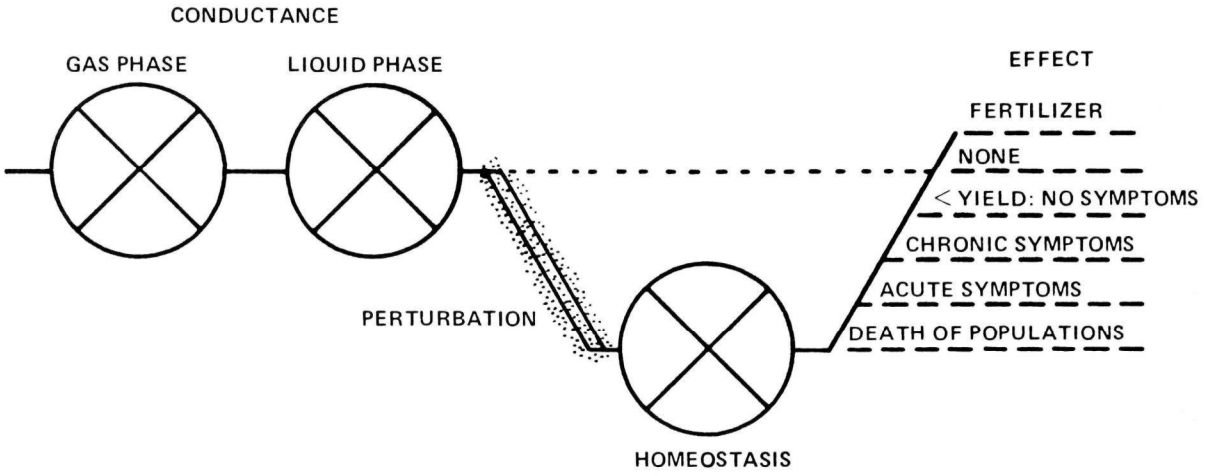


Figure 8-1. A conceptual model of potential responses by plants following exposure to various doses of Sulfur dioxide. Model modified from similar treatment of plant response to ozone.

Source: Tingey and Taylor, 1980.

*
closing and play a major role in plant sensitivity by limiting passive entry of SO_2 into the leaf (Domes, 1971; Meidner and Mansfield, 1968; Setterstrom and Zimmerman, 1939; Spedding, 1969; McLaughlin and Taylor, 1981). These factors must therefore be considered when determining plant sensitivity or tolerance to entry of SO_2.

Internal resistances to flux of gases into plant leaves may also be substantial and may exceed those imposed by stomata under some conditions. Barton et al. (1980) found that photosynthetic depression in kidney beans (Phaseolus vulgaris) during SO_2 exposure was explained predominantly by increases in mesophyll resistance. Stomatal resistances changed only slightly and were a minor component of total leaf resistance to CO_2 at both high (71 percent) and low (33 percent) relative humidity. Winner and Mooney (1980) also found that differences in non-stomatal components of leaf resistance to SO_2 uptake were associated with differences in resistance of deciduous and evergreen shrubs to SO_2.

The absorption rate of SO_2 into plants varies not only among species but also with previous exposure to SO_2. Bigtooth aspen (Populus grandidentata) had a higher SO_2 absorption rate during exposure to high concentrations (2.75 pmm) of SO_2 for 2 hr than did white ash (Fraxinus americana) or yellow birch (Betula alleghaniesis) when they were exposed 0 to 6 hr prior to fumigation with 0.75 ppm SO_2 (Jensen and Kozlowski, 1975). However, after 20 to 36 hr of pre-fumigation treatment, the rate of SO_2 absorption during the 2.75 ppm SO_2 exposure was greater for birch and ash. The sulfur content of foliage increased in all species. Eight days after fumigation with $^{35}SO_2$, varying amounts of the labelled S were translocated throughout the plants including roots (Jensen and Kozlowski, 1975). Subsequent effects were not indicated.

Sulfur dixoide has been shown to increase or decrease stomatal resistance and thus affect potential photosynthetic performance (Hallgren, 1978). Sulfur dioxide induced the closure of "Pelargonium x hortorum" stomata especially when they had been fully opened, and necrosis was not averted (Bonte et al., 1975). Kodata and Inoue (1972) demonstrated that SO_2 entered leaves of Pinus resinosa through stomata and was accumulated in the cells around stomata for some time before diffusing inward through the leaf; i.e., internal diffusion was slower than diffusion into the leaf.

Once SO_2 has entered, it may induce stomata to remain open for longer periods of time or to open wider than before fumigation. Exposure to SO_2 (0.5 ppm) at relative humidities above $40[SO_2]$ percent caused an increase in stomatal opening (Majernik and Mansfield, 1970; Mansfield and Majernik, 1970). A 3-minute 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 have also been noted (Buron and Cornic, 1973).

*

8.2.4 Cellular and Biochemical Changes

Based on the available literature, it is difficult to assess the relationship of SO_2-induced biochemical and/or physiological changes at the cellular level to subsequent effects on photosynthetic activity or resultant growth and yield. Numerous studies have utilized detached leaves and/or isolated chloroplasts in culture solutions for evaluation of effects, but their use for field estimations under ambient conditions remains limited.

Recent studies have also shown a variety of SO_2-induced biochemical effects: enzyme inhibition (Pahlich, 1971, 1973; Ziegler, 1972); interference with respiration (Haisman, 1974); interference with energy transduction (Ballentyne, 1973); interference with lipid biosynthesis (Malhotra and Kahn, 1978); alterations in amino acid content and quality (Godzik and Linskens, 1974); and chlorophyll loss (Rao and LeBlanc, 1965). Pahlich (1975) has rationalized some of this diverse list of effects in terms of sulfite and sulfate accumulation by exposed plant tissues.

Vogl et al. (1965) attempted to integrate biochemical responses with the type and magnitude of resultant plant effects (Table 8-1). Development of models is necessary to relate changes in physiology (biochemical responses) of specific plant species to altered growth and productivity.

Horsman and Wellburn (1976) prepared the most complete listing of reported metabolic or enzymatic effects of SO_2 on plants or plant tissues. In only one of eleven studies (5 references) was an increase in photosynthesis ($^{14}CO_2$ fixation) in response to exposure to SO_2 or its derivatives reported.

With SO_2, which upon absorption is further oxidized to SO_3 and SO_4 and subsequently incorporated into S-containing amino acids and proteins, the rate of entry is particularly important to determining toxicity. Plants have an inherent, and apparently species-dependent, capacity to absorb, detoxify, and metabolically incorporate SO_2 and may absorb low concentrations of SO_2 over long time periods without damage. Thomas et al. (1943), for example, exposed alfalfa to SO_2 continuously at 0.20 ppm for 8 weeks without adverse effects. Toxicity to SO_2 may occur during short episodes when the SO_2-SO_4 conversion rate is exceeded and the extremely toxic sulfite SO_3 form, a partially oxidized metabolic intermediate, accumulates (Ziegler, 1975). During longer exposures at lower SO_2 levels, SO_4 may accumulate as the rate of metabolic incorporation of SO_4 is exceeded, and chronic symptoms may appear.

8.2.5 Acute Foliar Injury

This type of injury occurs following rapid absorption of a toxic dose of SO_2 and results at first in marginal and interveinal areas having a dark-green, watersoaked appearance. After desiccation and bleaching of tissues, the affected areas become light ivory to white in most broadleaf plants. 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. In monocotyledons,

*

TABLE 8-1. RELATIONSHIP OF BIOCHEMICAL RESPONSE TO VISUAL SYMPTOMS OF PLANT INJURY

Degree of injury	Description of Injury					
			Injury To:		Ability to recover in:	
	Visual 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 impedance of gaseous exchange	not detectable	very quick, completely	
C	loss of assimilation capacity through:	diminished activity of enzymes	prolonged impedance of gaseous exchange	reduced growth (deficiency conditions)	slowly, completely	slowly, completely for perennials
	1) premature death of assimilation organs (leaves, needles)	effect upon chlorophyll				
	2) diminished growth of new tissues (shorter needles, etc.)					
D	necrosis of the assimilating and active plant tissues	death of cells through protein and enzyme degradation	irreversible injury: necrosis of some assimilation organs or parts thereof	loss of assimilation capability	quick, not completely, sometimes (for isolated tissues) not any more	slowly, completely for perennials
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)

*
(corn, grasses) foliage injury occurs at the tips and in lengthwise strips along the parallel veins (U.S. Environmental Protection Agency, 1976).

In conifers, acute injury on foliage usually appears as a bright orange red tip necrosis on the current-year needles, often with a sharp line of demarcation between the injured tips and the normally green bases. Occasionally, the injury may occur as bands at the tip, middle, or base of the needles (Linzon, 1972).

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 (Davis, 1972a).

8.2.6 Chronic Foliar Injury

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 variable fumigations consisting of both short-term, high-concentration or long-term, low-concentration exposures to SO_2. It has also been referred to as "sulfate injury" since a slow accumulation of sulfate is the end result of such exposures (Daines, 1968). Within 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 (Thomas, 1951). The capacity of the plant tissues to convert sulfite and bisulfite to sulfate may never be exceeded, and visible expression of symptoms will not occur. In some studies, sulfate levels in plants exposed to SO_2 have been demonstrated to be several times greater than those in controls (Linzon, 1958). As sulfite and bisulfite ions are formed, and as sulfate accumulates to phytotoxic levels, then chronic symptoms first appear as various forms of chlorotic (yellowing) patterns. As sulfite and bisulfite ions continue to accumulate, destruction of individual chloroplast membranes or a reduction of chlorophyll production ensues resulting in reddening or bleaching of cells without necrosis (Thomas, 1951). 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 pollutant removal or as a result of changing environmental conditions (Jacobson and Hill, 1970).

Chronic effects of SO_2 in conifers are generally first expressed on older needles (Linzon, 1966). Chlorosis of tissues starting at the tips progresses down the needle towards the base, i.e., symptoms progress from the oldest to youngest tissues. Advanced symptoms may follow, involving reddening of affected tissues (Linzon, 1978).

*

8.2.7 Classification of Plant Sensitivity to SO_2

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

Jacobson and Hill (1970) included a listing of plants sensitive to the major phytotoxic air pollutants. Linzon (1972) has listed 36 tree species as being tolerant, intermediate, and sensitive to SO_2. Many of these sensitivity lists have not attempted to identify the dose required to induce visible injury on indicator species. However, Jones et al. (1974) have published such details based upon observations over a 20-year period of 120 species growing in the vicinity of coal-fired power plants in the southeastern United States (Table 8-2).

McLaughlin (1980) used symptom data as collected by Dreisinger and McGovern (1970) on 31 species of forest and agricultural plants following SO_2 exposure and plotted the average, maximum, and minimum tolerances of individual species (Figure 8-2). The injury threshold for most sensitive plants was 0.41, 0.37, 0.28, and 0.12 ppm SO_2 at averaging intervals of 1, 2, 4, and 8 hours, respectively.

Other compilations have been presented. The report of Davis and Wilhour (1976) provides information on an international basis. Specific reports have been prepared for vegetation native to the southwestern deserts of the United States (Hill et al., 1974).

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 (Gerhold, 1977), and the most recent review of lichen bioindicators was prepared by LeBlanc and Rao (1975).

Other recent reports have been prepared for various ornamentals (Daessler et al., 1972); Heggestad, 1973; Pelz, 1962), bluegrass cultivars (Murray et al., 1975), scotch pine (Demeritt et al., 1971), hybrid poplar (Dochinger and Jensen, 1975), and trembling aspen (Karnosky, 1977). These represent examples of the continued efforts to identify sensitive plants suitable for use as bioindicators.

Other incitants such as drought, nutrient imbalances and other pollutants 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.

*

TABLE 8-2. SULFUR DIOXIDE CONCENTRATIONS CAUSING VISIBLE INJURY TO VARIOUS SENSITIVITY GROUPINGS OF VEGETATION[a] (ppm SO_2)

Maximum average concentration	Sensitivity grouping		
	Sensitive ppm SO_2	Intermediate ppm SO_2	Resistant ppm SO_2
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., 1973.

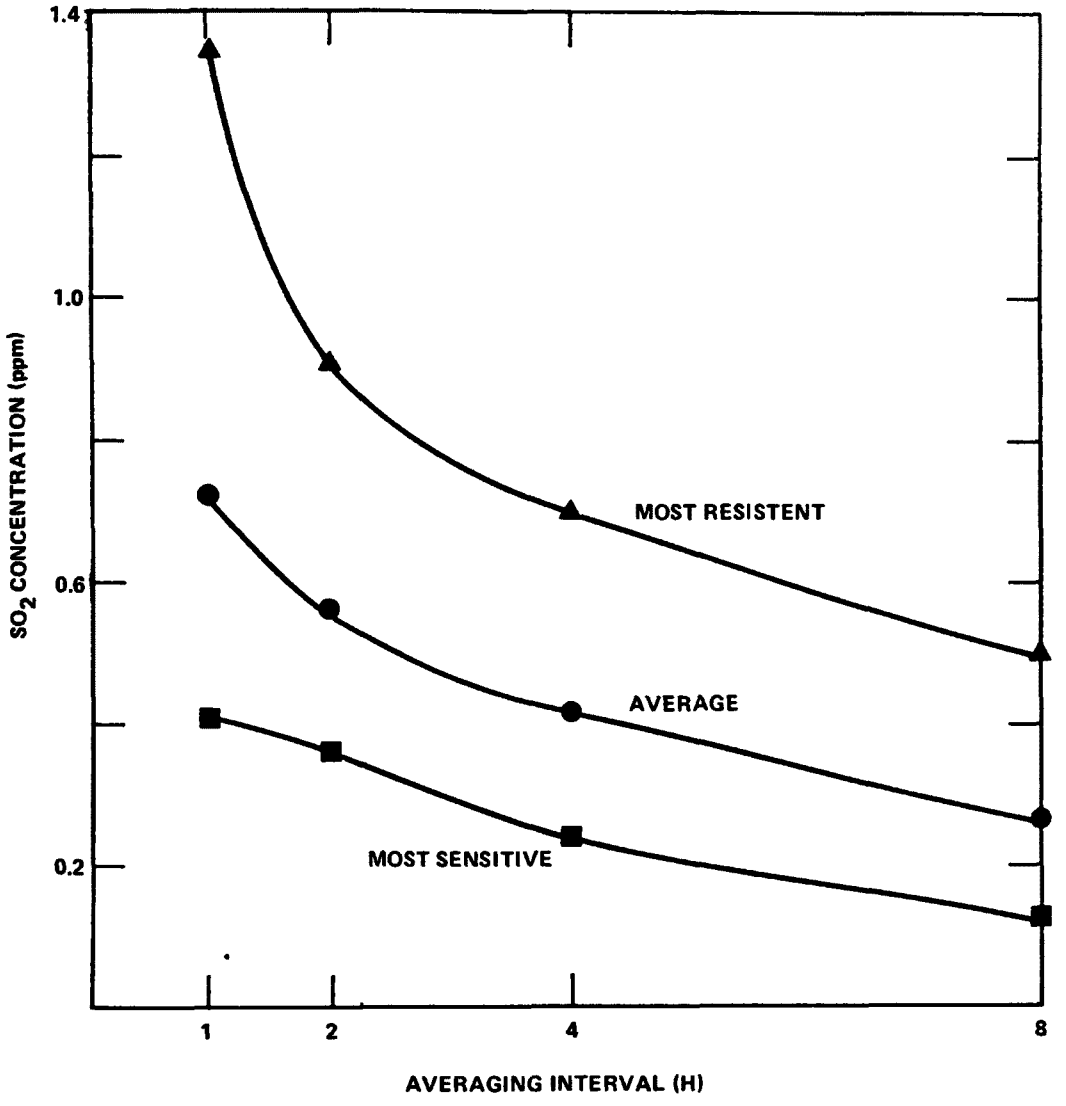


Figure 8-2. Exposure thresholds for minimum, maximum and average sensitivity of 33 plant species to visible foliar injury by SO_2.

Source: Dreisinger and McGovern (1970) as applied by McLaughlin (1980).

*

8.2.8 Beneficial "Fertilizer" Effects

Under certain conditions, atmospheric SO_2 can have beneficial effects to agronomic vegetation (Noggle and Jones, 1979). Sulfur is one of the elements required for plant growth and Coleman (1966) reported that crop deficiencies of S have been occurring with increasing frequency throughout the world. Sulfur requirements to maintain high crop production range from 10 to 40 kg/ha per year. Figure 8-3 presents a map of sulfur deficient soils of the United States (The Sulphur Institute, 1979).

Cowling et al. (1973) 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 (1970) conducted a series of experiments to determine effects of varying atmospheric concentrations of SO_2 on sunflower, corn, and tobacco. In these studies, plants were grown in nutrient media containing adequate supplies of all essential elements except sulfur, which was low. 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 SO_2 added to the atmosphere during plant growth. For tobacco, the total dry weight increased by up to 40 percent. Yields of leaves and stems alone increased by 80 percent while dry weights of tobacco increased even at the highest SO_2 concentration used (0.57 ppm); sunflower and corn had their highest biomass at SO_2 concentrations of 0.40 ppm and 0.20 ppm, respectively. Beyond these concentrations, visible injury was observed. Additional studies by Faller (1970) with ^{35}S suggest that up to 90 percent of plant sulfur requirements may originate from the atmosphere under the specific experimental conditions.

Although no monitoring or handling procedures for SO_2 delivery were presented in a study by Thomas et al. (1943), its results indicated that SO_2 could serve as a required source of nutrient S to alfalfa fumigated with approximately 0.10 ppm SO_2 for 6 to 7 hr/day, 6 days/week for the growing season. An additional caveat for plants being grown under S-deficient soil nutrient status must also be considered for this study.

Recently, Noggle and Jones (1979) reported the results of a 2-year study using potted soil and ^{35}S as S nutrient addendum 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 (1979) also showed that cotton grown in specifically designed growth containers in the vicinity of certain coal-fired power plants accumulated significant amounts of atmospheric sulfur (as SO_2) and produced significantly more biomass than those grown at a location remote to the industrial source of sulfur. Thus, under appropriate conditions,

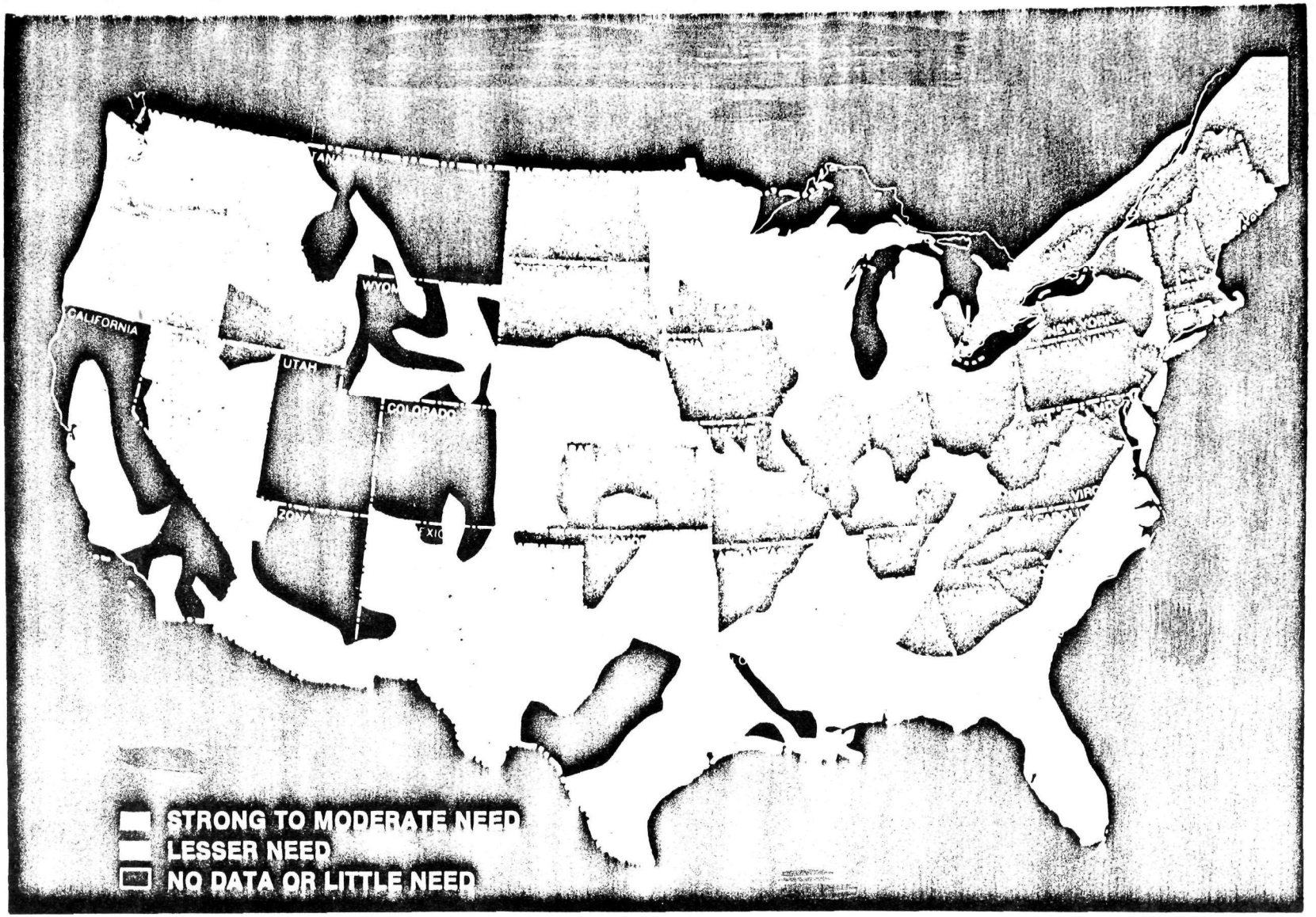


Figure 8-3. Map of the United States indicating major areas of sulfur-deficient soils.

Source: The Sulfur Institute (1979).

*
such as with sulfur-deficient soils, the atmosphere can be an important source of sulfur for plant requirements; however, SO_2 monitoring data were not presented in their study report.

Similar stimulatory responses of Oryzopsis hymenoides (a desert grass) were noted following exposure to SO_2 concentrations of 0.03 and 0.06 ppm continuously for 6 weeks (Ferenbaugh, 1978). The noted increases in productivity expressed as mg dry wt/plant were not statistically different from the control plants, but the trends were stable for these doses. Exposure to 0.13 and 0.25 ppm SO_2 under identical conditions resulted in foliar symptoms and decreased productivity.

The interpretation of studies that have demonstrated beneficial effects must be evaluated in light of their single influence to one crop (as has been done for studies demonstrating detrimental effects). There is little doubt that direct application of S as a nutrient to certain crops grown under borderline or S-deficient conditions, may result in increased productivity for that crop. However, long-term natural ecosystem studies showing similar positive effects for the entire ecosystem have not been accomplished. Since these agronomic and natural ecosystems are often physically proximal to one another, further research on the potential influence of S compounds to each singly and collectively is greatly warranted.

Numerous conditions may actually determine if S delivered to the plant as SO_2 will terminate as a nutrient or pathogenic agent. Those factors discussed in relation to Figure 8-2 will significantly influence the final disposition. Growth rates of leaf tissues, available nutrient supplies, and environmental factors affecting stomatal opening and closing should all be considered as influencing the rate of S accumulation in plant tissues (Bell and Clough, 1973). The addition of nutrient forms of nitrogen being delivered to the plant along with SO_2 in plumes has not been investigated.

Cowling and Lockyer (1976) demonstrated that S 23 ryegrass, when grown under S deficiency and at low nitrogen, did not respond to 0.02 ppm SO_2 for 85 days; however, plants grown at high N under the same exposure conditions responded with a 227 percent yield increase and S-deficiency symptoms were alleviated. Data presented by Cowling and Jones (1971) previously showed that at high levels of N, and inadequate levels of S, nitrate-nitrogen accumulated in ryegrass, thus indicating protein synthesis was inhibited. A review of crop response to sulfur has been published by The Sulphur Institute (1971).

8.2.9 Foliar Versus Whole Plant Responses

The presence of acute or chronic foliar injury is not necessarily associated with growth or yield effects. Furthermore, when present, the degree of foliar injury may not always be a reliable indicator of subsequent growth or yield effects.

A prediction of two-thirds of one percent crop loss for each percent of leaf area destroyed was generated from 30-minute exposures of soybeans (King) in the field to SO_2 concentrations ranging from approximately 0.5 to 6.0 ppm (Davis, 1972b). The exposures were

*
conducted to generate varying amounts of injury. Usually, no injury resulted at concentrations below 0.5 ppm, and all symptomatic tissue (necrosis, chlorosis, bronzing) was estimated. Therefore, all leaves with any degree of symptoms were considered as non-functional in plant productivity as completely destroyed. Soybean (Dare) plants exposed to 0.10 ppm SO_2 6 hr/day for 133 days in closed field chambers failed to exhibit significant yield reductions, even in the presence of foliar injury (Heagle et al., 1974).

Yield effects in the absence of foliar injury have recently been reported for soybean in field fumigations (Sprugel et al., 1980) and chamber exposures (Reinert and Weber, 1980). Sprugel et al. (1980), utilizing the Zonal Air Pollution System, reported significant yield reductions in soybeans (Wells) exposed to mean SO_2 concentrations of 0.09, 0.10, 0.19, 0.25, or 0.36 ppm for an average 4.2 hr/day intermittantly for 18 days during July and August 1978. Visual leaf injury was noted only at the highest SO_2 concentration. It must be noted that the characteristics of the ZAPS allow for significant variation in the pollutant concentrations (although this does relate to ambient conditions near a source). For example, in 1977, within experiments reporting a mean SO_2 concentration of 0.30 ppm, the actual concentration ranged from 0.00 to 1.20 ppm SO_2 (Miller et al, 1980). The greenhouse chamber study by Reinert and Weber (1980) was an O_3+SO_2 interaction study with Dare soybeans exposed 4 hr/day, 3 times per week, for 11 weeks. They reported significant growth reductions in the absence of visible injury for 0.25 ppm SO_2 when the treatment sums of squares were partitioned.

Similar ambiguities are found in some of the literature dealing with grasses. In a preliminary study, S 23 ryegrass exhibited significantly reduced growth when exposed to 0.12 ppm SO_2 for 9 weeks or 0.067 ppm SO_2 for 26 weeks (Bell and Clough, 1973). The only foliar injury noted was a slight chlorosis and an enhanced rate of leaf senescence. Ashenden (1978) noted similar significant growth reductions for cocksfoot when exposed to 0.11 ppm SO_2 for 4 weeks. Reductions ranged from 32 to 52 percent for various parameters while foliar necrosis was only 5 percent. On the other hand, exposure of S 23 ryegrass to 0.02 or 0.14 ppm SO_2 in two successive growth periods of 29 and 22 days resulted in foliar injury at the high concentration, but no yield effects at either concentration (Cowling and Koziol, 1978). Net photosynthesis and dark respiration were also not significantly affected.

Different plant species differ in tolerance to SO_2 injury. Leaf injury and radial growth were evaluated on Douglas fir and ponderosa pine growing in nursery plots exposed to various doese of SO_2 in controlled fumigations (Katz and McCallum, 1952). Slightly injured ponderosa pine (10 percent foliar symptoms) exhibited no significant deviations in growth while slightly injured Douglas fir (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.

*

Increasing SO_2 concentrations have been negatively correlated with annual ring width in Norway spruce (Keller, 1980). Exposures to 0.05, 0.10, and 0.20 ppm SO_2 were continuous for 10 weeks in the spring. Some injury was noted at 0.10 and 0.20 ppm, but a distinct decline of wood production was also found in cases where no visible injury occurred. When dormant seedlings of beech were exposed to the same SO_2 concentrations (0.05, 0.10, and 0.20 ppm) for about 16 weeks, there were adverse effects to the terminal buds (Keller, 1978). There was an increase in the number of terminal buds which failed to "break" in the spring for the 0.10 and 0.20 treatments.

The literature concerning SO_2-induced growth and yield effects and correlations with visible foliar injury is ambiguous. No studies consider all the potential variables that can affect plant response. This is a virtual impossibility for a single study and is especially true for field studies (which are most relevant) where many environmental variables cannot be controlled. Also, many of the studies that have demonstrated negative effects of SO_2 at low concentrations have utilized sensitive cultivars of plant species (which may or may not be representative of plant populations as a whole) and maintained exposure conditions conducive to maximum plant sensitivity. However, from the data available, we can conclude that growth and yield effects are not necessarily related to foliar injury. Depending upon the plant affected, the environmental conditions, and the pollutant exposure conditions, one may observe yield effects without injury, injury without yield effects, or more direct correlations between injury and yield.

8.3 DOSE-RESPONSE RELATIONSHIPS - SO_2

The primary focus of dose-response studies should be to develop useful generalizations of the relationship between meaningful parameters of plant response and measurable indices of exposure dose. This section will examine this relationship both from the perspective of deficiencies in our present knowledge of dose-response relations and from the perspective deficiencies in our present knowledge of dose-response relationships and from the perspective of what generalizations are presently possible with existing data sets.

The dose of SO_2 to which vegetation may be exposed is conventionally designated as the product of concentration in the plant's environment times the duration of exposure. Response may be characterized by a measurable change in any parameter such as biochemical pathways, gas exchange rates, photosynthetic rates, physiological functions, degree of visibly recognizable leaf injury, or subsequent growth and yields. Plant responses may be beneficial (see Section 8.2.8) or detrimental. They may involve the expression of growth and yield effects without foliar symptoms (see Section 8.2.9) or lead to overt symptoms that seldom become more serious than those associated with acute injury (see Section 8.2.5) or chronic injury (Section 8.2.6).

In interpreting dose-response studies wherein a measured plant response is correlated with exposure dose, it is important to realize that the relationship between exposure dose and the amount of pollutant entering the plant may be influenced significantly by environmental

*
factors which control rates of pollutant flux into plant leaves and by plant factors which determine the metabolic fate of the pollutant within leaf tissues (see Figure 8-2).

The role of short-term fluctuations in SO_2 may be particularly significant where impacts of point sources are under study (McLaughlin et al., 1976). Here concentrations may fluctuate widely during exposure and damage to vegetation may be most closely associated with short-term averages (1 hr) or even peak concentrations. Laboratory experiments by Zahn (1961, 1970) have demonstrated the greater relative toxicity of short-term exposures at high concentrations of SO_2 than longer-term exposures with the same total exposure dose. More recently, McLaughlin et al. (1979) studied the effects of varying the peak to mean SO_2 concentration ratio on kidney beans in short-term (3 hr) exposures to SO_2. Working at or below the present National Secondary Air Quality Standard (NSAQS) they found that increasing the peak:mean ratio from 1.0 (steady state exposure at 0.50 ppm for 3 hours) to 2.0 (3 hr exposure with peak = 1.0 ppm) did not alter post fumigation photosynthetic depression. Further increasing the ratio to 6.0 (1 hour exposure with peak = 2.0 ppm), however, tripled the post fumigation photosynthetic depression. Total dose delivered in the three exposures was 1.5, 1.8, and 1.1 ppm, respectively. Clearly the quantity of SO_2 to which the plants are exposed may have a very different effective potential as the kinetics of the exposure are changed.

Another important aspect of exposure dose is the frequency and duration of periods of low SO_2 stress. Zahn (1970) emphasized that periods of low SO_2 concentration may be critical to the recovery potential of plant systems following exposure to elevated levels of SO_2. Thus, continuous exposure systems probably over-estimate the toxicity of the delivery dose in many cases because physiological recovery is not permitted. Such recovery would be expected under most exposure regimes in the field where fluctuating synoptic or local meteorological conditions strongly influence exposure patterns.

Equally critical to definition of the biological significant features of exposure regimes is the definition of significant parameters of plant response. Sections 8.2.1 through 8.2.9 have emphasized the many types of responses which may be elicited by exposure to SO_2. In interpreting or predicting plant response to SO_2, it is important to keep in perspective the fact that plant growth and development represents an integration of cellular and biochemical processes just as community behavior is an integration of the performance of component species. The internal allocation of resources (carbon, water, and nutrients) to growth is an integrative and in many cases resilient process which plays a major role in determining how both individual plants and plant communities respond to environmental stress (McLaughlin and Shriner, 1980); (see also Section 8.10). The fact that a response is measured following exposure to a given dose of SO_2 may be of interest in understanding the mechanism of action and in identifying the biologically significant features of dose; however, it does not necessarily mean that an effect will be measured at a subsequent higher level of organization. Responses at higher levels of organization, however, must be viewed within the perspective of the increasingly complex biotic and

*
abiotic factors which control plant response (see Section 8.5) and influence our attempts to move the focus of our studies from processes to plants and from plants to communities. These factors similarly limit our capacity to easily extend experimental protocols beyond the confines of our carefully controlled laboratory studies to more natural, and more variable, field situations.

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, 1922; Thomas and Hill, 1935; Zahn, 1963a,b,). However, their consistency and usefulness are limited due to numerous physical and biotic factors which must be considered in evaluating dose-response data. Changes in exposure conditions, differences in exposure methodology and efficiency of monitoring equipment, ad consistency of measurements within a study and between studies on the same plant will directly influence results (Figure 8-4).

According to Larsen and Heck (1976), (1) a constant percentage of leaf surface will be injured by an air pollutant concentration that is inversely proportional to 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:

$$c = m_{g\ 1\ hr} s_g^{z} t^{p}$$

where

c = the SO_2 concentration in ppm

$m_{g\ 1\ hr}$ = the geometric mean concentration, the concentration that injures 50 percent of the leaf surface after a 1-hr exposure

s_g = the standard geometric deviation, ratio of the concentration that injures 50 percent of the leaf surface to the concentration that injures (16 percent)

z = the number of standard deviations the percent leaf injury is from the median (50 percent)

t = the exposure duration in hr

p = the slope of the percent leaf injury isopleths on logarithmic graph paper.

Parameters for the above equation have been determined from leaf injury observations on four tree species. The concentration expected to cause threshold (1) leaf injury in Norway maple exposed to SO_2 for 8 hr is determined by substituting its parameters into the above equation:

$$c = 6.76(1.29)^{-2.33_8}{}^{-0.38}$$
$$c = 1.7 \text{ ppm}$$

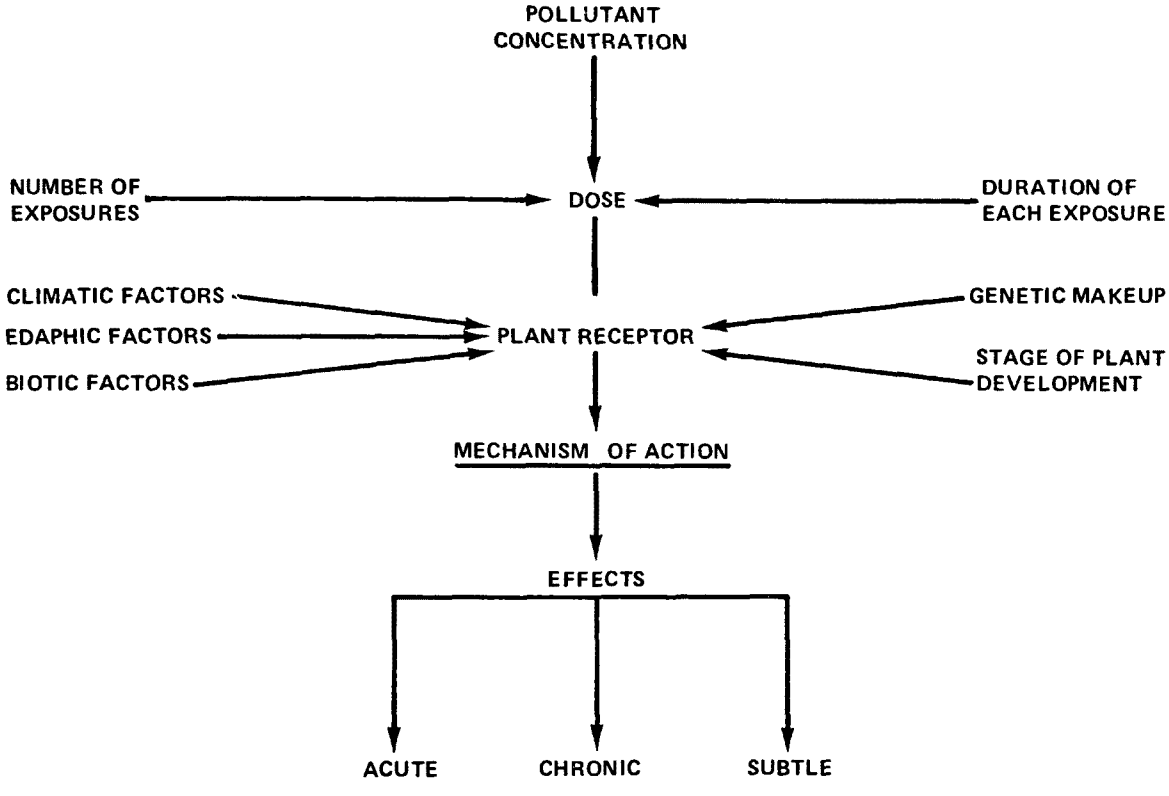


Figure 8-4. Conceptual model of the factors involved in air pollution effects (dose-response) on vegetation.

Source: Heck and Brandt, 1977.

*

Similar calculations indicate that threshold injury is expected after an 8-hr exposure to 2.2 ppm for ginkgo and 3.7 ppm for pin oak. The injury data are too far from threshold to calculate an accurate threshold for the fourth tree species, Chinese elm.

As discussed in preceding sections, plant response to SO_2 may occur at many levels. For purposes of air quality control, however, two parameters, visible damage to foliage, and plant productivity, provide the most functional basis for evaluating response. Both can be quantified as a "cost" to economic or ecological performance of many plant species.

Dose-response relationships involving visible injury may be expressed in terms of the level of injury (percent leaf area destroyed) produced for a single species, or as the upper and lower limits of sensitivity of a group of species. The latter approach is presented here because it provides data more applicable to responses of plant populations and because of the difficulties in quantifying a dependable relationship between degree of visible injury and growth responses (see Section 8.2.7). Data on generalized concentrations at which sensitive, intermediate, and resistant species may be injured by SO_2 were presented earlier in Table 8-2. In Figure 8-2 (Section 8.2.7) the data of Dreisinger and McGovern (1970) were graphed to show upper and lower concentration limits of susceptibility of 31 species of herbs, trees, and shrubs to visible foliar injury. Plotted as a function of SO_2 concentration and exposure time, these data demonstrate a number of important points: first, the most sensitive plants at each concentration were injured at SO_2 levels 6 to 7 times lower than the most resistant plants. Secondly, the dose (ppm x h) required to cause injury was 30 to 60 percent lower for 1-hr than 8-hr exposures, emphasizing the importance of exposure kinetics. Finally, exposure to SO_2 at 0.5 ppm for 3 hr represents a rather close estimate of the injury threshold for "average" plants.

A second approach to defining dose-response relations focuses on the numbers of individuals in a plant population which may be injured as function of exposure concentration. As an example of a "worst-case" situation of SO_2 exposures and vegetation effects near a rural coal-fired power plant, TVA's Widows Creek Plant in northern Alabama provides some interesting data (McLaughlin and Lee, 1974). During the period 1970-1973 (before partial sulfur scrubbing and stack elevation by TVA improved surrounding air quality), surveys of vegetation in the vicinity of this plant documented foliar injury to 84 plant species growing in the vicinity of continuous SO_2 monitoring stations. Tabulation of these data (Figure 8-5) as a function of exposure concentration provides an index of probability of injury of species in a plant community as a function of SO_2 concentration. If one arbitrarily sets a limit of acceptable risk as 10 percent of the plant population (here 8 of 84 species), then peak, 1-hr, and 3-hr concentrations of (1.00, $\leq$ 0.50, and $\leq$ 0.30 ppm should be avoided. At the present National Secondary Ambient Air Quality Standard (3 hr at 0.5 ppm), approximately 30 percent of the species present sustained foliar injury. This form of data representation allows intercomparisons between short-term concentrations and risk of foliar injury to be readily made.

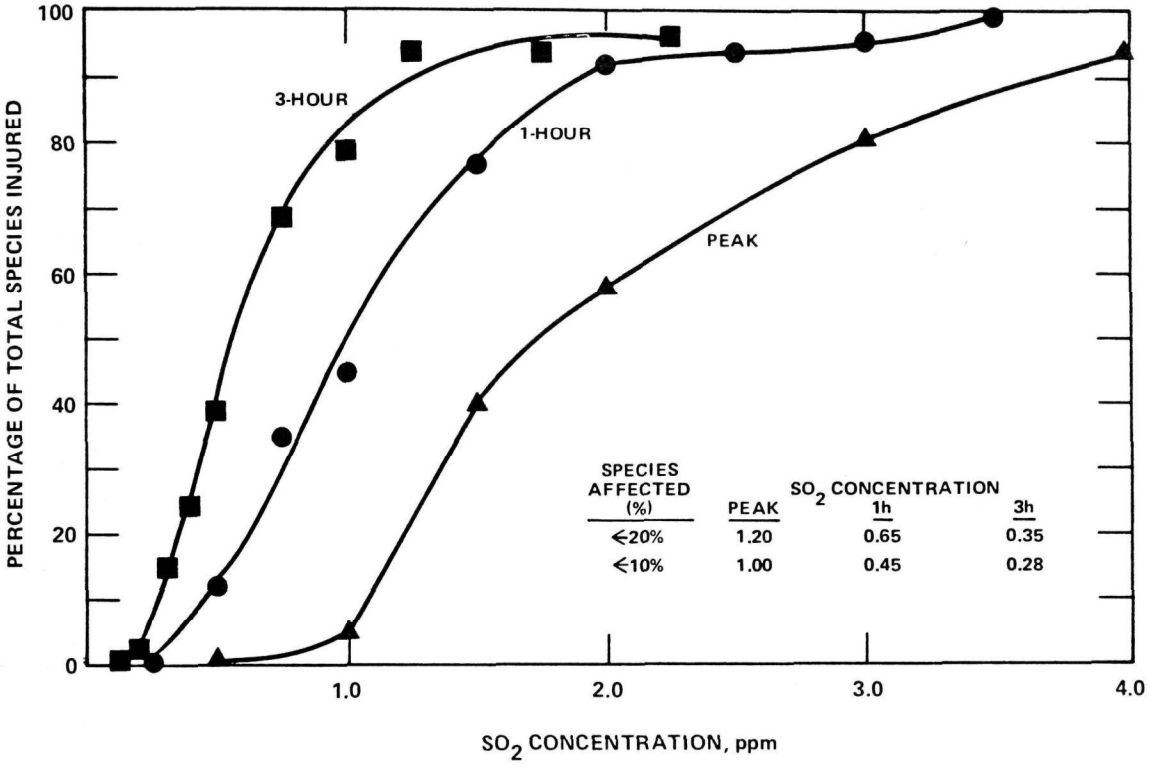


Figure 8-5. Percentage of plant species visibly injured as a function of peak, 1h and 3h SO_2 concentrations.

Source: McLaughlin and Lee, 1974.

*

Data on SO_2 effects of plant growth and yield in most cases provide the most relevant basis for studing dose-response relationships. As a whole-plant measurement, plant productivity is an integrative parameter which considers the net effect of multiple-factors over time. Productivity data are presently available for a wide range of species under a broad range of experimental conditions. Because results would not be expected to be closely comparable across these sometimes divergent experimental techniques, data have been tabulated separately for controlled field exposures (Table 8-3), laboratory studies with agronomic and horticultural crops (Table 8-4) and tree species (Tables 8-5 and 8-6), and a variety of studies with native plants (Table 8-7).

Relatively few crops of economic importance have been studied under field conditions utilizing various field exposure systems. Of the twelve "studies" reviewed in Table 8-3, seven reported induced yield effects following SO_2 exposures at varying doses. The lowest dose exposure to induce a yield effect was 0.09 ppm SO_2 for 4.2-hr average fumigation period on 18 days scattered from July 19 through August 27 of the soybean growing season (Sprugel et al., 1980). Five studies indicated no effect following various exposure regimes, and one study (Neely and Wilhour, 1981) reported increased yields (27 percent and 8 percent) of winter wheat cs. Yamhill following exposure dose of 0.03 and 0.06 ppm SO_2 for 24 hr/day for 30 days, respectively.

Table 8-4 presents a summary of studies that have investigated effects of SO_2 on agronomic and horticultural crops grown and fumigated within artificial exposure chamber or growth chamber systems. It is difficult to determine the significance of the results of such studies in relation to actual similar fumigations under field conditions. Additionally, with the exception of a relatively few studies, doses used for exposure treatments would be considered as in excess of expected doses for ambient field exposures. As indicated in Table 8-4, acute foliar effects have not been reported in long-term studies using less than 0.15 ppm SO_2 for 24 hr/day for 7 days (Mandl et al., 1975).

A few major investigations of the effects of SO_2 on tree species growing under natural conditions have been reported (Linzon, 1971, 1980; Dreisinger, 1965; Dreisinger and McGovern, 1970; Materna et al., 1969; and Vins and Mrkva, 1973). Table 8-5 illustrates the degree of injury to eastern white pines (Pinus strobus) over a 10-year period (1953-1963) in the sulfur fume effects area near Sudbury, Ontario, CAN. (Linzon, 1971). Linzon (1971, 1978) has indicated that a pollution (SO_2) gradient existed within the designated study area and effects correlated well with this gradient. Chronic effects on forest growth were prominent where SO_2 air concentrations averaged annually 0.017 ppm SO_2, and such effects were not reported in areas receiving 0.008 ppm SO_2 annually. Although monitoring of SO_2 was conducted in these studies, other air pollutants nor their potential effects were evaluated.

The studies of Vins and Mrkva (1973) and Materna et al. (1969), although reporting foliar and growth increment losses to forest trees as being due to SO_2, were done in areas

TABLE 8-3. SUMMARY OF STUDIES REPORTING RESULTS OF SO_2 EXPOSURES USING EXPOSURE SYSTEMS AND/OR CHAMBERS OVER PLANTS UNDER FIELD CONDITIONS

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
0.04	3 hr for 8 exp. growing season	F/CC	Wheat			No effect on apparent photosynthesis, no effect on the avg. heat length or # of gains/head.		Sij et al., 1974
0.02 0.05 0.10 Geom. means 0.022; 0.038; 0.068, respectively	Growing season	F-ZAP	Western wheat grass, Prairie June grass			S content > with > SO_2 conc.; digestibility dry matter was < by 2 years of treatment; crude protein content in w. wheat < significantly.		Preston and Lewis, 1978
0.03-0.10	72 hr/wk for growing season	F/CC	Barley Durum wheat Spring wheat			No effect on yield		Wilhour, 1980
0.03- 0.06 0.10 0.15 0.20	24 hr/day for 30 days	F/CC	Winter wheat cv. Yamhill		X X X X X	27% > yield grain wt. 8% > yield grain wt. 17% < yield grain wt. 17% < yield grain wt. 70% < yield grain wt.		Neely and Wilhour, 1981
0.03 0.06 0.10 0.15 0.20	24 hr/day for 30 days	F/CC	cv. Hyslop		X X X X X	No effect 22% < yield grain wt. 36% < yield grain wt. 27% < yield grain wt. 56% < yield grain wt.		
0.06	68 days	F/CC	Alfalfa		X	28% < foliage stubble, 45% < root dry wt.; 21% < total protein, amino acids, nonstructured carbohydrates, and symptiotically fixed nitrogen content.	Potted plants set on soil surface, grown hydropinically	Neely et al., 1977
0.09 0.10 0.19 0.25 0.36	Mean conc. 4.2h/18 fumigations 19 July-27 August	Z-ZAP	Soybean	X X X X X	X X X X X	6.4% yield reduction 5.2% yield reduction 12.2% yield reduction 19.2% yield reduction 15.9 % yield reduction	Sd of fumigation conc. ranged 44-45% of x. Sg=standard geometric deviation	Sprugel et al., 1980 and Miller et al.,. 1980
0.10	6 hr/day 43 days 92 days 133 days	F/OT	Soybean		X	No significant effect on foliar injury, fresh wt. seeds/plant or wt. of seeds/plant 92nd day defoliation was 12% > control; 135th day seed wt. only 1% < control.		Heagle et al., 1974
0.12 0.30 0.79	Mean conc. 4.7hr/24 fumigations 13 July to 29 August	F-ZAP	Soybean	X X X	X X X	12.3% yield reduction 20.5% yield reduction 45.3% yield reduction	Sd of fumigation conc. ranged 41-64% of x Sg=standard geometric deviation	Sprugel et al., 1980 and Miller et al., 1980

TABLE 8-3 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
0.15 0.40	72 hr/wk for growing season	F/CC	Barley Durum wheat Spring wheat		X X	44% < yield in Barley 42% < yield in Durum wheat No effect on Spring wheat		Wilhour, 1981
0.25 0.40 0.80 1.20	Once every week (3hr) to once in 5 wks (3hr)	F/CC	Alfalfa Barley Durum wheat Spring wheat			*No effect on yield*		Wilhour, 1981
0.45	3 hr for 7 exp. growing season	F/CC	Wheat			No accumulative effect on yield, no effect on avg. head length or # grains/head		Sij et al., 1974
0.80- 2.00	4 hr 20 min	F-ZAP	Soybean 	 X	X X X 	4.5% < yield at 1.4 ppm 11% < yield at 1.7 ppm 15% < yield at 2.0 ppm Epidermal and mesophyll cell death; the # of dead mesophyll cells highly correlated with > SO_2	Pollutant avg.; no est. on range of exposure doses	Miller et al., 1979 Irving et al., 1979

[a] Table arranged by > 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/CC = field, closed chambers; F/OT = field, open top chambers, F-ZAP = field, zonal air pollution system.
[c] X indicates study found boliage and/or yield effects.
[d] Most prominent or significant effect reported.
[e] Caveats for consideration about proper study design and interpretations.

TABLE 8-4. SUMMARY OF STUDIES REPORTING RESULTS OF SO_2 EXPOSURE UNDER LABORATORY CONDITIONS FOR AGRONOMIC AND HORTICULTURAL CROPS

Conc. ppm	Exposure Time	Exposure Condition	Plant	Effects on[c] Foliage Yield	Species effect[d]	Caveat	Reference
0.035 0.175	8 hours	EC/SD	Broadbean		Depressed net photosynthesis		Black and Unsworth, 1979
0.05	5h/d; 5d/wk for 4 wk	EC/SD	Alfalfa	X	26% < in foliage dry wt. at final harvest		Tingey and Reinert, 1975
				X	49% < of root dry wt. at final harvest		
			Tobacco, Bel W3	X	22% < of leaf dry wt. at final harvest	Sensitive plant	
			Tobacco, Burley 21		No effect		
0.05 0.10 0.25	4 hour	EC/SD	Oats Radish Soybean Tobacco		No foliar injury		Tingey et al., 1971a
0.05 0.20	8hr/day 5 days/wk for 18 days	EC/SD	Soybean		No effect on top fresh or dry wt., root fresh or dry wt.; plant height, shoot/root fresh or dry wt. ratio		Tingey et al., 1973b
0.06- 0.08	103.5hr/wk for 20 wks	GC	Cocksfoot	X	40% < total dry wt.		Ashenden, 1979
			Meadowgrass	X	28% < total dry wt.		
0.07- 0.53	24hr/day 9-20 days	GC	Tobacco	X	Increased dry wt. yield up to 0.53 ppm (44% > control)	No monitoring methods presented; Low S in soil medium	Faller, 1970
			Sunflower	X	Greatest dry wt. yield at 0.35 ppm (44% > control); 27% increased yield over control at 0.53 ppm		
			Corn	X	Greatest dry wt. yield at 0.17 ppm (24% > control) 7% increased yield over control at 0.53 ppm		
0.10	18 days	GC	Pea	X	3% < fresh wt. shoot 5% < dry wt. shoot 4% < total nitrogen 30% < H^+ (buffer capacity) 10% > glutamate dehydrogenase activity 110% > inorganic sulfur content		Jager and Klein, 1977
0.11	24hr/day 4 wks	GC	Italian ryegrass	X	No difference from control at low wind; 17%-40% < total dry wt. high wind		Ashenden and Mansfield, 1977
0.125-	1-3 hours	EC/SD	Oats Radish Sweet pea Swiss chard		No foliar injury at concentrations < 0.50 ppm 2% maximum foliar injury experienced at all doses.		Bennett et al., 1975
0.15	18 days	GC	Pea	X	3% < fresh wt. of shoot 8% < dry wt. of shoot 2% < total nitrogen 35% < H^+ (buffer capacity) 32% > glutamate dehydrogenase activity 140% > inorganic sulfur content	Water Culture	Jager and Klein, 1977

TABLE 8-4 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat	Reference
0.15-0.30	24 h/day 7 days	EC/SD	Barley Bean Corn	X X X		Severe foliar injury No injury Severe foliar injury		Mandl et al., 1975
0.17	2 hour	EC/SD	Broadbean			< photosynthetic rate, < stomatal resistance if RH > 40%, > stomatal resistance if RH < 40%		Black and Unsworth, 1979
0.20-0.30	2 hour	GC	Alfalfa Barley			Threshold dose for inhibition of photosynthesis, reversible effect		Bennett and Hill, 1973
0.20	30, 78, 100 hours	EC/SD	Wheat	X	X	Trend of increased dry wt. for 19 or 21 exposures; small amount foliar injury	Trend, not significant from control	Laurence, 1979
0.20	15 days	GC	Tomato	X		Treshold dose for initial symptom of tissue death, < or change vitamin B_1, B_6, and nicotinic acid content		Unzicker et al., 1975
0.20	Continuous to maturation	EC/SD	Kidney bean		X	< 15% of total yield; no change in protein content		Berigari et al., 1974
0.25	4 hours	EC/SD	Broccoli Tobacco, Bel B Alfalfa Onion Soybean Lima bean Bromegrass Cabbage Radish Spinach Tomato	X X		6% leaf injury 1% leaf injury No effects No effects No effects No effects No effects No effects No effects No effects No effects		Tingey et al., 1973a
0.25	18 days	GC	Pea		X	32% < fresh wt. of shoot 26% < dry wt. of shoot 24% < total nitrogen 42% < H^+ (buffer capacity) 80% > glutamate dehydrogenas activity 150% > inorganic sulfur content	Water Culture	Jager and Klein, 1977
0.25	4 hr 3 times/wk 11 weeks	EC/SD	Soybean		X	No foliar injury; significant < in plant ht. at 5,7,9,11 wks; significant shoot dry wt. < at 7,11 wks; significant root dry wt. < at 9,11 wks; significant total dry wt. < at 11 wks		Reinert and Weber, 1980

TABLE 8-4 (continued)

Conc. ppm	Exposure Time	Exposure Condition	Plant	Effects on[c] Foliage	Yield	Species effect[d]	Caveat	Reference
0.30	5hr/day 6day/wk 12 days	EC/SD	Barley	X	X	11% foliar injury; 38% < dry wt. shoot	Montoring system explained in unavailable publication	Markowski et al., 1975
			Bean	X	X	<1% foliar injury; 25% < dry wt. shoot		
			Sunflower	X	X	5% foliar injury; 41% < dry wt. shoot		
	26 days		Barley	X	X	21% foliar injury; 25% < dry wt. shoot		
			Bean	X	X	2% foliar injury; 15% < dry wt. shoot		
			Sunflower	X	X	16% foliar injury; 29% < dry wt. shoot		
0.35	1 hour	EC/SD	Alfalfa			8% < in apparent photosynthesis		White et al., 1974
0.40 0.50 0.60	4 hours	EC/SD	Tomato			> accumulation total and soluble S content		Bennett and Hill, 1973
0.40	6 hours	EC/SD	Apples	X		2% leaf injury		Kender and Spierings, 1975
1.00	2 hours	GC	Barley	X		Threshold dose for foliar necrosis; 30-60% < net photosynthesis		Bennett and Hill, 1973a
1.00	3 hours	GC	Poinsettia 8cv's	X		Foliar injury 1 cultivar		Heggestad et al., 1973
1.00	2 hours	EC	Begonia			No effect		Adedipe et al., 1972
			Petunia		X	30% < flower #'s; 19% < shoot wt.		
			Coleus		X	27% < flower #'s; 19% < shoot wt.		
			Snapdragon		X	14% < flower #'s; 16% < shoot wt.		
1.00	4 hours	EC/SD	Broccoli	X		38% leaf injury		Tingey et al., 1973a
			Bromegrass	X		65% leaf injury		
			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		
1.00	6 hr/day for 3 days	EC/SD	Strawberry	X		No effect on growth and development; necrotic lesions, lower leaf surface		Rajput et al., 1977
1.00	1.5 hour	EC/SD	Soybean	X	X	9% < shoot fresh wt., 4% leaf injury	Short-term growth response only	Heagle and Johnston, 1979
	3 hours				X	21-29% < shoot fresh wt.		
1.50	.75-3 hours	EC/SD	Soybean	X	X	24-94% < shoot fresh wt., 63-93% foliar injury	Short-term response only	Heagle and Johnston, 1979
1.50	3 hours	EC/SD	Alfalfa	X		Leaf necrosis at 315 ppm CO_2 was 2.5x that induced under 645 ppm CO_2		Hou et al., 1977
2.00	2 hours	EC	Begonia		X	14% < flower #'s; 22% < shoot wt.		Adedpie et al., 1972
			Petunia		X	32% < flower #'s; 24% < shoot wt.		
			Coleus		X	30% < flower #'s; 20% < shoot wt.		
			Snapdragon		X	15% < flower #'s; 15% < shoot wt.		

TABLE 8-4 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat	Reference
2.00	3 hours	GC	Poinsettia 8cv's	X		Foliar injury, 2 cultivars		Heggestad et al., 1973
2.50	6 hours	EC/SD	Apples	X	X	> foliar injury; 62% > leaf abscission; 19% < shoot growth		Kender and Spierings, 1975
3.00	1 hour	GC	Poinsettia 8cv's	X		Foliar injury, 5 cultivars		Heggestad et al., 1973
	2 hour	GC	Poinsettia 9cv's	X		Foliar injury, 7 cultivars		
	3 hour	GC	Poinsettia 8cv's	X		Foliar injury, 8 cultivars		
4.00	2 hour	EC	Begonia	X	X	27% < flower #'s; 33% < shoot wt.; severe necrosis		Adedipe et al., 1972
			Petunia	X	X	42% < flower #'s; 32% < shoot wt.; slight injury		
			Coleus		X	30% < flower #'s; 21% < shoot wt.; no foliar injury		
			Snapdragon	X		20% < flower #'s; 19% < shoot wt.; slight injury		
			Marigolds	X		Slight injury		
			Celosia, Salvia	X		Slight injury		
			Impatiens	X		Slight injury		
0.40	30, 78, 100 hours	EC/SD	Wheat 7cv's	X		No effect on yield, small amount foliar injury		Laurence, 1979
0.50	1.5 hour	EC/SD	Soybean	X	X	7% < in short fresh wt., trace foliar injury	Short-term growth response only	Heagle and Johnston, 1979
0.50	100 hours	EC/SD	Corn			Minimal foliar injury, no effect on dry mass		Laurence, 1979
0.60	6 hours	EC/SD	Apples	X		7.3% > foliage injury; 5% > leaf abscission		Kender and Spierings, 1975
0.60	30, 78, 100 hours	EC/SD	Wheat 7cv's	X	X	Trend of decreased dry wt. in 17 or the 21 exposures, small amount of foliar injury	Trend not significant from control	Laurence, 1979
0.75	3 hour	EC/SD	Alfalfa	X		No injury developed		Hou et al., 1977
0.80	2 hour	GC	Alfalfa	X		Threshold dose for foliar necrosis; 25-50% < in net photosynthesis		Bennett and Hill, 1973

[a] Table arranged by > SO_2 concentration as first order and exposure time as second order division. 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] GC = Growth chambers, EC = Exposure chambers, EC/SD = Exposure chamber, special design.
[c] X indicates study found foliage and/or yield effects.
[d] Most prominent or significant effect reported.
[e] Caveats for consideration about proper study design and interpretation.

TABLE 8-5. THE DEGREE OF INJURY OF EASTERN WHITE PINE OBSERVED AT VARIOUS DISTANCES FROM THE SUDBURY SMELTERS FOR 1953-63

Forest Sampling Station[a] (Distance and Direction from Sudbury)	Trees with Current Year's Foliage Injured in August 1963 (%)	Trees with 1-Year-Old (1962) Foliage Injured		Trees with 2-Year Old Foliage		Net Annual Average Gain or Loss in Total Volume, 1953-1963 (%)	Annual Average Mortality 1953-1963 (%)	Degree of SO_2 Damage	Average SO_2 Concentration for Total Measurement Period 1954-1963[b] (ppm)
		June 1963 (%)	August 1963 (%)	Injured in June 1963 (%)	Lacking in August 1963 (%)				
West Bay (19 miles NE)	2.0	38.0	77.9	96.0	20.6	-1.3	2.6	Acute and chronic injury	0.045
Portage Bay (25 miles NE)	1.1	21.5	55.6	77.0	15.2	-0.5	2.5	Mostly chronic and little acute injury	0.017
Grassy to Emerald Lake (40-43 miles NE)	0.4	2.5	16.7	37.5	9.1	+1.8	1.4	Very little chronic injury	0.008
Lake Matinenda (93 miles W)	0.6	0.3	2.1	10.1	3.9	+2.1	0.5	Control: no SO_2 injury	0.001[c] (Sturgeon Falls)
Correlation Coefficient (r)	0.96*	0.96*	0.93**	0.90**	0.94**	0.90**	0.81		

[a] Linzon (1971)
[b] Dreisinger (1965)
[c] Data for 5-month growing season-1971
*$p < 0.05$
**$p < 0.10$

TABLE 8-6. SUMMARY OF STUDIES REPORTING RESULTS OF SO_2 EXPOSURE UNDER LABORATORY CONDITIONS FOR VARIOUS TREE SPECIES

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
0.025	6 hour	EC/SD	E. white pine	X		Threshold dose for needle damage; most sensitive clones only		Houston, 1974
0.05-0.15	6 hour	EC/SD	E. white pine	X		60% of tolerant clones developed foliar injury	Sensitive clones	Houston, 1974
0.05	16 weeks Winter	EC/SD	Beech			Number of dead buds in Spring > at 0.10 ppm and higher; 50% > kill at 0.20.		Keller, 1978
0.05	10 weeks	EC/SD	Norway spruce	X	X	No foliar effect 25% < vol. growth (Avg.)	2 cones only	Keller, 1980
0.10				X	X	Foliar injury 38% < vol. growth (Avg.)		
0.20				X	X	Foliar injury 53% < vol. growth (Avg.)		
0.18-0.20	24 hour	EC/SD	Jack pine			Inhibit foliar lipid synthesis, inhibition reversible; > dose = > recovery time		Malhotra and Kahn, 1978
0.25	2 hour	EC/SD	E. white pine	X		6.5% foliar injury	Plants maintained in sensitive condition	Berry, 1971
			Jack pine	X		4.5% foliar injury		
			Red pine	X		0.5% foliar injury		
0.25	2 hour	EC/SD	Loblolly pine	X		All equally sensitive; most sensitive period 8-10 weeks of age or older	Plants maintained in sensitive condition	Berry, 1974
			Shortleaf pine	X				
			Slash pine	X				
			Virginia pine	X				
0.35	3 hour	EC/SD	Trembling aspen	X		2% foliar injury		Karnosky, 1976
0.45	6 hour	EC/SD	E. white pine	X		All tolerant clones developed foliar injury		Houston, 1974
0.45	9 hr/day for 8 wks	EC	Ponderosa pine	X		Severe needle tip chlorosis and necrosis		Evans and Miller, 1975
0.50	2 hour	EC/SD	E. white pine	X		12% foliar injury		Berry, 1972
			Jack pine	X		11% foliar injury		
			Red pine	X		2% foliar injury		
0.50	3 hour	EC/SD	Trembling aspen	X		11% foliar injury		Karnosky, 1976
0.50	5 hour	GC	Austrian pine	X		No injury		Smith and Davis, 1978
			Ponderosa pine					
			Scotch pine					
			Balsam, Fraser fir					
			White fir					
			Blue, white spruce					
			Douglas fir					
0.50	24 hr/day up to 30 day	GC	Chinese elm	X		7 days to chlorosis		Temple, 1972
			Gingko	X		14 days to chlorosis		
			Norway maple	X		12 days to chlorosis		
			Pin oak	X		30 days to chlorosis		

TABLE 8-6 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
0.50	24 hr/day 1/wk	EC/SC	Sugar maple Black oak White ash			48% < rate of photosynthesis, no symptoms 54% < rate of photosynthesis, no symptoms 20% < rate of photosynthesis, no symptoms		Carlson, 1979
0.50	24 hr/day	EC/SD	Sugar maple Black oak White ash			74% < rate of photosynthesis, no symptoms 33% < rate of photosynthesis, no symptoms 7% < rate of photosynthesis, no symptoms		Carlson, 1979
0.65	3 hour	EC/SD	Trembling aspen	X		23% foliar injury		Karnosky, 1976
1.00	4 hour	GC	Austrian pine Ponderosa pine Scotch pine Balsam, fraser fir White fir Blue, white spruce Douglas fir	X		Less than 4% foliar injury all species		Smith and Davis, 1978
1.00	8 hour	EC	American elm			Inhibition of stomatal closing		Noland and Kozlowski, 1979
1.0	1 hour 3 hour 5 hour	EC	Scots pine	X X X		No injury, primary needles; slight injury, secondary needles 14% maximum injury primary needles; 52% maximum injury secondary needles 37% maximum injury primary needles, 60% maximum injury secondary needles		Smith and Davis, 1977
2.00	2 hour	GC	Austrian pine Ponderosa pine Scotch pine Balsam, fraser fir White fir Blue, white spruce Douglas fir	X		No foliar injury on Douglas fir, firs, spruce Pine foliar injury threshold, necrotic tips		Smith and Davis, 1978
2.00	6 hour	GC	American elm	X	X	Induce severe foliar injury; defoliation in older leaves; significant reduced expansion of new leaves; # of emerging leaves and root dry wt. reduced		Constantinidou and Kozlowski, 1979a
2.00	6 hour	GC	American elm			No significant reduction in lipid content; significant < in new leaf protein content; significant < leaf, stem root carbohydrate content		Constantinidou and Kozlowski, 1979b
2.00	6 hour	GC	Chinese elm	X		100% leaf necrosis		Temple, 1972
2.00	6.5 hour	EC	Gingko			Water stressed plant > uptake of SO_2		Noland and Kozlowski, 1979

TABLE 8-6 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
2.00	12 hour	GC	American elm			Induced stomatal closing; S content > in plants fumigated in light		Temple, 1972
3.00	6 hour	GC	Gingko Norway maple	X		50% leaf necrosis		Temple, 1972

[a]Table arranged by 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 effects.

[b]GC = growth chambers, EC = exposure chambers, EC/SD = exposure chamber, special design.

[c]X indicates study found foliar and/or yield effects.

[d]Most prominent or significant effect reported.

[e]Caveats for consideration about proper study design and interpretation.

TABLE 8-7. DOSE-RESPONSE INFORMATION SUMMARIZED FROM LITERATURE PERTAINING TO NATIVE PLANTS AS RELATED TO FOLIAR, YIELD AND SPECIFIC EFFECTS BY INCREASING SO_2 DOSE

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat	Reference
0.024	85 days	EC/SD	S23 Ryegrass		X	Plants at high nitrogen, SO_2 exp. allev. S deficiency of plants not provided SO_4 227% > in yield. No effect on plants grown with adequate SO_4		Cowling and Lockyer, 1978
					X	Plants at low nitrogen, no effect of SO_4 or SO_2		
0.02	29 days and 22 days later	EC/SD	S23 Ryegrass		X	No significant effects at 0.02 or 0.14 at first harvest (29 days);		Cowling and Koziol, 1978
0.14					X	at 0.14, significant reduction (16%) in specific leaf area at second harvest (22 days later). No significant effect on dry wt., tillers, dark respiration or transpiration coef.		
0.03	6 week	EC/SD	Indian ricegrass		X	Non-significant increase in productivity (19%);		Ferenbaugh, 1978
0.06						Non-significant increase in productivity (21%); significant decrease in chlorophyll content (43%)		
0.067	26 week	EC/SD	S23 ryegrass		X	Significant increase in number (88%) abd dry wt. (78%) of dead leaves; significant decrease in number of tillers (41%); leaf area (51%), dry wt. of stubble (55%), and number (45%) and dry wt. (51%) of living leaves; significant decrease in yield (52%)	Preliminary study mean weekly conc. wintertime exposure	Bell and Clough, 1973
			Wild ryegrass		X	None		
0.08	13 hr/day for 28 days	EC	Foxtail grass	X	X	Foliar injury as caused by heavy metals was increased by SO_2 exposure; yield not significantly affected	No technical SO_2 monitoring information	Krause and Kaiser, 1977
0.11	4 week	EC/SD	Cocksfoot	X	X	5% foliar necrosis; significant (30%) decrease in leaf area, dry wt. (45%), tillers, green leaves, and root/shoot ratios	Wind tunnel exposures	Ashenden, 1978
0.11	4 week	EC/SC	Ryegrass		X	Significant (20%) decease in leaf area, dry wt. (40%), root/shoot ratio at a wind speed of 25m min^{-1} (.93mph) No effect at a wind speed of 10m min^{-1} (.37mph)	Wind tunnel exposures	Ashenden and Mansfield, 1977
0.11 (weekly mean 0.067)	103.5 hr/wk for 20 wk	EC/SD	Smooth-stalked meadowgrass		X	Significant decrease in leaf area (28%), all dry wt. fractions (44%), leaves (37%), and tillers (27%)		Ashenden, 1978

TABLE 8-7 (continued)

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat	Reference
0.12	9 week	EC/SD	S23 ryegrass		X	Significant decrease in dry wt. (46%) and number (34%) of living leaves, tillers (42%), leaf area (44%), dry wt. of stubble (47%); significant increase in number (46%) and dry wt. (46%) of dead leaves; significant decrease in yield		Bell and Clough, 1973
			Wild ryegrass		X	None		
0.13	6 week	EC/SD	Indian ryegrass	X	X	Necrotic foliar lesions noted; non-significant decrease in productivity (6%), significant decrease in chlorophyll content (51%)	Wind tunnel exposures	Ferenbaugh, 1978
0.25						Necrotic foliar lesions noted; significant decrease in productivity (35%) and chlorophyll content (61%)		
0.50						Plants mostly dead after 4 weeks		
1.00						Plants dead after 4 weeks		
0.15	6 weeks		Duckweed		X	Decrease in diameter of fronds, no dry wt. effects	Ambient air + SO_2 exposure system not described	Frankhauser et al., 1976
0.30						Decrease in diameter of fronds		
0.60						Decrease in starch content, no dry wt. effects, no irreversible damages up to 0.60 ppm SO_2		
0.20	2 hour	GC	Kentucky bluegrass	X		Visible foliar injury, high degree of variation among 17 cultivators	No SO_2 monitoring information, plants previously exposed to SO_2	Murray et al., 1975
0.25	5 week	EC/SD	Ryegrass		X	Significant decrease in yield (17%), no effect on number of tillers	Wind tunnel exposure	Horsman et al, 1978
0.27	8 week					Significant decrease in green wt. (38%), total dry wt. (30%), no reduction in number of tillers, senescence rate doubled		
0.50-11.00	2 hour	F/CC	87 desert species	X		Most plants required more than 2.00 ppm SO_2 to produce foliar injury	Field plants watered heavily	Hill et al., 1974
11.00						SO_2 to produce foliar injury	watered heavily and exposed to ambient air before and after fumigation	1974
0.71	1 hour 2 hour 5 hour	EC/SD	Lily			Significant pollen tube elongation, inhibition at 1 and 2 hours	Pollen on agar, relationship those effects have to ambient conditions is unknown	Masaru et al., 1976
1.0	6 hour	EC/SD	Eucalyptus	X		>40% foliar necrosis, 32 of 131 species of Australian trees and shrubs were rated as sensitive to acute (≥1 ppm) exposure to SO_2		O'Conner et al., 1974

[a]Table arranged by > 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.

*
of fluoride contamination or used only sporadic monitoring schedules, respectively. Pollution gradients were evident and SO_2 exposure was most probably involved, but conclusive proof of losses was not presented as in the Sudbury area.

Table 8-6 summarizes the results of tree studies that have utilized artificial exposure chamber systems under laboratory conditions. Only two studies (exposures) used doses close to ambient concentrations (Houston, 1974); however, the use of selected clones of known sensitivity to SO_2 hinders further field speculation from this study. The remainder of the studies presented in Table 8-6 have used doses above expected occasional exposures under field conditions. Concentrations of greater than 0.25 ppm SO_2 for 2 hours were required to induce slight injury to several pine species (Berry, 1972), but overall trends for increasing foliar injury do not follow increasing dose for conifers per se. Smith and Davis (1978) exposed several conifers (pine, spruce, fir and Douglas fir) to doses of 1.0 ppm SO_2 for 4 hours or 2.0 ppm SO_2 for 2 hours and only pines developed necrotic tips at the 2.0 ppm dose.

Studies done with tree seedlings under artificial conditions are difficult to extrapolate to expected yield loss effects under field conditions. Of the studies reviewed and accepted without caveats, none demonstrated significant height or annual increment growth effects.

In an evaluation of SO_2 effects to photosynthesis, Keller (1977) used field chambers to expose potted white fir, Norway spruce and Scotch pine to 3 concentrations of SO_2 (0.05, 0.10, and 0.20 ppm and a control 0.0 ppm) for 10 weeks each during the spring, summer, and fall, respectively. Several types of photosynthetic responses rates were obtained; however, trends of decreasing rate occurred as dose increased especially when administered during the 10-week spring period. Effects were less during the summer and fall periods and spruce responded positively to SO_2 exposures of 0.05 ppm during the initial part of the fall period. Keller, also reported that even with the most severe depression of photosynthesis, there were not visible foliar symptoms in evidence. Keller (1980) utilized a similar exposure system and SO_2 doses to study effects to the annual ring width in two clones of Norway spruce. He reported significantly depressed CO_2 uptake with higher doses (0.10 and 0.20 ppm SO_2, 10 weeks), but only a trend was noted for the 0.05 ppm SO_2 treatment; visible symptoms and trends of reduced cambial growth occurred at only the higher dose.

On the limited data available regarding non-woody components of native ecosystems, there appear to be no adverse yield effects below 0.06 ppm SO_2 for 6 weeks (Table 8-7). Most of the acceptable literature deals with long-term exposures (several weeks) and results in SO_2 doses well above, or not comparable, with the current standards. There is some indication of beneficial yield effects below 0.06 ppm SO_2 on one species (i.e., Indian ricegrass). As reviewed in Section 8.2.8, low doses of SO_2 may result in an increase of productivity within certain crops. Concentrations of 0.03 to 0.06 continuously for 6 weeks of exposure increased the

*
productivity of desert grass by 8 percent over the control plants were grown in indigenous soils (Ferenbaugh, 1978). Other studies have demonstrated beneficial effects, but conditions included a sulfur-deficient growing medium.

In spite of differences due to exposure regimes, techniques, and species, certain generalizations can be made with respect to average and outer-limit responses of the plants under study. These have been made in the form of correlations of yield response with total exposure dose in part-per-million hours (ppmh). The latter data were calculated as the product of exposure time and SO_2 concentration and transformed to log values. For experiments employing controlled exposures under field conditions, data are graphed in Figure 8-6. For the 36 data points shown, exposure dose ranged from 0.24 to 259 ppmh. No effects on yield were detected in any of the six studies at doses $\leq$ 6 ppmh. Yield losses occurred in 26 cases at levels $\geq$ 6 ppmh while no effects and positive effects were noted in two cases each at levels $\geq$ 6 ppmh. A linear regression of yield on dose for all studies reporting yield losses showed strong positive correlation (r = .75) of yield with dose and took the form:

$$\text{Yield loss} = -13.6 + 23.8 \text{ (log dose)}$$
$$r^2 = 0.53 \text{ (Significance} = \geq 0.001)$$

This correlation excludes four data points, two with no effect and two with positive responses. All were studies with wheat reported by Wilhour (1978). Data from studies reporting no effect or a positive effect are all plotted in Figure 8-6, however.

Data from Tables 8-4 through 8-7 are graphed together in Figure 8-7. These data were derived from 59 yield responses involving 24 species or cultural varieties. Of these responses no effect was found in 10 cases, a positive effect was noted in 6 cases (4 under low-sulfur fertility), and a negative response was found in the remaining 33 cases. The linear fit to all data points for which yield losses were detected gave the formula:

$$\text{Yield loss} = 13.7 + 11.1 \text{ (log dose)}$$
$$r^2 = 0.22 \text{ (Significance} = \geq 0.003)$$

Yield loss showed a strong positive correlation (r = 0.48) with exposure dose. An alternate approach to deriving a dose-response surface for these data involves describing the upper limit of responses over the range of exposure doses studied. Such an approach, termed boundary-line analysis (Webb, 1972), defines the yield losses under "worst-case" conditions (i.e., sensitive species, sensitive conditions).

A boundary line for exposures below 500 ppmh in Figure 8-7 shows a threshold for effects of 0.6 ppmh and maximum potential losses of approximately 12, 39, and 50 percent at 1, 10, and 100 ppmh, respectively. Average losses as estimated from the linear regression were 14, 25, and 36 percent at these same dosage levels.

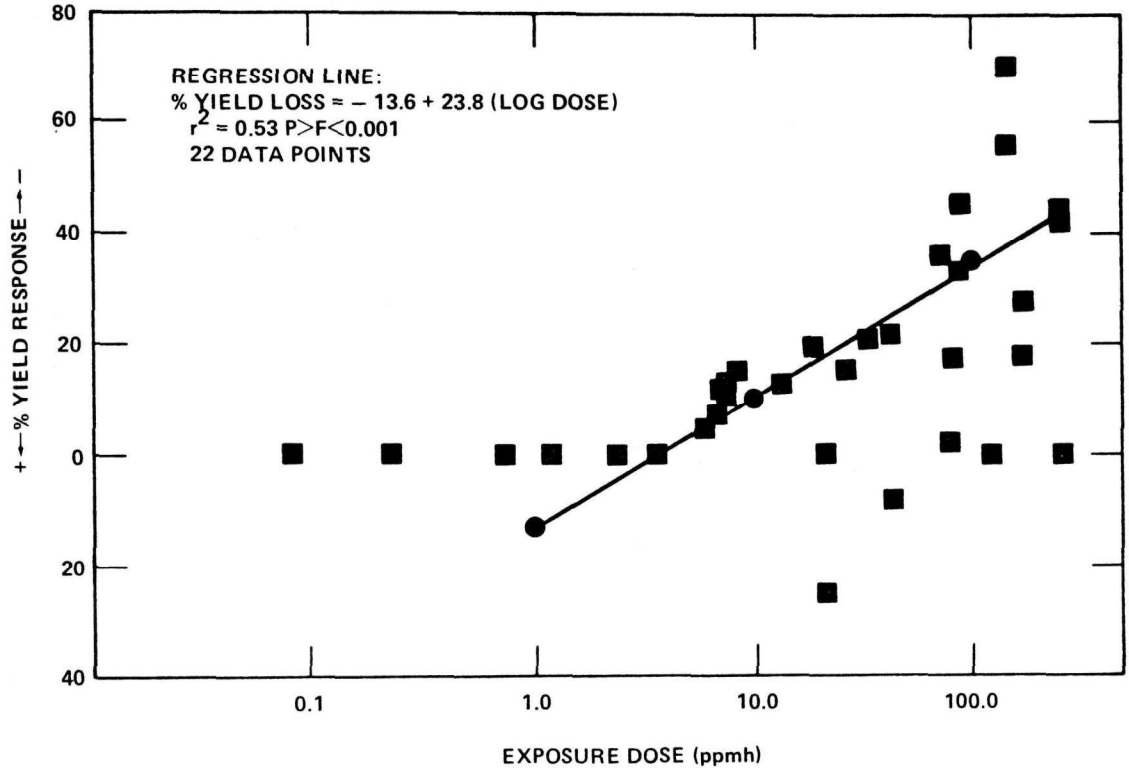


Figure 8-6. Regression of yield response vs. transformed dose (ppmh) for controlled exposures using field chambers (zero and positive effects excluded from regression analysis). See table 8-3 for details of exposures.

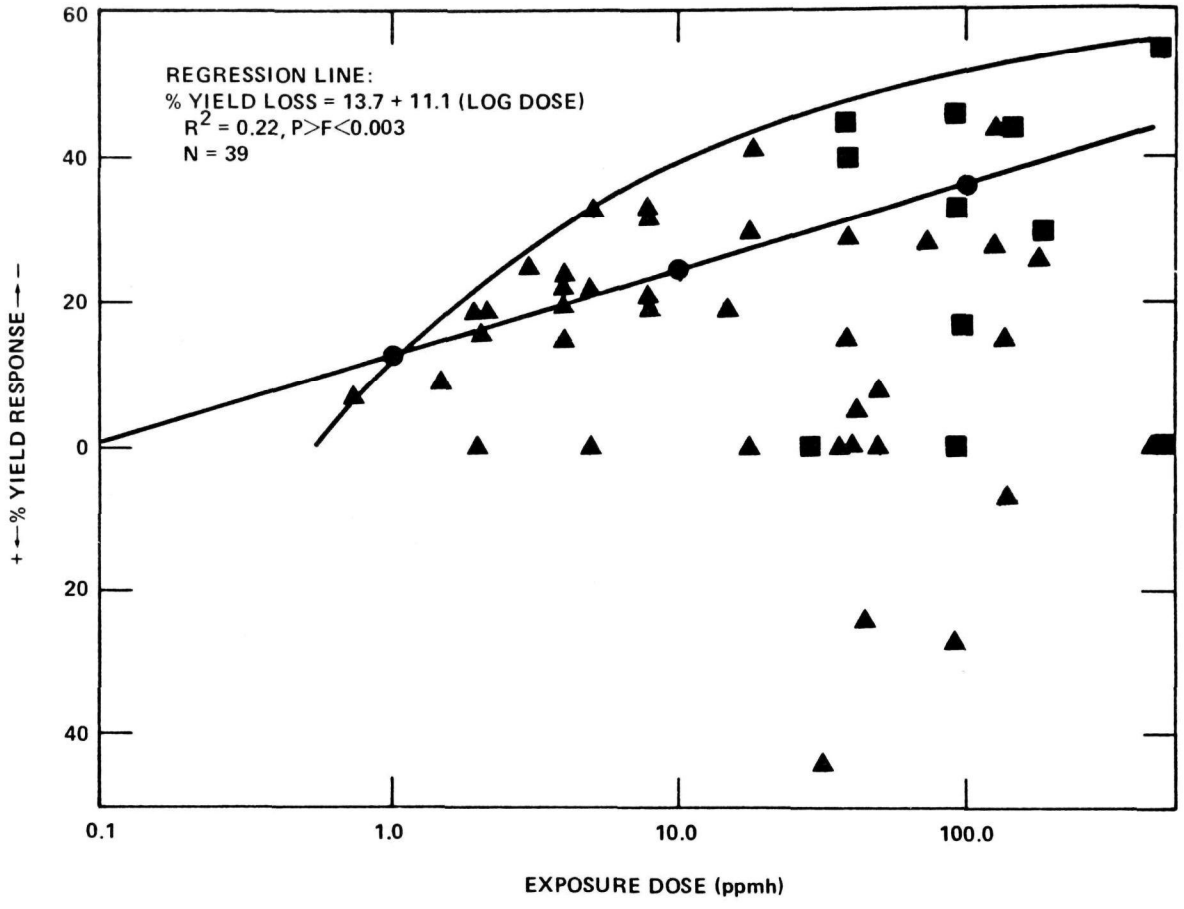


Figure 8-7. Regression of yield effects vs. transformed dose (ppmh) for laboratory and greenhouse studies using agricultural, ornamental, and native herbs. (Zero and positive effects excluded from regression). See tables 8-4 and 8-7 for details of exposure.

*

Only two studies in which quantitative data on SO_2 concentrations were related to effects on tree growth were found. These represent the work of Keller (1980) with Norway spruce and Linzon (1971) with white pine, and are shown in Figure 8-8. These data are interesting in that they demonstrate a linear, and very different, response surface for these two coniferous species over a rather broad range of log dose exposures (4-fold for spruce and 50-fold for white pine). These data further confirm that plant response is not equally affected by equal increments of SO_2 exposure dose.

In summary, our present dose-response data sets are heavily weighted towards controlled exposures in the laboratory or in field chambers. In spite of the variety of species studied and experimental protocols utilized, it is possible to derive potentially useful generalizations from these data:

(1) The concentration threshold for visible injury is generally lower than the threshold for efforts on growth and yield. Doses causing visible injury to 10 percent of a variety of southeastern plant species were 0.75 ppm for a 3-hr exposure and 0.50 for a 1-h exposure. The present NAAQS is 1.5 ppmh for 1 hr, and represents an approximate average threshold for most plant species.

(2) Visible injury data emphasize the greater relative biological effectiveness of short-term higher concentrations than longer exposures with the same total dose.

(3) Plant responses to SO_2 may be positive, neutral, or negative over a rather wide range of exposure dose. Positive responses were generally restricted to a very few species or conditions when plants were known to have been grown in S-deficient soils. Negative responses constituted approximately 85 percent of all responses noted above threshold levels.

(4) Data derived from controlled exposures of six species or cultivars in field chambers provided the most reliable basis for estimating yield responses from total logarithmically transformed exposure dose. Regression analysis of these data provided a no-effects limit of approximately 4.5 ppmh. Yield losses of 10 percent and 20 percent were similarly estimated at 10 and 27 ppmh, respectively.

(5) Data derived from laboratory and greenhouse exposures with 23 species or cultivars indicated generally greater sensitivity of test plants and were described both by a boundary line which delimited the maximum observed response over the range of concentrations employed and a regression line. Upper-limit yield losses determined by this approach were approximately 10 percent and 20 percent for exposure doses of 0.9 and 17 ppmh, respectively. (Average responses determined by regression analysis indicated that 10 and 20 percent yield losses would be produced by exposures of 0.6 ppmh and 45 ppmh, respectively.)

In interpreting the dose-response information presented above, it should be noted that responses of plants to SO_2 in the field may occur as a consequence of one or more short-term episodes or as a result of the cumulative dose experienced over an entire growing season.

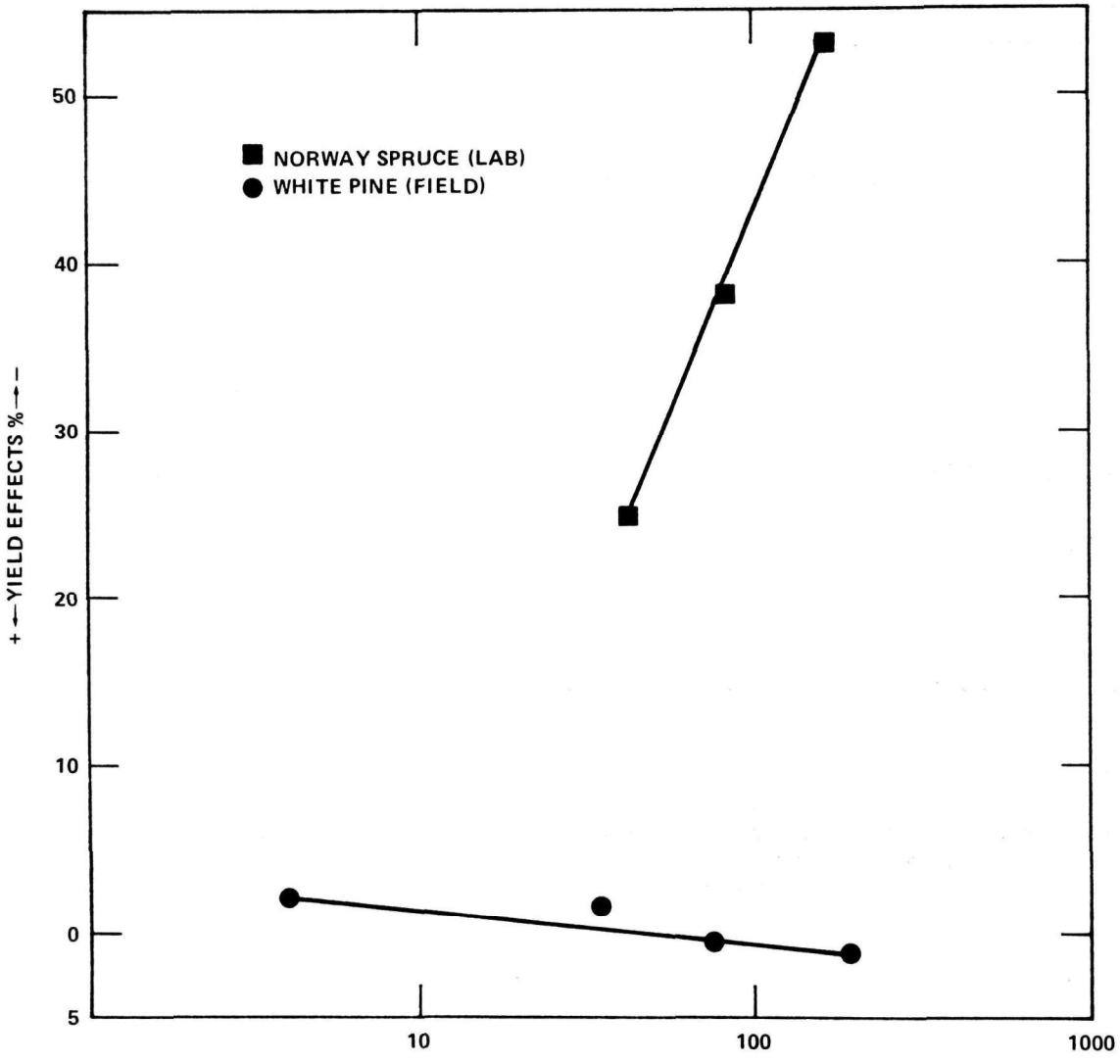


Figure 8-8. Yield responses vs. SO_2 dose for Norway Spruce (Keller, 1980) and White Pine (Linzon, 1971). See table 8-6 for details of exposure.

*
The regression lines developed in Figures 8-6 and 8-7 were derived from predominantly low-dose exposures in which a wide variety of exposure times were used and are intended to be used to describe risks associated with cumulative exposures. These relationships do not infer that single recent exposures with a total dose below the boundary line will not produce effects. The risks associated with these short-term exposures are probably best delimited by the visible injury data (Figures 8-2 and 8-5) which were developed around episodic exposure conditions.

Under field conditions, exposure kinetics may be dominated by episodic contributions from one or more point sources or they may be primarily a function of regional SO_2 loading and atmospheric stagnation patterns. Calculations of the probabilities of growth impacts around point sources should consider the average length and frequency of exposures as well as the exposure concentration. Data collected in 1973 in the vicinity of a 1900 megawatt power plant in Alabama demonstrate one useful approach to describing episodic exposures (McLaughlin and Lee, 1974). At this site SO_2 exposures occurred on a total of 40 percent of the days, lasted an average of 3 hr each, comprised approximately 10 percent of the total daylight hours, and provided approximately 230 h of exposure to SO_2 during the growing season. One-hr average concentrations $\geq$ 0.50 ppm occurred on an average of 12 hr at monitoring stations in the vicinity of this plant and provided a total of 6 ppmh of "high-level" exposure.

Calculation of the phytotoxic potential for regional scale exposures involves many assumptions regarding toxic and non-toxic components of the total dose to which vegetation is exposed. Obviously not all, and probably most, exposures to SO_2 on a regional scale are below levels producing phytotoxic reactions. An important aspect of evaluating the likelihood that plants will be negatively influenced by SO_2 exposures is the determination of what components of a plant's total exposure history are phytotoxic. McLaughlin (1980) recently examined Environmental Protection Agency (1978) data on regional SO_2 concentration averages. Using the assumption that only the upper 10 percent of all SO_2 exposure days would have SO_2 concentrations high enough to cause stress to vegetation, and that only daylight exposures (8 hr/day^{-1}) during the active growing season (6 mo/yr^{-1}) would be effective, he calculated that the average potentially phytotoxic dose within designated air quality control regions would range from 0.9 ppmh (Region IX) to 5.5 ppmh (Region VIII). Maximum doses (highest reporting stations within regions) ranged from 2.6 ppmh to 27 ppmh.

More definitive dose-response studies both with and without the addition of other pollutants (see Section 8.4) are needed before the biologically significant features of typical regional scale exposure regimes can be positively delineated. However, the above calculations represent the type of data reduction which will eventually be needed to place air quality data into biological perspective. An examination of the minimum levels of SO_2 associated with yield depression (regardless of time of exposure) indicates that this level is approximately 0.05 ppm for long-term exposures.

*

8.4 EFFECTS OF MIXTURES OF SO_2 AND OTHER POLLUTANTS INCLUDING PARTICULATE MATTER

Ambient atmospheres usually contain more than one pollutant. Long-distance transport of photochemical oxidants and oxidant precursors (Husar et al., 1977; U.S. Environmental Protection Agency, 1971), the demonstration of acidic rainfall over large areas of the eastern United States (Cogbill, 1976), and atmospheric monitoring have documented that emissions from specific sources are mixed with ambient concentrations of one or more associated pollutants (Shriner et al., 1977). 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 (sum of effects), less than additive (antagonistic), or more than additive (synergistic). In addition to pollutant combinations under controlled conditions, 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. Reinert (1975) and Reinert et al. (1975) have prepared the most recent reviews of this area of investigation. Some examples of the available literature follow.

8.4.1 Sulfur Dioxide and Ozone

A more than additive reaction on vegetation was first noted with ozone and SO_2 (Menser and Heggestad, 1966). Tobacco were severely injured by 0.03 ppm ozone and 0.24 ppm SO_2 when the pollutants were combined for either 2 or 4 hours, whereas when used alone, neither pollutant produced foliar symptoms.

Since that first report, the effects of mixtures 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 0.10 ppm O_3 + 0.10 ppm SO_2 (Tingey et al., 1973a), but less than additive growth reduction (top and root weights) from an 8-hr, 5 day/wk, 5-week exposure of radish (alfalfa total exposure time unknown) to a mix of 0.05 ppm O_3 + 0.05 ppm SO_2 (Tingey et al., 1971a; Tingey and Reinert, 1975). 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 (Tingey et al., 1973a). Soybean has exhibited non-significant less than additive foliar injury effects (Tingey et al., 1973a) while exhibiting significantly greater than additive growth effects (Tingey et al., 1973b).

Most research examining the effects of pollutant mixtures has utilized standard means comparisons to express the responses. These tests usually do not adequately evaluate the interaction: the failure of one pollutant to be consistent at different concentrations of the second pollutant. Reinert and Nelson (1980) utilized sums of squares partitioning by factorial analysis to examine the effects of 0.5 ppm SO_2 and 0.25 ppm O_3 (4-hr exposures, 4 times, 6 days apart) on Begonia. A significantly less than additive effect was found for flower weight of 1 to 5 cultivars. The same technique was utilized by Reinert and Weber (1980) to evaluate the effects of 0.25 ppm O_3 and 0.25 ppm SO_2 (exposed 4 h/day,

*
3 days/wk, for 11 wks) on soybean (Dare); an additive effect of the pollutant mixture was demonstrated.

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. Injury and yield due to the mixture were increased (9 percent) and decreased (19 percent), respectively, compared to the ozone-alone treatment, but the differences were not significant (Heagle et al., 1974). 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 (Jacobson and Colavito, 1976).

Alfalfa exposed in closed field chambers to low levels of ozone and sulfur dioxide single 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 (Neely et al., 1977).

Many studies have been conducted on the effects of mixtures of sulfur dioxide and ozone on eastern white pine (Pinus strobus L.) (Costonis, 1973; Dochinger and Heck, 1969; Houston, 1974; Houston and Stairs, 1973). Genetic control of sulfur dioxide and ozone tolerance in this species has been demonstrated for low concentrations of SO_2 (0.025 ppm) and O_2 (0.05 ppm) for only 6 hr with consistent injury to the exposed sensitive clones (Houston and Stairs, 1973). Houston (1974) 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 (0.05 ppm) for 6 hr in mixture caused more serious damage than that resulting from either pollutant alone at similar concentrations. A less than additive effects 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 (Neilson et al., 1977).

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 (Karnosky, 1976). Table 8-8 lists some selected O_3 + SO_2 combination studies.

Oshima (1978) conducted a field experiment using constant-stirred, round, closed chambers to assess the effect of SO_2 (0.10 ppm, 6 hr/day, total 335 hrs) on yield of potted red kidney beans, Phaseolus vulgaris exposed to a gradient of ozone doses; that is, the ozone present in 0, 25, 50, 75, and 100 percent charcoal-filtered air at Riverside, California. The temperature, light, and humidity approximated that of ambient air; plants were in the chambers for 78 days. An interaction with ozone and SO_2 was documented in the 50 percent carbon filtered treatment (5144 ppm-hrs) and produced a significant reduction in yield (37 percent) and plant biomass. The data also indicated the suggestion of an interaction in the 75 percent filtered treatment (2822 ppmh-hrs) (yield reduced 17 percent), but at an unacceptable level of significant ($p = .20$ level). Sulfur dioxide at 10 pphm did not produce detectable plant or yield responses alone and did not have an interactive effect at ozone doses exceeding 5144 pphm-hrs.

TABLE 8-8. EFFECTS OF MIXTURES OF SO_2 and O_3 ON PLANTS

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Productivity	Species effect[d]	Caveat[e]	Reference
0.025 SO_2 + 0.05 O_3	6 hr	EC/SD	E. white pine	X	X	No effect to needle elongation. Foliar injury on sensitive clones only; 10 trees with 75-100% of needles with tip necrosis. SO_2 alone caused tip necrosis on 75-100% of the needles on 1 tree. O_3 alone caused no injury.		Houston, 1974
0.05 SO_2 + 0.05 O_3	8 hr/d, 5 d/wk 5 wks	EC/SD	Radish	X	X	Plant weight reductions additive (leaf fresh and dry weight) or significantly less than additive (plant fresh wt., root fresh and dry weight).		Tingey et al., 1971b
0.05 SO_2 + 0.05 O_3	8 hr/d, 5 d/wk 18 days	EC/SD	Soybean	X	X	Additive foliar injury effects, greater than additive root dry weight		Tingey et al., 1973b
0.05 SO_2 + 0.05 O_3	8 hr/d, 5 d/wk 4 wk	EC/SD	Tobacco		X	Additive growth reductions		Tingey and Reinert, 1975
	8 hr/d, 5 d/wk until control plants 40-45 cm high		Alfalfa		X	Less than additive growth reductions		
0.06 SO_2 + 0.05 O_3	7 hr/day 68 days	F/CC	Alfalfa		X	No significant alteration of plant responses (carbohydrate, protein, dry weight) compared to the effects of single pollutants	Potted plants set on soil surface; grown hydroponically	Neely et al., 1977
0.075-0.60 SO_2 + 0.15 O_3	5 or 10 days	EC/SD	White bean	X	X	Less than additive growth reductions and foliar injury		Hofstra and Ormrod, 1977
			Soybean	X		Less than additive foliar injury		
0.10 SO_2 + 0.10 O_3	6 hr/d 133 days	F/CC	Soybean	X	X	SO_2 alone and in the mix did not significantly affect the yield and injury responses		Heagle et al., 1974
0.10-0.50 SO_2 + 0.05-0.10 O_3	4 hr	EC/SD	Alfalfa Broccoli Cabbage Radish Tomato Tobacco W_3	X		Greater than additive foliar injury at 0.10 ppm of each gas for alfalfa, brocolli, and radish. Less than additive effect for tomato. At 0.25 ppm, SO_2 + 0.10 ppm O_3 greater than additive injury noted on alfalfa, radish, and tobacco. At 0.50 ppm, SO_2 and 0.05 ppm O_3 greater than additive injury on broccoli and tobacco and less than additive injury on alfalfa. At 0.50 ppm, SO_2 and 0.10 ppm O_3 greater than additive effects on alfalfa, cabbage, radish, tobacco.		Tingey et al., 1973a

TABLE 8-8. Continued

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
0.20 SO_2 + 0.05 O_3	3 hr	EC/SD	Trembling Aspen (5 clones)	X		Greater than additive injury to 3 clones no injury due to SO_2 alone		Karnosky, 1976
0.35 SO_2 + 0.05 O_3	3 hr	EC/SD	Trembling Aspen (5 clones)	X		Greater than additive injury to 4 clones		Karnosky, 1976
0.24 SO_2 + 0.27 O_3	2 hr	GC	Tobacco Bel-W3 Bel-B Consolidation 402	X		9-38% foliar injury--no injury due to either pollutant singly		Menser and Heggestad, 1966
0.28 SO_2 + 0.28 O_3	4 hr	GC	Tobacco Bel-W3 Bel-B Consolidation 402	X		23-76% foliar injury--no injury due to either pollutant singly		Menser and Heggestad, 1966
0.25 SO_2 + 0.05 O_3	4 hr	EC/SD	Alfalfa Onion Soybean Tobacco Bel-B Tobacco White gold	X		Only tobacco Bel W_3 showed greater than additive foliar injury	Bel W_3 tobacco very sensitive	Tingey et al., 1973a
1.00 SO_2 + 0.10 O_3			Tobacco Bel-W_3 Lima bean Broccoli Bromegrass Cabbage Radish Spinach Tomato			At 1.00 ppm SO_2 tobacco Bel B and Bel W_3 exhibited greater than aditive effects, and there were less than additive effects for Bromegrass, cabbage, spinach, and tomato.		
0.25 SO_2 + 0.25 O_3	4 hr/d, 3 d/wk 11 wks	EC/SD	Soybean	X	X	Additive growth effects		Reinert and Weber, 1980
0.45 SO_2 + 0.15 or 0.45 O_3	4 hr	EC/SD	Radish		X	Additive growth effects		Tingey and Reinert, 1975
0.25 SO_2 + 0.14 O_3	10 6hr/day 68hr 5day/wk 154 164	EC/SD	Scotch Pine	X		Less than additive effects--no effects due to O_3 alone		Nielsen et al., 1977
0.25 SO_2 + 0.29 O_3	10 6hr/day 68hr 5day/wk 154 164	EC/SD	Scotch Pine	X		Less than additive effects--no effect due to O_3 alone		Nielsen et al., 1977
0.50 SO_2 + 0.25 O_3	4hr/day 4 times, 6 days apart	EC/SD	Begonia (5 cultivars)	X	X	Less than additive effects for flower weight of one cultivar. 0.50 SO_2 alone significantly reduced flower production in the absence of foliar injury for one cultivar		Reinert and and Nelson, 1980

*

8.4.2 Sulfur and Nitrogen Dioxide

The occurrence of SO_2 and nitrogen dioxide (NO_2) has been associated with power plant plumes as well as mobile sources. However, ambient concentrations of NO_2 seldom reach the injury threshold, and the literature for NO_2 suggests that any injury associated with NO_2 results from interactions with other pollutants (Jacobson and Hill, 1970).

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. However, at 0.10 ppm of each gas for 4 hr, injury was noted on all species; at 0.05 ppm of each gas, slight injury was noted on all species except tomato (Tingey et al., 1971a). 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 (White et al., 1974). At 0.15 ppm of each gas singly, there were no measurable effects, but a 7-percent suppression of apparent photosynthetic rates was noted in the mixture (White et al., 1974).

Field exposure of seven different species of plant indigenous to the cold desert areas of the southwestern United States to 0.50-11.0 ppm SO_2 singly, or 0.50-11.0 ppm SO_2 and 0.10-5.00 ppm NO_2 combined in 2-hr fumigations resulted in no evidence of more than additive foliar injury (Hill et al., 1974).

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) (Bennett et al., 1975). 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-1,5diphosphate carboxylase activity was decreased (Horsman and Wellburn, 1975). Some selected SO_2 + NO_2 combination studies are shown in Table 8-9.

8.4.3 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 (Matsushima and Brewer, 1972). 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. 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 (Mandl et al., 1975).

8.4.4 Sulfur Dioxide, Nitrogen Dioxide and Ozone

Fujiwara et al. (1973) 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

TABLE 8-9. EFFECTS OF MIXTURES OF SO_2 AND NO_2 ON PLANTS

Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Plant	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
0.05-0.25 SO_2 + 0.05-25 NO_2	4 hr	EC/SD	Tobacco Pinto Bean Tomato Radish Oats Soybean	X X X X X X		0-2% foliar injury at 0.05 ppm SO_2 + 0.05 ppm NO_2. 1-35% foliar injury at 0.10 ppm SO_2 and 0.10 or 0.15 ppm NO_2. Injury less at 0.20-0.25 ppm SO_2 than at 0.10 ppm SO_2. Thresholds-SO_2=0.50 ppm, NO=2.00 ppm		Tingey, et al., 1971a
0.15-0.25 SO_2 + 0.10-0.20 NO_2	4 hr	EC/SD	Pinto Bean Tomato Radish Oats	X X X X		No foliar injury	Recirculating air Experimental conditions approximated those of Tingey, et al., 1971b, but used different cultivars of tomato, radish, and oats	Bennett et al., 1975
0.11 SO_2 + 0.11 NO_2	103.5 h/wk 20 wk	EC/SD	Cocksfoot Meadow-grass		X X	Greater than additive decreases in # of tillers, # leaves, and leaf area	Wintertime exposures	Ashenden, 1979
0.125-1.0 SO_2+0.125 -1.0 NO_2	1hr or 3hr	EC/SD	Radish Swiss chard Oats Sweet pea	X X X X		Greater than additive foliar injury to radish at higher concentrations. Thresholds for radish were 0.50 ppm of each gas, and for the other species 0.75 ppm of each gas.	Recirculating air	Bennett et al., 1975
0.15-0.50 SO_2+0.15-0.40 NO_2	1hr and 2hr	EC/SD	Alfalfa			Slight but significantly greater than additive depression of photosynthesis at SO_2 concentrations of 0.15 and 0.25. No greater than additive effects at 0.35 or 0.50 ppm SO_2.	Reversible effects	White et al., 1974
0.2 SO_2 + 0.1 or 1.0 NO_2	6 days	EC/SD	Pea			Significantly greater than additive increase in peroxidase and RuDPC enzyme activity at 0.20 ppm SO_2 and and 0.10 ppm NO_2	Reversible effect?	Horsman and Wellburn, 1975
0.5-11.0 SO_2 + 0.1-5.0 NO_2	2 hr	F/CC	87 desert species	X		No evidence of SO_2 + NO_2 synergism at an NO_2/SO_2 ratio of 0.28. Most species required over 2.00 ppm SO_2 to cause injury.	Plants exposed to ambient air before and after fumigation	Hill et al., 1974
0.8 SO_2 + 0.3 NO_2	2 hr	EC/SD	Alfalfa	X		Apparent photosynthesis reduced at 315 ppm CO_2 but increased at 645 ppm CO_2	Reversible effects	Hou et al., 1977

[a] Table arranged by > 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] EC/SD = exposure chamber, special design; F/CC = field, closed chambers.
[c] X indicates study found foliar and/or yield effects.
[d] Most prominent or significant effect reported.
[e] Caveats for consideration about proper study design and interpretation.

*
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 and Gray (1981) examined the effects of 0.2 or 0.4 ppm each of O_3, SO_2, and NO_2 (3- or 6-hr exposures) on the growth of radish. Through partitioning, the main effects of each pollutant and the potential interactive effects of each mixture were examined. Sulfur dioxide depressed the root/shoot ratio at both 0.2 and 0.4 ppm; however, when NO_2 and SO_2 were both present there was a greater than additive depression of the root/shoot ratio at 0.4 ppm.

8.4.5 Summary

As can be seen from the preceding research, plant species vary in their responses to pollutant mixtures, and the type of response (additive, less than additive, greater than additive) may depend on the parameter measured. Our understanding of how pollutant combinations influence plant growth and development, and how environmental factors can modify those responses is still fragmentary. Insufficient information exists 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.

There is a need to determine the best technique for evaluating the effects of pollutant mixtures. Only recently has the partitioning technique been utilized to express the effects of pollutant mixtures. This technique allows for separation of the main effects of each pollutant, and also provides a statistical test of the significance of potential interactions between pollutants.

The data have demonstrated that interactions can occur between pollutants and, due to the occurrence of pollutant mixtures in the ambient situation, knowledge of interactive effects is very important. However, the nature of the effects of pollutant mixtures is extremely complex. Most research studies have necessarily taken a rather simplistic approach to this complex problem. It is, therefore, difficult to relate these relatively few results to "real world" situations.

8.5 EFFECTS OF NON-POLLUTANT ENVIRONMENTAL FACTORS ON SO_2 PLANT EFFECTS

The physical environment plays an extremely important role in determining response to SO_2. Most evidence has accumulated on factors leading to or inhibiting the ingress of SO_2 into stomates and immediate plant reactions as determined by the metabolism of the plant at the time of exposure; the metabolic state of the plant is likewise affected by the physical environment. As illustrated in the following sections, the response of any given plant species may also be quite different from any other given species grown under identical physical conditions.

8.5.1 Temperature

Temperature plays an important part not only in determining the metabolic rate of the plant, but in determining (with moisture, fertility, and light) species diversity and richness of a given ecosystem (NAS, 1978). The primary path of entry of SO_2 into the

*
leaf is through 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 may also increase the plant response to SO_2 (Heck and Dunning, 1978). It is generally believed that plant sensitivity increases with temperature over a wide range, from about 4 to 35°C (Guderian, 1977; Rist and Davis, 1979). Several studies suggest greater resistance of conifers to SO_2 in the winter, attributed to lower rates of physiological activity (NAS, 1978). However, according to Guderian and Stratmann (1968), in areas with SO_2 emissions, winter wheat and winter rye are more severely injured than the summer varieties. Guderian (1967) interpreted this to be due to gas exchange taking place through stomata at temperatures as low as -2°C.

8.5.2 Relative Humidity

Relative humidty exerts important control over plant sensitivity to SO_2 both by affecting stomatal opening and closing (Bonte et al., 1975; Majernik and Mansfield, 1970; Mansfield and Majernik, 1970; Buron and Cornic, 1973) as well as by affecting the internal leaf resistance to SO_2 flux (McLaughlin and Taylor, 1981). Although plant sensitivity increases with relative humidity, Setterstrom and Zimmerman (1939) found rather large changes ($\geq$ 20 percent) were required to cause change in plant sensitivity once RH levels become $\geq$ 40 percent. McLaughlin and Taylor (1981), in laboratory studies, found 2 to 3 fold increases in SO_2 uptake by kidney beans over a range of SO_2 concentrations (0.16-0.64 ppm) as relative humidity was raised from 35 percent to 78 percent during exposure times of $\leq$ 3 hours. According to Zimmerman and Crocker (1954), although relative humidity is important in governing sensitivity and consequently the sensitive plant population, it is not as important as the tissue turgidity as may be influenced by soil moisture as well as relative humidity. Based on the water relations in certain trees, Halbwachs (1976) has rated plants as sensitive, intermediate, and tolerant at relative humidities of over 75 percent, 50 to 75 percent, and below 50 percent, respectively.

8.5.3 Light

Light also controls stomatal opening and thus plant sensitivity. Plants are more tolerant when fumigated in darkness with SO_2 or when held in the dark for several hours before exposure (Zimmerman and Crocker, 1954). This relationship is complex, since injury is greater if the night exposure follows a daylight exposure (NAS, 1978).

Setterstrom and Zimmerman (1939) 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 (NAS, 1978).

Plants seem to be more sensitive from midmorning to midafternoon, in spite of a high light intensity that might continue after midafternoon (Rennie and Halstead, 1977; Thomas and Hendricks, 1956). 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 (Van Haut and Stratmann, 1970).

8.5.4 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 (NAS, 1978). Adequate soil moisture and the resultant stomatal opening have been shown to increase the degree of plant sensitivity, whereas wilting conditions confer tolerance (Setterstrom and Zimmerman, 1939; Zahn, 1963; Zimmerman and Crocker, 1954). 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 adequate supply, even though the moisture content of the soil is the same at the time of fumigation (Setterstrom and Zimmerman, 1939). Withholding water from some crops during periods of high pollution risk has been suggested (Brandt and Heck, 1968).

Soil fertility has a significant influence on plant response to SO_2. Some plants become more tolerant to SO_2 upon fertilization (Enderlein and Kastner, 1976; Zahn, 1963). However, 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 (Cotrufo and Berry, 1970). Nitrogen and sulfur deficiencies were correlated with increased tolerance to SO_2 in tobacco and tomato (Leone and Brennan, 1972). Conversely, nutrient deficiencies increased SO_2 sensitivity in alfalfa (Setterstrom and Zimmerman, 1939). 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 (Van Haut and Stratmann, 1970; Zahn, 1963).

8.5.5 SO_2 and Biotic Plant Pathogen Interactions

Plant disease is caused by the interaction of a plant and a pathogen acting under suitable environmental conditions. The influence of SO_2 directly or indirectly on the interrelations of a given plant and its possible biotic pathogens has been difficult to investigate. Additionally, whenever the variables of the physical environment would be considered within such experimental sequences, the subject becomes even more difficult to examine. Heagle (1973) and Laurence (1978) have provided the most recent reviews of the interaction between air pollutants and plant parasites.

In seven of nine plant diseases reported in SO_2-related studies as reviewed by Laurence (1978), there was no effect or a reduction in disease development demonstrate; disease increased only in needle case of pine (Chiba and Tanaka, 1968) and increased virus titer of southern bean mosaic virus has been reported by Laurence et al. (1981).

In a recent study by Laurence et al. (1979) maize and wheat were exposed to 0.10 or 0.15 ppm SO_2 for either 2 or 10 days and innoculated at various times with Helminthosporium maydis or Puccinia graminis. The ability of these fungi to infect either

*
corn or wheat, respectively, was inhibited by SO_2 exposures; greater inhibition occurred if plants were fumigated prior to inoculation attempts.

Studies done under ambient conditions without monitoring of other pollutants have suggested a decrease in disease incidence in areas of higher SO_2 pollution with the possible exception of those pathogens which are able to better invade weakened plants. If SO_2 exposure has resulted in an overall weakened condition, other agents such as root invading fungi may be able to gain entrance into an otherwise resistant host. Such is the suspected reason for increased incidence and severity of attack by the root pathogen Armillaria mellea in trees weakened by SO_2 (Donaubauer, 1968; Jancarik, 1961; Kudela and Novakova, 1962).

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 (Stewart et al., 1973).

A direct influence of SO_2 on plant pathogenic fungi has been demonstrated and a review has been presented by Saunders (1973); no direct effects of SO_2 on plant pathogenic bacteria have been reported.

8.6 PLANT EXPOSURE TO PARTICULATE MATTER

8.6.1 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 if available on the deposition rate for these particles. Shinn (1978) 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 2 are at least 10 times less than in Category 2 (Shinn, 1978). According to Clough (1975), in the range of wind speeds normally encountered, the larger particles in the atmosphere are much more efficiently collected than the smaller fraction.

Little (1977) evaluated the effects 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 varies according to both wind speed and particle size.

*

Further information on atmospheric transport transformation and deposition of particulate matter may be found in Chapter 6 of this document.

8.6.2 Routes and Methods of Entry Into Plants

Direct Entry Through Foliage--Foliage is continuously subjected to natural and man-made coarse particles that are insoluble or sparingly soluble in water. Coarse particles in general are too large to enter leaves through stomata. Based upon a review by Meidner and Mansfield (1968) which presented stomatal data for 27 species of plants (e.g., pine, oak, corn, soybean, and tobacco) the overall average pore (opening) width is 6 microns which accounted for 0.15 to 2.0 percent of the average stomate total area. In certain cases, such as with cement kiln dusts (Lerman and Darley, 1975) and other types of aggregate particles (Smith, 1977), 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 (1961) 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 delineate and 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 (Little, 1973).

Smith (1973) evaluated metal contamination of urban woody plants by using a variety of washing procedures. Indirect evidence from all these studies 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 particle and their chemistry, rates of deposition, and dose in conjunction with changes in tissue concentrations over time relative to background conditions.

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 elements associated with the 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 (Brady, 1974). As uptake of elements proceeds, there may be a redistribution of nutrients or toxicants in the soil.

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, may usually be available at a neutral pH; however, when the soil becomes acidic, toxic elements such as aluminum become available.

8.7 REACTION OF PLANTS TO PARTICULATE EXPOSURE

8.7.1 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 (Darley, 1966; Lerman and Darley, 1975; U.S. Department of Health, Education, and Welfare, 1969; U.S. Environmental Protection Agency, 1977a). Krupa et al. (1976) and Linzon (1973) have also prepared an extensive review of various forms of heavy metal depositions and impact. Tolerance of plants for heavy metals and fine particles and their bioenvironmental impacts have also been reviewed (U.S. Environmental Protection Agency, 1975).

Dusts directly affect plants by coating exposed plant parts, including leaves, stems, flowers, and fruits (Jennings, 1934; Katz, 1967; Linzon, 1973). 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 of particulates on leaves result in reduced gas exchange, increased temperature, reduced photosynthesis, and eventual yellowing and tissue desication (Daessler et al., 1972; Parish, 1910).

Terminal growth reduction and chlorosis of 2-year needles of hemlocks coated with heavy dust deposits has been reported. Manning (1971) also reported that fungal propaguels increased and bacterial numbers decreased on such needles. Brandt and Rhoades (1972) reported long-term changes in plant community structure and species composition, and later indicated that radial growth rates were reduced in the tree species involved (Brandt and Rhoades, 1973). On the exposed site they demonstrated a reduction in radial growth of red maple (18 percent, chestnut oak (29 percent), and red oak (23 percent) 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. Reduction in growth of

*
the dominant species (oak, maple) most probably gave a competitive advantage to tulip poplar and greater than expected increase may have occurred.

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 (Gilbert, 1976). A reversal of this trend occurred in areas where SO_2 was of importance prior to limestone dust emission. No exact pollutant dose 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 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 mb/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 (Darley, 1966).

The accumulation of dust caused increased reflection of solar radiation in wavelengths of 400 to 760 nm and has been demonstrated to reduce photosynthesis (Ricks and Williams, 1974). 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 (Spinka, 1971).

Growth and yield effects induced by the accumulation of dust have recently been reviewed (U.S. Environmental Protection Agency, 1975). 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 (Anderson, 1914).

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.

The phytotoxicity of heavy metals, arsenic, and boron has been demonstrated after accumulations in soils and subsequent uptake by various plants. Table 8-10 presents a summation of toxic effects of individual elements (Krupa et al., 1976). Published reports of direct effects on plants from specific sources are discussed in the following paragraphs.

Arsenic--Only one study was available to show foliar uptake of airborne arsenic (Linzon, 1977). Phytotoxicological studies in the vicinity of gold smelters in Ontario, Canada revealed the occurrence of several injuries to vegetation (primarily fireweed, Epilobium angustifolium) as induced by airborne arsenic compounds in a sulphurous plume. Chemical tissue analysis of affected leaves revealed arsenic at 200 ppm as compared to 1 ppm arsenic in leaves collected 50 miles from the source area. Linzon (1977) suggested 10 points of evidence leading to the conclusion of the airborne nature of the toxicant including elevated concentrations on sides of plants closer to the source and correlation of arsenic emissions (variation) and corresponding changes in tissue concentrations on an annual basis.

TABLE 8-10. Plants sensitive to heavy metals, arsenic, and boron as accumulated in soils and typical symptoms expressed.

Metal	Plant	Symptoms	Reference
Arsenic	Snap bean, lima bean, onion, pea, cucumber, alfalfa, legumes, sweet corn, strawberry (on light and sandy soils).	Reduced germination of seeds, rotting of roots, leaf wilt, brown to red coloration of leaves, reduced yield in fruit trees, death.	Liebig (1966) Linzon (1977)
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.	Yellowing of leaf tips, necrosis between lateral veins and midrib of monocotyledons, marginal leaf scorch, downward cupping of leaves, reduced flowering, fruit lesions.	Bradford (1966) Krupa and Kohut (1976) Yopp et al. (1974)
Cadmium	Red oak, birch, trembling aspen, beet, carrot, celery, green pepper, lettuce, radish, soybean, Swiss chard, tomato, winter wheat.	Reduced root elongation, general growth retardation.	Yopp et al. (1974) Jordan (1975)
Copper	Bean, citrus fruits, corn, mustard.	Stunted root development, chlorotic leaves, reduced vegetative growth.	Reuther and Labanauskas (1966)
Lead	Bean dwarf French, var. Carters; beet, corn, fescue, lettuce, lupine, lobblolly pine, red maple.	Stunted root growth, shoot retardation, increased leaf abscission, reduced yields.	Yopp et al. (1974)
Magnesium	Orange (only case known from published literature).	Leaf rolling, spiraling inhibition of leaf emergence. Narrow leaf development.	Embleton (1966)
Manganese	Alfalfa, broadbean, cabbage, cauliflower, cereals, citrus, clover, lespedeza, pineapple, potato, tobacco, tung, barley, var Atlas 46, var. Herta; yellow birch, cranberry, peanut, potato, var. Kesweck; alfalfa, apple, apricot, barley, bean, brussels sprout, carrot, clover, cotton, lettuce, medic, orange, peas, potato, sugar beet, vetch, wheat.	Necrotic spots on leaves, necrosis of internal bark,marginal leaf yellowing, incurling of leaf margins.	Yopp et al. (1974) Labanauskas (1966) NAS (1973)
Mercury	Broadbean, oxalis, sunflower, bean, butterfly weed, cinquefoil, fern, Hydrangea, Mimosa, Oxalis, privet, sunflower, willow.	Possible reduced growth.	Yopp et al. (1974) Lagerwerff,(1972) Jacobson and Hill (1970)
Nickel	Citrus fruit, alfalfa, oats, var. Victory; pear.	Repression of vegetative growth, leaf chlorosis, white or light yellow and green striping.	Vanselow (1966) Yopp et al. (1974)
Potassium-	Orange, tung (only case known for published literature).	Fruit coarseness and leaf necrosis, leaves curl downward, marginal leaf necrosis, intervenal chlorosis, plant dieback.	Ulrich and Ohki (1966)
Zinc	Oats, orange, tung, barley, var. Trail; corn, var. Whatley's Pro- Univorm chlorosis, reduced terminal growth, twig lific, var. Ida Hybrid 330; cowpea, var. Suwannee; wheat, var. Gaines; barley, citrus, oats, sugarbeet.	Chapman (1966) dieback, chlorotic striping of leaves, stems stiff and erect.	Yopp et al. (1974)

Source: *Adapted from Krupa et al. (1976)*

*

Arsenic sprays have been applied to the foliage of many plants to 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 (Liebig, 1966). Boertitz et al. (1976) 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.

Cadmium--Most biologically active cadmium enters plants through root uptake (Jordan, 1975). 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 (Yopp et al., 1974).

Copper--Wu and Bradshaw (1972) demonstrated a selection of individual plants of Agrostis stolonifera growing near metal smelters, thus indicating an indirect effect of within-species simplification within a population through selection.

Lead--Davis and Barnes (1973) reported reduced growth of loblolly pine and red maple seedlings in pots of two forest soils treated with 2×10^{-4} to 2×10^{-3}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 (Schoenbeck, 1973). Plants growing in soil already high in these metals tended to be more sensitive to the addition of metals by air pollution.

Nickel--Plants can absorb and translocate airborne nickel salts (NAS, 1975). Once inside the plant, nickel affects photosynthesis and other processes such as stomatal function (Bazzaz and Govindjee, 1974). In cases of incipient nickel toxicity to vegetation, no definite symptoms have been observed other than growth repression. In cases of moderate or acute nickel toxicity, chlorosis-resembling symptoms of iron deficiency is common (Anderson et al., 1973; Anderson, 1974).

8.7.2 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 the toxicity of specific chemical constituents of particulates in relation to sensitivity groups of vegetation under field conditions. Table 8-10 has listed plants that may be sensitive to heavy metals following deposition and various symptoms as expressed following their respective accumulations.

*

8.8 DOSE-RESPONSE RELATIONSHIPS--PARTICULATES

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 constitutions are frequently ill-defined although their sources have often been identified. Little information could be found on the effects of fine particles on vegetation.

Where cause-and-effect relationships have been suggested, 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 must be considered as a plant response. Soil scientists have contributed most 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, tissue concentrations prior to actual exposure will affect the amount and elemental composition of particulates that plants can tolerate. Dose-response relationship are therefore determined and predetermined by the background concentrations of various elements in the soil where the plant is growing.

Effects of surface accumulation of cement kiln dust on bean leaves have been investigated by Darley (1966). Doses of 0.6-3.8 g/m 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 visible foliar injury. Bean leaves dusted with cement kiln dust at the rate of 4.7 g/m^2/day for 2 days and then exposed to dew developed leaf rolling and interveinal necrosis (Lerman and Darley, 1975). Leaves not exposed to dew following the dust treatment 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 (Krause and Kaiser, 1977). Yield reductions of up to 36 percent were noted.

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 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 to 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.

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

8.9.1 Biotic Interactions

Few studies have exmained 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 (Schoenbeck, 1960). Increased occurrence of fungus-induced leaf spots on wild grape and sassafras have been observed near a source of heavy emissions of limestone dust (Manning, 1971). 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 non-exposed site did not result in decreased spore germination (Sharp, 1967, 1972).

8.10 EFFECTS OF SULFUR DIOXIDE AND PARTICULATES ON NATURAL ECOSYSTEMS

The previous sections of this chapter have discussed the effects of sulfur dioxide and particulate matter on individual plants. This section discusses the effects of these substances on natural ecosystems since, due to their complexity, these systems respond to environmental perturbations differently from individuals or populations of organisms.

Ecosystems are basically energy processing systems whose components have evolved together over a long period of time. They are composed of living organisms together with their physical environment (see Chapter 7, Table 7-1). The boundaries of the system are determined by the environmental conditions that determine the kinds of life forms that can exist in a particular habitat or region. The plant and animal populations within the system are the objects through which the system functions. Ecosystems respond to environmental changes or perturbations only through the response of the organisms of which they are composed (Smith, 1980).

*

Relationships among the various ecosystem components are structured, not haphazard. The living (biotic) and the non-living (abiotic) units are linked together by functional interdependence. Processes necessary for the existence of all life, the flow of energy and cycling of nutrients are based on the functional relationships that exist among the organisms within the system (Odum, 1971; Smith, 1980; Billings, 1978). Because of these relationships, unique attributes emerge when ecosystems are studied that are not observable when individuals, populations or communities are studied. For a more detailed account of ecosystems see Chapter 7, Section 7.1.2.

The discussion that follows emphasizes the response of terrestrial ecosystems to sulfur dioxide and particulate matter. Natural ecosystems are seldom, if ever, exposed to a single air pollutant. Therefore, the responses observed under ambient conditions cannot conclusively be attributed to a single substance such as sulfur dioxide or particulate matter alone.

8.10.1 Sulfur Dioxide In Terrestrial Ecosystems

Sulfur is an element that is essential for the normal growth and development of plants and animals. 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 plant requirements. Excessive sulfur in the form of sulfur dioxide however, 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 sources are in the atmosphere, living and dead organisms, and available and unavailable salts in the soil and rocks. The nutrients are cycled from the living to the non-living elements and back again. Air pollution, however, can disrupt nutrient cycling by altering the amounts in the various compartments and the rate of flow among them. (Smith, 1980; Chadwick, 1975).

The biogeochemical cycle of sulfur is both sedimentary and gaseous. Sulfur enters the atmosphere from the combusiton of fossil fuels, volcanic eruptions, the surface of oceans and gases released by decomposition processes (see Sources and Emissions, Chapter 4). Anaerobic decomposition of organic matter releases hydrogen sulfide (H_2S) into the atmosphere where it is quickly oxidized into sulfur dioxide. Sulfur dioxide is soluble in water and is carried back to earth in rainwater as weak sulfuric acid (H_2SO_4) (Smith, 1980). Regardless of the source, sulfur in soluble form is taken up by vegetation and is incorporated through a series of metabolic processes including photosynthesis into sulfur-containing amino acids. Sulfur is transferred from the producers to the consumers and through excretion and death back to the soil and to the sediments in the bottoms of ponds, lakes, and seas where bacterial action releases it as hydrogen sulfide or sulfate. Sulfur in the long-term sedimentary phase is tied up in organic and inorganic deposits in the soil and sulfur is added to ecosystems through geological weathering and meteorological processes with the latter being the predominant source. 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 8-9).

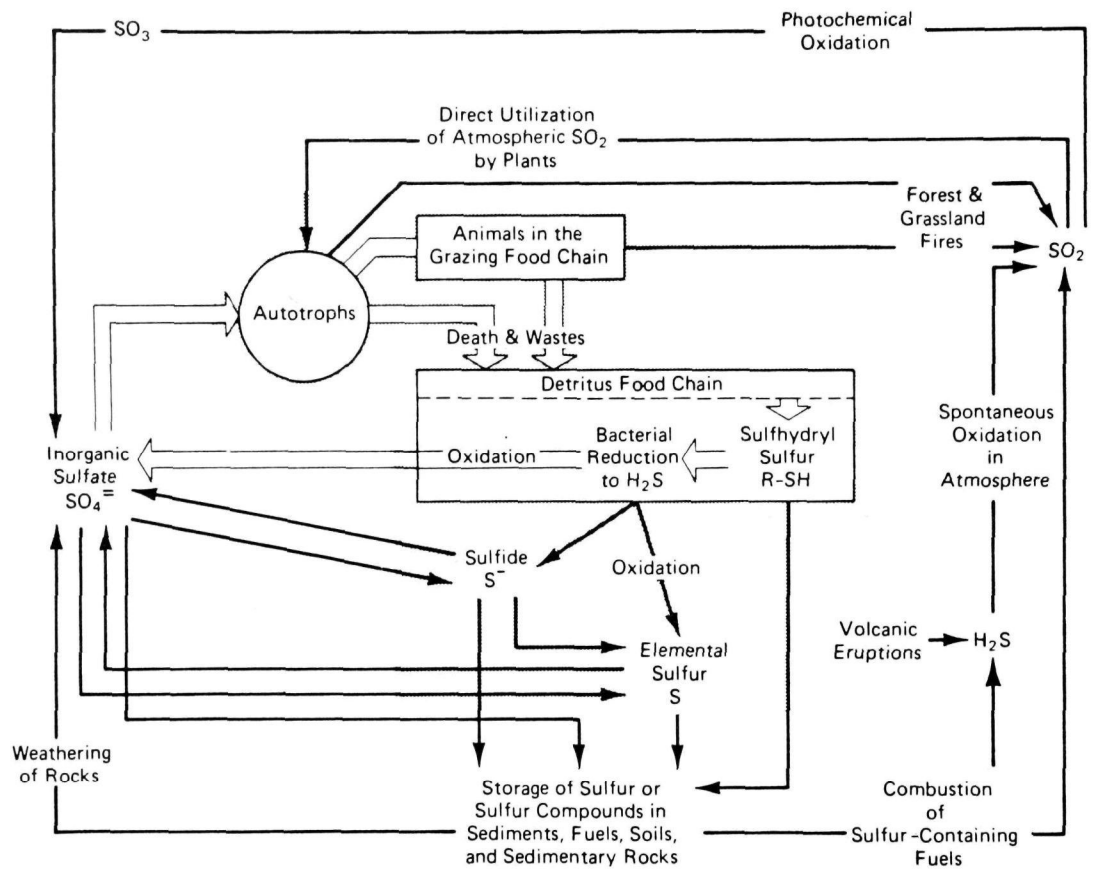


Figure 8-9. The sulfur cycle. Organic phase shaded.

Source: Clapham (1973).

*

Based on empirical watershed studies (Likens et al., 1977; Shriner and Henderson, 1978) and modelling (Coughenour, 1978), the soil is a major reservoir for atmospherically derived sulfur within in ecosystems. The majority of soil sulfur is unavailable to vegetation and is organically bound in the humus (May and Downes, 1968). Microbial activity oxidizes organically bound sulfur to sulfates. Sulfates may be taken up by plants or leached from the soil. The rate of sulfur released from the organic to the inorganic compartment is the major factor controlling the movement of sulfur between the soil and vegetation (May et al., 1972; Moss, 1976). A distinction between natural and agroecosystems is that soils in agroecosystems through continued cropping are depleted of their supply of organic sulfur and it is not renewable; therefore, sulfur must be added as fertilizer. Sulfur dioxide brought down in precipitation is also added to the soil. The amount of sulfur added to soils through precipitation will depend on the industrial activity of the surrounding area (Kamprath, 1972).

The influence of anthropogenic sources of sulfur on the sulfur cycle is most pertinent when addressed on a regional basis (Granat et al., 1976) as Shinn and Lynn (1979) have done for the northeastern United States. Comparing global versus regional sulfur cycling, atmospheric sulfur additions are not equally distributed over the global land areas, and the northeastern U.S. experiences anthropogenic atmospheric additions of sulfur that are 28.4 times that expected if additions were distributed uniformly over the globe. The most notable contrast between the global and regional sulfur cycle is the importance of atmospheric sulfur sources. Globally, natural processes far exceed anthropogenic contributions, whereas in the northeast man generates 12.5 times the amount of sulfur released by nature. A total of 27 x 10^6 tons of SO_4 enters the northeastern regional atmosphere annually and 13 x 10^6 tons are deposited within this region by wet and dry deposition; the remaining sulfur is exported to other areas of the globe.

The conclusion that SO_2 emitted into the atmosphere through anthropogenic activity is ultimately transferred to terrestrial and aquatic ecosystems is well documented (Meszaro et al., 1978). Unfortunately, the fate of sulfur in the ecosystem after deposition is not fully resolved. The issue is critical since ecosystems subject to excess nutrients or toxic materials do not commonly distribute them uniformly throughout the system but rather preferentially sequester them in specific pools or compartments. In addition, sulfur dioxide as a gas can cause injury to the vegetative components of an ecosystem so that energy flow and the cycling of other nutrients as well as sulfur may be disrupted.

Within the U.S. man is a major source of atmospheric sulfur and in the northeast alone anthropogenic sources exceed all others by a factor of 12.5. Within this region SO_2 levels annually average 16 $\mu g/m^{-3}$ (Shinn and Lynn, 1979) which is several times that recorded in pristine areas. The immediate fate of approximately 60 percent of this atmospheric sulfur is deposition on terrestrial and aquatic ecosystems; however, the subsequent fate of sulfur within the ecosystem is not fully known. Experimental evidence from forested watersheds coupled with results from simulation models indicates that sulfur in ecosystems is highly mobile. Although sulfur levels in the soil and vegetation compartments, in aggrading and mature ecosystems

*
impacted by SO_2 increase with time the majority of sulfur deposited annually is exported out of the system in stream flow.

8.10.2 Ecosystem Response to Sulfur Dioxide

The Kaybob gas plants (Fox Creek, Alberta, Canada), 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; however, white spruce (Picea glauca) stands predominate (Winner and Bewley, 1978a,b; Winner et al., 1978). Since these white spruce forests have less species variation than other sites, they were selected for analysis along a transect showing decreasing SO_2 stress. 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 (Legge et al., 1976). 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 (Winner and Bewley, 1978b). Numbers of white spruce seedlings close to the refinery were 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 (Winner and Bewley, 1978a). These results indicate that species diversity, particularly in the mosses, has changed as a consequence of sulfur gas emissions.

In subsequent study of the ecological fate of sulfur emissions in the same white spruce forests, Winner et al. (1978) 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 assessed the fate of emitted sulfur (Krouse, 1977). This condition of enhanced moss sensitivity has ecological consequences since mosses serve several unique functions within a forest. These included water storage, soil formation, eorosion prevention, and nutrient cycling.

A second study of the effects of chronic sulfur gas emissions on a forested ecosystem were conducted in a region experiencing effluents from a natural gas-processing facility (West Whitecourt Gas Plant, Whitecourt, Alberta, Canada)(Legge et al., 1976). 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 0.2 ppm/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 concentrations of SO_2 remained in the forest for 4 hours; however, over 46 percent of all hours monitored were characterized by pollutant concentrations below 0.05 ppm. The highest instantaneous level was 0.45 ppm; pollution concentrations were greater during daylight hours. These data depicting the ambient SO_2 exposure for the forest are specific for 1975.

Two locations were selected based upon their similarity in many edaphic, climate, 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 a reference and SO_2-stressed location. Using basal-area increments as an example (Legge et al., 1976), trees nearer the source showed smaller incremental additions, beginning in 1964 and continuing through 1975; statistically significant differences were obtained in 1971 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.

The movement of materials within the forest also showed signs of SO_2-induced modifications (Legge et al., 1976). This phase of the study compared indices of changes in a series of sites selected for their similarity in vegetation and 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.

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; higher soil acidity was recorded proximal to the source of SO_2.

Pollutant-incuded modifications of the biogeochemical cycles were not restricted to sulfur alone but were also evident in other inorganic elements. The most striking and consistent pattern was recorded with manganese distribution. Over four successive years, the manganese content of lodgpole x jackpine needles decreased with increasing distance away from the source. 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 forest. 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 the near future, the grasslands of the upper plains will be subject to SO_2 emissions from new coal-burning power facilities that are being constructed in areas rich in coal

*
reserves (Durran et al., 1979). To address this problem, plots of Montana grasslands were exposed to SO_2 during growing seasons of successive years. The monthly median exposure levels were approximately 0, 0.02 (52 $\mu g/m^3$), 0.04 (106 $\mu g/m^3$), and 0.07 ppm (185 $\mu g/m^3$) SO_2 and were delivered by a zonal air pollution system or ZAPS (Lee et al., 1978). Field observations over four years verified that these concentrations were not sufficient to elicit any leaf lesions characteristic of acute SO_2 (Heitschmidt et al., 1978). 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 (Preston, 1979).

The most prevalent producer species within the grassland is a perennial, Agropyron 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 with time of exposure and canopy-level SO_2 concentrations (Lauenroth et al., 1980). This relationship was most conspicuous with the two higher exposure regimens, and total foliar sulfur in the highest exposure plot was three times greater than that in vegetation sampled from control locations (Lauenroth and Heasley, 1980). As the sulfur content of leaf tissue increased, the ratio of nitrogen to sulfur decreased (Laurenroth and Heasley, 1980).

These biochemical changes in the major producer species were 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 two weeks at 105 and 185 $\mu g/m^3$ SO_2 (Laurenroth and Heasley, 1980). 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 (Heitschmidt et al., 1978).

Dominant producers were not the only flora exhibiting sensitivity to SO_2. In simulated pollutant exposure using a bisulfate solution, Sheridan (1979) showed that nitrogenase activity in a major component of the lichen flora (Dollema 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 the light of the importance of soil lichens in regulating nitrogen fixation in the grasslands (Sheridan, 1979).

Further evidence of SO_2-associated effects on 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, 1980). Decomposition rates were apparently also altered with less litter disappearance 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 (Laurenroth and Heasley, 1980).

Larger consumers also exhibited responses reflecting the presence of SO_2 in the atmosphere; however, the responses were not dose dependent (Chilgren, 1978). 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 (habital preference) whereby individuals seek habitats free of the pollutant.

In summary, at SO_2 levels above 0.02 ppm (52 $\mu g/m^3$), SO_2 induced changes in the performance of producers, consumer, and decomposers. Many of the responses are individually small, but collectively over time they are gradually modifying the structure and function of the grasslands. The significance of these changes to the long-term persistence of the ecosystem remains controversial (Preston, 1979).

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, geochemistry, 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.

The influence of prolonged SO_2 exposures on plant communities is not well documented; however, a theoroetcal basis from which to evaluate effects is emerging. This conceptual effort is exemplified by the development of a generalized forest growth model (Botkin et al., 1972) that was designed to assess the consequences of perturbation on plant communities (Botkin, 1976; Shugart and West, 1977). This model has been applied to the response of a mixed species, deciduous forest in the southeastern U.S. to differential levels of growth reduction (0, 10, and 20 percent) following simulated air pollution stress (West et al., 1980). Over several decades, simulated pollution stress altered the biomass importance of the major tree species within the forest; some species populations increased while others decreased in importance. These results suggest that competitive interactions between species may significantly modify both the level and direction of change in growth rate of individual species in response to air pollution stress. Stand age was also shown to strongly influence the role of competition in modifying responses of individual species within the forest community. 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 interaction with sensitive species, can be expected to be enhanced under stresses such as air pollution which does not affect all species equally (West et al., 1980). An understanding of this governing role of species interactions is essential to predicting how ecosystems respond to low levels of pollution (Botkin, 1976). 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 (Miller and McBride, 1975; Kickert and Miller, 1979).

The results from community level studies in areas experiencing chronic levels of SO_2 lend credence to the modelling effort. Using communities comprised of only 2 or 3 different species, Guderian (1967) analyzed community level responses to SO_2 and their underlying causes. Changes in community composition were a function of pollutant dose; the higher the does the more rapidly the community changed. Altered community composition was attributed to both direct SO_2 effects on sensitive species' populations and indirect changes in species' interactions. Community biomass exhibited little quantitative change but striking differences in species composition. Similar conclusions have been reached in studies of natural plant communities experiencing prolonged SO_2 exposure (Guderian and Stratmann, 1966; Rosenberg et al., 1979). Rosenberg et al. (1979) assessed species composition in 27 stands of natural regrowth, Northern hardwood forest dominated by oaks (Quercus spp.), white pine (P. strobus), and hemlock (Tsuga canadensis). The stands, which varied in their distance from a 25-year-old coal-consuming 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 plants (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 (Shannor-Weiner). In spite of these SO_2-induced changes in community composition, an index of aboveground biomass (basal area of overstory species) exhibited no variation among stands. Among the vascular plants, shrub and ground vegetation was more responsive (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.

Some of the most notable examples of SO_2 affecting plant communities are the responses of cryptogamic flora (lichens and mosses), and several reviews are available (DeSloover and LeBlanc, 1968; Hawksworth, 1971). A map of epiphytic lichen communities for England and Wales has been devised which associates progressive shifts in species composition with SO_2 levels (Hawksworth and Rose, 1970). 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 bioassay to estimate ambient SO_2 levels.

Similar mapping efforts are reported for several regions of North America. In a rural area of Ohio surrounding a coal-consuming 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 (Showman, 1975). In regions experiencing an annual SO_2 average exceeding 0.020 ppm, both species were absent. 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 (1973) to affect the ability of sensitive lichen species to survive and reproduce; acute and chronic symptoms of SO_2 toxicity in epiphytic lichens occurred when annual averages of SO_2 exceeded 0.03 and 0.006-0.03 ppm, respectively.

The susceptibility of crytogamic flora to elevated levels of SO_2 may influence the movement of materials within the ecosystem. In the northwestern coniferous forests, lichens fix 2-11 kg/ha of nitrogen, which represents 5-20 percent of the total nitrogen requirement for the dominant producer, Douglas fir (Denison, 1973).

The network of biotic-abiotic interactions, which is characteristic of managed and natural ecosystems, leads to the hypothesis that SO_2 effects on producers must have repercussions to other trophic levels. Demonstration of such responses, however, is difficult experimentally, and an accurate assessment of the specific importance of SO_2 in eliciting these responses is complicated by the often complex relationships between producers, consumers, and decomposers.

Consumer and decomposers may respond to SO_2 via a direct, adverse effect of the pollutant. The presence of elevated atmospheric levels of SO_2 is particularly relevant to soil organisms (Babich and Stotzky, 1979) since soils are preferential sulfur accumulation sites. This focus on soil-borne organisms takes on even more relevance since the rhizosphere is not only biologically active but also the major site for sulfur accumulation within the ecosystem (Legge et al., 1976). In a forested area experiencing atmospheric SO_2 levels averaging 0.048 ppm, the species composition of soil microflora shifted toward a greater number and frequency of species capable of utilizing the soil sulfur additions (Wainwright, 1979). Specifically, the levels of thiobacilli and sulfur-oxidizing fungi were positively correlated with levels of SO_2 stress and soil depth.

The edaphic and climatic environment strongly influences the community of plants, animals and microorganisms that develop at a given site. In natural ecosystems in sulfur deficient soils, communities have evolved within the constraints imposed by a limited supply of sulfur. Although atmospherically derived sulfur may not be sufficient to cause injury, the prolonged input of sulfur may relax the constraints of a limited sulfur supply thereby inducing shifts in species composition.

8.10.3 Response of Natural Ecosystems to Particulate Matter

Particulate matter originating from both natural and anthropogenic emission sources is a common component of the atmosphere. As discussed in Section 8.7, the heterogeneous physical and chemical nature of particulates presents problems in addressing the significance of elevated atmospheric particulate levels for natural and agroecosystems.

Wet and dry deposition are the two processes by which particulates are transferred from the atmosphere to terrestrial ecosystems. The fate of particulates deposited on foliar surfaces depends on the solubility of the constituents (chemicals and elements), the occurrence of precipitation, and the sorptive capacity of the leaf (Little, 1973). 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 (Klake, 1974). Leaf surfaces may be only a transitory site for particulate matter and its associated constituents. If not retained by the leaf, material is ultimately transferred to the forest floor through washoff in rain events or litterfall. 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 heavy metals deposited in natural ecosystems (e.g., Coughtrey et al., 1979; Thompson et al., 1979).

Given the regional character of particulate emissions, particularly along the east coast (National Air Quality, Monitoring and Emissions Trend Report, 1978), the fate of particulates in terrestrial ecosystems experiencing low levels particulate pollution needs to be assessed. In a deciduous forest in the Southeast, wet and dry deposition of aerosols, gases, precipitation and large particulates 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 (Linberg et al., 1979). These seemingly large percentages are typical for rural or remote areas even though 3 major coal consuming power facilities (total coal consumption of 7×10^6 tons/year) were within 20 km of the forest.

Irrespective of the source of particulates deposited in the forest, the atmosphere contributed a major portion of the trace element inputs (Lindberg et al., 1979). Water solubility was critical since insoluble constituents associated with the particulate were not readily mobilized within the forest. Any event promoting solubilization (e.g., aerosol formation, rainfall scavenging, moisture formation on leaves) enhanced an element's mobility.

The leaf surface is not the only accumulation site for particulates and their associated constituents within the ecosystem. Through precipitation scavenging of particulates in air, washoff of surface deposits or litterfall, particulates are transferred to the soil where they are tightly bound to decaying organic matter. The upper soil horizon, including the decaying organic material, is a region of intense biological activity as a result of the physical degradation of litter, remineralization of the bound materials and root uptake of the plant-available nutrients. Consequently, particulate emissions that interfere with microbial activity can have delayed effects on primary production (Tyler, 1972) and soil consumer species.

In summary, even though the impact of particulate matter on terrestrial ecosystems is most apparent proximal to large emission sources, ecosystems within the same geographic region may be the site of deposition. Foliar surfaces are the most common 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. However, concern for terrestrial ecosystems must also address elements and chemicals that may be associated with the particulates. Solubility of these particulate constituents is a critical factor since insolubility limits mobility within the ecosystem. One common behavior of particulates is their tendency to selectively accumulate within a given component of the landscape. Soils are long-term sites for the retention of many constituents found in particulates. While

*
this accumulation in the soil-litter layer has had demonstrable adverse consequences for ecological processes such as decomposition, mineralization, nutrient cycling and primary production around some point sources, the effects of the much lower levels chronically deposited over large regions have not yet produced documented adverse impacts to natural ecosystems.

8.11 SUMMARY

The widespread occurrence of particulate matter and sulfur dioxide in the atmosphere results frequently 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 on plant life. 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 after entering plant cells from the stomata 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 insignificant changes in the 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 quite variable since response is governed by pollutant dose (concentration x duration of exposure), kinetics of the exposure (e.g., day vs night, peak vs long-term); physiological status of the plant, phenological stage of plant growth, environmental influences on the pollutant/plant interaction, and the environmental influences on the metabolic status of the plant itself.

There are several possible plant responses to SO_2 and related sulfur compounds: (1) fertilizer effects appearing as increased growth and yields, (2) no detectable responses, (3) injury manifested as growth and yield reductions without visible symptom expressions on the foliage or with very mild foliar symptoms that would be difficult to perceive as air pollution incited without the presence of a control set of plants grown in pollution-free conditions, (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reduction in growth and yield, and (5) death of plants and plant communities.

A member of species of plants are sensitive to low levels of SO_2. Some of these plants 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. Various species of lichens appear to be among the most sensitive plants.

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

*
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 matter and wet deposition of gases and particles bring sulfur compounds into contact with plant surfaces and soil substrates. The effects of such exposures 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 pollutant uptake through internal physiological changes as well as stomatal opening and closing and hence play a major role in determining sensitivities of species and cultivars or the time of sensitivity of each on a seasonal basis. Dose-reponse relationships are significantly conditioned by environmental conditions before, during, and following exposure to SO_2.

Analysis of existing data sets relating SO_2 exposure concentration to both visible injury of foliage and reduced growth and yield indicate that both thresholds of reponse and generalized average reponse can presently be described mathematically. For visible injury, the threshold varied with duration of exposure ranging from 0.4 ppm for 1 hr (0.4 ppm/hr) to 0.15 ppm for 8 hr (1.2 ppm/hr). The response threshold was 0.5 ppm for 3 hr (1.5 ppm/hr). For plant species growing in the vicinity of a coal-fired power plant approximately 10 percent of the species visibly injured by SO_2 experienced that injury at peak, 1-hr, and 3-hr average concentrations of 1.00, 0.45, and 0.28 ppm, respectively.

Since, under many conditions, visible injury may not lead directly to measurable losses in plant productivity, correlations of productivity with exposure dose represent the most direct link to the effects of SO_2 on economic and ecological parameters of plant response. Regression analysis of data from both controlled exposures in field chambers and from laboratory and greenhouse studies showed positive and statistically significant correlations between degree of yield loss and logarithmically transformed exposure dose in ppm/hr. The plants and conditions utilized in field studies, which were heavily oriented toward crop plants, provided generally lower yield losses for the same exposure dose than did laboratory and greenhouse studies. In field studies a 20 percent yield loss was associated with approximately 27 ppm/hr of accumulative exposure dose. In laboratory studies with agronomic, ornamental, and native species a 20 percent yield loss occurred after only 9 ppm/hr of cumulative exposure dose.

A critical need in evaluating the likelihood of adverse effects occurring in association with longer-term SO_2 exposures is the indentification of the fraction of the total SO_2 exposure

*
which may constitute a stress to plant growth and development. A review of dose-response data indicates that this level may be approximately 0.05 ppm for sensitive species. Additional data from studies involving SO_2 alone and in combination with other pollutants may provide a more accurate basis for determining this level.

At present, data concerning the interactions of SO_2 with other pollutants indicates that, on a regional scale, SO_2 occurs at least intermittently at concentrations high enough to produce significant interactions with other pollutants, principally O_3. A major weakness in the approach to pollutant interactions, however, is the lack of in-depth analysis of existing regional air quality data sets for the three principal pollutants (SO_2, O_3, and NO_2). These data should determine how frequently and at what concentrations the pollutants occur together both spatially and temporally within regions of major concern. The relative significance of simultaneous versus sequential occurrence of these pollutants to effects on vegetation is also not well documented and is critical in evaluating the likelihood and extent of potential pollutant interactions under field conditions.

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 vegetational 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 result 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.

Natural ecosystems are integral to the maintenance of the biosphere and disturbances of stable ecosystems may have long-range effects which are difficult to predict. Within the United States anthropogenic contributions to atmospheric sulfur exceed natural sources. In the Northeast these contributions exceed natural sources by a factor of 12.5 and approximately 60% of the anthropogenic emissions into the atmosphere are deposited (wet and dry deposition) on terrestrial and aquatic ecosystems; its subsequent fate and distribution in these systems is not well understood. Wet deposition of sulfur compounds is discussed in Chapter 7.

Data relating ecosystem responses to specific doses of SO_2 and other pollutants are difficult to obtain and interpret because of the generally longer periods of time over which these responses occur and because of the many biotic and abiotic factors which modify them.

Vegetation within terrestrial ecosystems is sensitive to SO_2 toxicity, as evidenced by changes in physiology, growth, development, survival, reproductive potential and community composition. Indirect effects may occur as a result of habitat modification through influences on litter decomposition and nutrient cycling or through altered community structure. At

*
the community level chronic exposure to SO_2, particularly in combination with other pollutants such as O_3, may cause shifts in community composition as evidenced by elimination of individuals or populations sensitive to the pollutant. Differential effects on individual species within a community can occur through direct effects on sensitive species and through alteration of the relative competitive potential of species within the plant community.

Particulate emissions have their greatest impact on terrestrial ecosystems near large emission sources. Particulate matter in itself constitutes a problem only in those few areas where deposition rates are very high. Ecological modification may occur if the particles contain toxic elements, even though deposition rates are moderate. Solubility of particle constitutents is critical, since water-insoluble elements are not mobile within the ecosystem. Most of the material deposited by wet and dry deposition on foliar surfaces in vegetated areas is transferred to the soil where accumulation in the litter layer occurs.

8.12 REFERENCES

Adepipe, N. O., R. E. Barrett, and D. P. Ormrod. Phototoxicity and growth response of ornamental bedding plants to ozone and sulfur dioxide. J. Am. Soc. Hortic. Sci. 97:341-345, 1972.

American Phytopath. Soc. Glossary of air pollution terms and selected reference list. Phytopathology News 8:5-8, 1974.

Anderson, P. J. The effect of dust from cement mills on the setting of fruits. Plant World 17:57-68, 1914.

Anderson, A. J., D. R. Meyer, and F. K. Mayer. Heavy metal toxicities: levels of nickel, cobalt, and chromium in the soil and plants associated with visual symptoms and variation in growth of an oat corp. Aust. J. Agric. Res. 24:557-571, 1973.

Anderson, T. J. The effect of dust from cement mills on setting of fruits. Plant World 17:57-68, 1974.

Ashenden, T. W., and T. A. Mansfield. Influence of wind speed on the sensitivity of ryegrass to SO_2. J. Exp. Bot. 28:729-735, 1977.

Ashenden, T. W. Growth reductions in Cocksfoot (Dactylis golmerata L.) as a result of SO_2 pollution. Environ. Pollut. 15:161-166, 1978.

Ashenden, T. W. The effects of long-term exposures to SO_2 and NO_2 pollution on the growth of Dactylis golmerata L. and Poa pratensis L. Environ. Pollut. 18:249-258, 1979.

Babich, H., and G. Stotzky. Air pollution and microbial ecology. CRC Crit. Rev. Environ. Control 4:353-421, 1974.

Ballentyne, D. J. Sulfite inhibition of ATP formation in plant mitrochondria. Phytochemistry 12:1207-1209, 1973.

Bazzaz, M. B., and Govindjee. Effects of lead chloride on chloroplast reactions. Environ. Lett. 6:175-191, 1974.

Bell, J. N. B., and W. S. Clough. Depression of yield in ryegrass exposed to sulfur dioxide. Nature 241:47-49, 1973.

Bennett, J. H., and A. C. Hill. Inhibition of apparent phytosynthesis by air pollutants. J. Environ. Qual. 2:526-530, 1973a.

Bennett, J. H., A. C. Hill, A. Soleimani, and W. H. Edwards. Acute effects of combination of sulfur dioxide and nitrogen dioxide on plants. Environ. Pollut. 9:127-132, 1975.

Berigari, M. S., C. F. Jordan, and C. A. Feickert. The Effect of Sulfur Dioxide on Yield and Growth of Kidney Beans (Phaseolus vulgaris L.). Argonne Nat. Lab. Radiol. Environ. Res. Div. Annu. Rep. (Ecol.), January-December 1974. pp. 51-61.

Berry, C. R. Relative sensitivity of red, jack, and white pine seedlings to ozone and sulfur dioxide. Phytopathology 61:231-232, 1972.

Billings, W. D. Plants and the Ecosystem. 3rd ed. pp. 1-62. Wadsworth Publishing Company, Inc. Belmont, PA., 1978. 177 p.

Black, V. J., and M. H. Unsworth. Effects of low concentrations of sulphur dioxide on net photosynthesis and dark respiration of Vicia faba. J. Exp. Bot. 30:473-483, 1979.

Boertitz, S., H. G. Daessler, and E. Friedrich. Effect of metallurgical dust on agricultural plants. Tech. Umweltschutz 15:247-254, 1976.

Bonte, J., L. DeCormis, and P. Louguet. Effect of sulfur dioxide pollution on the degree of opening of Pelargonium x hortorum stomata. C. R. Hedb. Sciences Acad. Sci. Ser. D 280:2377-2380, 1975.

Botkin, D. B., J. F. Janak, and J. R. Wallis. Some ecological consequences of a computer model of forest growth. J. Ecol. 60:849-872, 1972.

Botkin, D. B. The role of species interactions in the response of a forest ecosystem to environmental perturbation. In: Systems Analysis and Simulation in Ecology, vol. IV. B. C. Patten, ed., Academic Press, New York, NY, 1976. pp. 147-173.

Bradford, G. R. Boron. In: Diagnostic Criteria for Plants and Soils. H. G. Chapman, ed., University of California, 1966. pp. 33-61.

Brady, N. C. The Nature and Properties of Soils, 8th edition. MacMillan Publishing Co., New York, NY, 1974. 639 pp.

Brandt, C. S., and W. W. Heck. Effects of Air Pollutants on Vegetation. In: Air Pollution, vol. I: Air Pollution and Its Effects. A. C. Stern, ed., Academic Press, New York, NY, 1968. pp. 401-443.

Brandt, C. J., and R. W. Rhoades. Effects of limestone dust accumulation on composition of a forest community. Environ. Pollut. 3:217-225, 1972.

Brandt, C. J., and R. W. Rhoades. Effects of limestone dust accumulation on lateral growth of forest trees. Environ. Pollut. 4:207-213, 1973.

Buron, A., and G. Cornic. Effect of sulfur dioxide on gas exchange in white mustard (Sinapsis alba). Bull. Soc. Vaudoise Sci. Natur. 71:451-461, 1973.

Carlson, R. W. Reduction in the photosynthetic rate of Acer Quercus and Fraxinus species caused by sulphur dioxide and ozone. Environ. Pollut. 18:159-170, 1979.

Chadwick, 1975.

Chamberlain, A. C. The Movement of Particles in Plant Communities. In: Vegetation and the Atmosphere, Vol. 1: Principles. J. L. Monteith, ed., Academic Press, London, England, 1975. pp. 155-203.

Chiba, O., and V. Tanaka. The effect of sulphur dioxide on the development of pine needle blight caused by Rhizosphaera kalkhoffii Bubak (I). J. Jap. For. Soc. 50:135, 1968.

Chilgren, J. D. The response of prairie deer mice to a field SO_2 gradient. In: Proceedings of the 4th Joint Conf. Sensing of Environmental Pollutants. American Chemical Society, Washington, DC, 1978. pp. 61-65.

Clapham, W. B. J. Natural Ecosystems. The Macmillan Company, N.Y., 1973. p. 43.

Clough, W. S. The deposition of particles on moss and grass surfaces. Atmos. Environ. 9:1113-1119, 1975.

Cogbill, C. V. The history and character of acid precipitation in eastern North America. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, U.S. Department of Agriculture and Ohio State University, Columbus, Ohio, May 12-15, 1975. L. S. Dochinger and T. A. Selige, eds., USDA Forest Service General Technical Report NE-23, U.S. Department of Agriculture, Upper Darby, PA, 1976. pp. 363-370.

Coleman, R. The importance of sulfur as a plant nutrient in world crop production. Soil Science 101:230-239, 1966.

Constantinidou, H. A., and T. T. Kozlowski. Effects of sulfur dioxide and ozone on Ulmus americana seedlings. I. Visible injury and growth. Can. J. Bot. 57:170-175, 1979a.

Constantinidou, H. A., and T. T. Kozlowski. Effects of sulfur dioxide and ozone on Ulmus americana seedlings. II. Carbohydrates, proteins, and lipids. Can. J. Bot. 57:176-184, 1979b.

Costonis, A. C. Injury to eastern white pine by sulfur dioxide and ozone alone and in mixtures. Eur. J. For. Pathol. 3:50-55, 1973.

Cotrufo, C., and C. R. Berry. Some effects of a soluble NPK fertilizer on sensitivity of eastern white pine to injury from SO_2 air pollution. Forensic Sci. 16:72-73, 1970.

Coughenour, M. B. Grasslands Sulfur Cycle and Ecosystem Response to Low-Level SO_2. Ph.D. Thesis, Colorado State University, Fort Collins, CO, 1978. 353 p.

Coughtrey, P. J., C. H. Jones, M. H. Martin, and S. W. Shales. Litter accumulation in woodlands contaminated by Pb, Zn, Cd and Cu. Oecologia 39:51-60, 1979.

Cowling, D. W., and L. H. P. Jones. Sulphur deficiency on two forage plants in England. Sulphur Institute J. 6:11, 1971.

Cowling, D. W., L. H. P. Jones, and D. R. Lockyer. Increased yield through correction of sulfur deficiency in ryegrass exposed to sulfur dioxide. Nature 243:479-480, 1973.

Cowling, D. W., and D. R. Lockyer. The effect of SO_2 on Lolium perenne L. grown at different levels of sulfur and nitrogen nutrition. J. Exp. Bot. 29:257-265, 1978.

Cowling, D. W., and M. J. Koziol. Growth of ryegrass (Lolium perenne L.) exposed to SO_2. I. Effects on photosynthesis and respiration. J. Exp. Bot. 29:1029-1036, 1978.

Czaja, A. T. Zementstaubwir-Kungen auf pflanzen: Die enstehung der Zementkrusten. Qual. Plant Mater. Veg. 8:201-238, 1961.

Daessler, H. G., J. Ranft, and K. H. Rehn. The susceptibility of woody plants exposed to fluorine compounds and sulfur dioxide. Flora (Jean) 161:289-302, 1972.

Daines, R. H. Sulfur dioxide and plant response. J. Occup. Med. 10: 516-534, 1968.

Darley, E. F. Studies on the effect of cement-kiln dust on vegetation. J. Air Pollut. Control Assoc. 16:145-150, 1966.

Davis, D. D. Sulfur Dioxide and Deciduous Plants. Air Pollution and Plants Series. PA. Coop. Ext. Ser. U. Ed. 3-17, 1972a. 2 pp.

Davis, D. D. Sulfur Dioxide and Evergreens. Air Pollution and Plants Series. Pa. Coop. Ext. Serv. U. Ed. 3-526, 1972b. 2 pp.

Davis, J. B., and R. L. Barnes. Effects of soil-applied fluoride and lead on growth of loblolly pine and red maple. Environ. Pollut. 5:35-44, 1973.

Davis, D. D., and R. G. Wilhour. Susceptibility of woody plants to sulfur dioxide and photochemical oxidants: a literature review. EPA 600/3-76-102, U.S. Environmental Protection Agency, Corvallis, OR, September 1976.

Demeritt, M. E., Jr., W. M. Chang, J. D. Murphy, and H. D. Gerhold. Selection system for evaluating resistance of Scots pine seedlings to ozone and sulfur dioxide. In: Proceedings of the 19th Northeastern For. Tree Improvement Conf., 1971.

Denison, W. E. Life in tall trees. Sci. Am. 228:74- , 1973.

DeSloover, J., and F. LeBlanc. Mapping of atmospheric pollution on the basis of lichen sensitivity. In: Proceedings of the Symp. Recent Adv. Trop. Ecol. R. Misra and B. Gopal eds., The International Society for Tropical Ecology, Varanashi-5, India, 1968. pp.42-56.

Dochinger, L. S., and W. W. Heck. An ozone-sulfur dioxide synergism produces symptoms of chlorotic dwarf disease of eastern white pine. Phytopathology 59:399, 1969.

Dochinger, L. S., and K. F. Jensen. Effects of chronic and acute exposure to sulfur dioxide on the growth of hybrid poplar cuttings. Environ. Pollut. 9:219-229, 1975.

Domes, W. Uterschiedliche CO_2-Abhangigkeit des Gasaustaushes beider Blattseiten von Zea Mays. Planta 98:186-189, 1971.

Donaubauer, E. Sekundarshaden in Osterreichischen Rauchschadensgegieten. Schwierigkeiten der Diagnose and Bewertung. Niedzynarodoweg Konf. Wplyw Zanieczyszczen Powietrza na Lasy, 6th., Katowice, Poland, 1968.

Dreisinger, B. P. Sulfur dioxide levels and the effects of the gas on vegetation near Sudbury, Ontario. Presented at the 58th Annual Meeting, APCA, Toronto, Ontario, 1965. Paper no. 65-121.

Dreisinger, R. B., and P. C. McGovern. Monitoring Atmospheric Sulfur Dioxide and Correlating its Effects on Crops and Forests in the Sudbury Area. In: Impact of Air Pollution on Vegetation Conf. S. N. Linzon, ed., Ontario Department of Energy and Resource Management, Toronto, 1970. 122 pp.

Durran, D. R., M. J. Meldgin, M. Liu, T. Thoem, and D. Henderson. A study of long-range air pollution problems related to coal development in the northern Great Plains. Atmos. Environ. 13: 1021-1037, 1979.

Embleton, T. W. Magnesium. In: Diagnostic Criteria for Plants and Soils. H.D. Champman, ed., University of California Division of Agricultural Sciences, Riverside, CA. 1966. pp. 225-263.

Enderlein, H., and W. Kastner. What effect has a nutrient deficiency on the resistance of one-year-old conifers to SO_2? Arch. Forstwes. 16:431-435, 1976.

Faller, N. Effects of atmospheric SO_2 on plants. Sulfur Inst. J. 6:5-7, 1970.

Fankhauser, N. C. Brunold, and K. N. Erisman. The influence of sublethal concentrations of sulfur dioxide on morphology, growth and production yield of the duckweed Lemne minor L. Oecologia 23:201-208, 1976.

Ferenbaugh, R. W. Effects of prolonged exposure of Oryzopsis hemenoides to SO_2. Water Air Soil Pollut. 10:27-31, 1978.

Garland, J. A. Dry and wet removal of sulfur from the atmosphere. Atmos. Eviron. 12:349-362, 1978.

Gerhold, H. D. Effect of air pollution on Pinus strobus L. and genetic resistance. EPA-600/3-77-002, U.S. Environmental Protection Agency, Corvallis, OR, January 1977.

Gilbert, O. L. An alkaline dust effect on epiphytic lichens. Lichenologist 8:173-178, 1976.

Godzik, S., and H. F. Linskens. Concentration changes of free amino acids in primary bean leaves after continuous and interrupted SO_2 fumigation and recovery. Environ. Pollut. 7:25-28, 1974.

Granat, L., H. Rehe, and R. O. Hallberg. The global sulfur cycle. Ecol. Bull. (Stockholm) 22:89-134, 1976.

Guderian, R. Reaktione von Fflanzer Gemeinschaften des Feslufferbaues auf Schwefeldioxideinwirkungen. Essen: Girardet-Verlag, Schriftenr. Landesnst. Immisions-Bodennutsungssch. d. Landes Nordrheim-Westfalen 4:80-100, 1967.

Guderian R., and H. Stratmann. Freilandversuche zur Ermittlung von Schwefeldioxidwirkungen auf die Vegetation. III. Grenzewerte schadlicher SO_2-Immissionen fur Obst-und Forstkulturen Sowie fur land wirtschaftliche and gratnerische Pflanzenarten. Forschunsber. Landes Nordrhein-West-falen Nr. 1920. Westdeutscher Verlag, Cologne, 1968. 113 pp.

Guderian, R. Air Pollution: Phytotoxicity of Acidic Gases and its Significance in Air Pollution Control. Springer-Verlag, Berlin, 1977. 127 pp.

Guderian, R. Terrestrial Vegetation--Air Pollutant Interactions: Non-Gaseous Air Pollutants. Presented at the International Conference on Air Pollutants and Their Effects on the Terrestrial Ecosystem. Banff, Alberta, Canada, May 10-17, 1980.

Haisman, D. R. The effect of sulfur dioxide on oxidizing enzyme systems in plant tissue. J. Sci. Food Agric. 25:803-810, 1974.

Halbwachs, G. Der Wasserhaushalt rauchgeschadigter Holzgewasche. Allg. Forstz. 78:196-197, 1976.

Hallgren, J-E. Physiological and Biochemical Effects of Sulfur Dioxide on Plants. In: Sulfur in the Environment, vol. 2. J. O. Nriagu, ed., John Wiley & Sons, New York, NY, 1978. pp. 163-210.

Hawksworth, D. L. Lichens as litmus for air pollution: a historical review. Int. J. Environ. Stud. 1:281-296, 1971.

Hawksworth, D. L., and F. Rose. Qualitative scale for estimating sulfur dioxide air pollution in England and Wales using epiphytic lichens. Nature 227:145-148, 1970.

Heagle, A. S. Interactions between air pollutants and plant parasites. Annu. Rev. Phytopathol. 11:365-388, 1973.

Heagle, A. S., D. E. Body, and G. E. Neely. Injury and yield responses of soybean to chronic doses of ozone and sulfur dioxide in the field. Phytopathology 64:132-136, 1974.

Heagle, A. S., and J. W. Johnston. Variable responses of soybeans to mixtures of ozone and sulfur dioxide. J. Air Pollut. Control Assoc. 29:729-732, 1979.

Heck, W. W., and C. S. Brandt. Effects on Vegetation: Native, Crops, Forest. In: Air Pollution. A. C. Stern, ed., Academic Press, New York, NY, 1977. pp. 157-229.

Heck, W. W., and J. A. Dunning. Response of oats to sulfur dioxide: interactions of growth temperature with exposure temperature or humidity. J. Air Pollut. Control Assoc. 28:241-246, 1978.

Heggestad, H. E., K. L. Tuthill, and R. N. Stewart. Differences among poinsettias in tolerance to sulfur dioxide. Hort. Sci. 8:377-338, 1973.

Heitschmidt, R. K., W. K. Lauenroth, and J. L. Dodd. Effects of controlled levels of sulfur dioxide on western wheatgrass in a southeastern Montana grassland. J. Appl. Ecol. 14:859-868, 1978.

Hill, A. C., S. Hill, Lamb, and T. W. Barrett. Sensitivity of native desert vegetation to SO_2 and SO_2 and NO_2 combined. J. Air Pollut. Control Assoc. 24:153-157, 1974.

Hofstra, G., and D. P. Ormrod. Ozone and sulfur dioxide interaction in white bean and soybean. Can. J. Plant Sci. 57:1193-1198, 1977.

Horsman, D. C., and A. R. Wellburn. Synergistic effect of SO_2 and NO_2 polluted air upon enzyme activity in pea seedlings. Environ. Pollut. 8:123-133, 1975.

Horsman, D. C., and A. R. Wellburn. Appendix II. Guide to Metabolic and Biochemical Effects of Air Pollutants on Higher Plants. In: Effects of Air Pollutants on Plants. T. A. Mansfield, ed., Cambridge University Press, Cambridge, 1976. pp. 185-199.

Horsman, D. C., T. M. Roberts, and A. D. Bradshaw. Evolution of sulfur dioxide tolerance in perennial ryegrass. Nature 276:493-494, 1978.

Hou, L-Y., A. C. Hill, and A. Soleimani. Influence of CO_2 on the effects of SO_2 and NO_2 on alfalfa. Environ. Pollut. 12:7-16, 1977.

Houston, D. C., and G. R. Stairs. Genetic control of sulfur dioxide and ozone tolerance of eastern white pine. For. Sci. 19:267-271, 1973.

Houston, D. B. Response of selected Pinus strobus L. clones to fumigation with sulfur dioxide and ozone. Can. J. For. Res. 4:65-68, 1974.

Husar et al., 1977

Irving, P. M., D. J. Martinson, and J. E. Miller. A histological study of soybeans injured by exposure to sulfur dioxide. Radiol. Environ. Res. Div. Ann. Rep., Argonne National Lab., ANL-78-65. Part III, 1979.

Jacobson, J. S., and L. J. Colavito. The combined effect of sulfur dioxide and ozone on bean and tobacco plants. Environ. Exp. Bot. 16:177-185, 1976.

Jacobson, J. S., and A. C. Hill. Recognition of Air Pollution Injury to vegetation: A Pictorial Atlas. Air Pollution Control Association, Pittsburgh, PA, 1970.

Jager, J. H., and H. Klein. Biochemical and physiological detection of sulfur dioxide injury to pea plants (Pisum sativum). J. Air Pollut. Control Assoc. 27:464-466, 1977.

Jancarik, V. Vyskyt drevokaznych hub v hourem poskozovani oblasti Krusnych hor. Lesnictvi 7:677-692, 1961.

Jennings, O. E. Smoke injury to shade trees. Natl. Shade Tree Conf. 10:44-48, 1934.

Jensen, K. R., and T. T. Kozlowski. Absorption and translocation of sulfur dioxide by seedlings of four forest tree species. J. Environ. Qual. 4:379-382, 1975.

Jones, H. D., D. Weber, and D. Balsillie. Acceptable limits for air pollution dosages and vegetation effects: sulfur dioxide. Presented at the 67th Annual Meeting, Air Pollution Control Association, Denver, CO, 1974. Paper No. 74-225.

Jordan, M. Effects of zinc smelter emissions and fire on a chestnut oak woodland. Ecology 56:78-91, 1975.

Kamprath, E. J. Possible effects from sulfur in the atmosphere. Combustion 44:16-17, 1972.

Karnosky, D. F. Threshold levels for foliar injury to Populus tremuloides by sulfur dioxide and ozone. Can. J. For. Res. 6:166-169, 1976.

Karnosky, D. F. Evidence for genetic control of response to sulfur dioxide and ozone in Populus tremuloides. Can. J. For. Res. 7:437-440, 1977.

Katz, M. Effect of contaminants other than sulfur dioxide on vegetation and animals. In: Pollution and Our Environment Conf., Background Paper A4-2-2, Vol. 1, Council Res. Ministers, Montreal, Can. 1967. pp. 1-18.

Katz, M. Sulfur dioxide in the atmosphere and its relation to plant life. Ind. Eng. Chem. 41:2350-2465, 1949.

Katz, M., and A. W. McCallum. The effect of sulfur dioxide on conifers. Proceedings of the U.S. Tech. Conf. Air Pollution, 1952. pp. 84-96.

Keller, T. The effect of long duration, low SO_2 concentrations upon phytosynthesis of conifers. In: Proceedings of the 4th International Clean Air Congress, 1977. pp. 81-83.

Keller, T. Wintertime atmospheric pollutants--do they effect the performance of deciduous trees in the ensuing growing season. Environ. Pollut. 16:243-247, 1978.

Keller, T. The effect of a continuous springtime fumigation with SO_2 and CO_2 uptake and structure of the annual ring in spruce. Can. J. For. Res. 10:1-6, 1980.

Kender, W. J., and F. H. F. G. Spierings. Effects of sulfur dioxide, ozone, and their interactions on "golden delicious" apple trees. Neth. J. Plant Pathol. 81:149-151, 1975.

Kickert, R. N., and P. R. Miller. Responses of Ecological Systems. In: Methodology for the Assessment of Air Pollution Effects on Vegetations. W. W. Heck, S. V. Krupa, and S. N. Linzon, eds., Air Pollution Control Association, 1979.

Klake, 1974.

Kodata, M., and T. Inoue. Invading path of sulfur dioxide into pine leaves as revealed by microradioauthography. J. For. Soc. 54:207-208, 1972.

Krause, G. H. M., and H. Kaiser. Plant response to heavy metals and sulfur dioxide. Environ. Pollut. 12:63-71, 1977.

Krouse, H. R. Sulphur isotope abundance elucidate uptake of atmospheric sulphur emissions by vegetation. Nature 265:46, 1977.

Krupa, S. V., and R. J. Kohut. Impact of stark emissions from the NSP-SHERCO power plant on terrestrial vegetation. Annual Report, Northern States Power Co., Minneapolis, MN, 1976.

Kudela, M., and E. Novakova. Lesnf skudci a skody zeri v lesich poskozovanych Kourum. Lesnictvi 6:493-502, 1962.

Labanauskas, C. K. Manganese. In: Diagnostic Criteria for Plants and Soils. H. D. Chapman, ed., University of California, 1966. pp. 264-285.

Lacasse, N. L., and W. J. Moroz. Handbook of effects assessment; vegetation damage. CAES. Pennsylvania State University, University Park, PA, 1969.

Lagerwerff, J. V. Lead, Mercury, and Cadmium as Environmental Contaminants. In: Micronutrients in Agriculture. J. J. Mortuedt, P. M. Giodana, and W. L. Lindsay, eds., Soil Science Society of America, Madison, WI, 1972. pp. 593-636.

Larsen, R. I., and W. W. Heck. An air quality data analysis system for interrelating effects, standards, and needed source reduction: Part 3. Vegetation injury. J. Air Pollut. Control Assoc. 26:325-333, 1976.

Lauenroth, W. K., and J. E. Heasley. Impact of atmospheric sulfur deposition on grassland ecosystems. In: Atmospheric Sulfur Deposition: Environmental Impacts and Health Effects. D. S. Shriner, A. Richmond, and S. E. Lindbergh, eds., Ann Arbor Science Publishers, in press, 1980.

Laurence, J. A. Effects of air pollutants on plant pathogen interaction. In: Proceedings of the 71st Annual Meeting, Air Pollution Control Association, Houston, TX, 1978. pp. 3-24.

Laurence, J. A. Response of maize and wheat to sulfur dioxide. Plant Dis. Reptr. 63:468-471, 1979.

Laurence, J. A., L. G. Weinstein, D. C. McCune, and A. L. Aluisio. Effects of sulfur dioxide on southern corn leaf blight maize and stem rust of wheat. Plant Dis. Reptr. 63:975-978, 1979.

Laurence, J. A., A. L. Alvisio, L. H. Weinstein, and D. C. McCune. Effects of sulphur dioxide on southern bean mozaic and maize dwarf moziac. Environ. Pollut., 1981. (in press)

LeBlanc, F., and D. N. Rao. Effects of air pollutants on lichens and bryophytes. In: Responses of Plants to Air Pollution. J. B. Mudd and T. T. Kozlowski, eds., Academic Press, New York, NY, 1975. 383 pp.

LeBlanc, F., and D. N. Rao. Effects of sulfur dioxide on lichen and moss transplants. Ecology 54:612-617, 1973.

Lee, J. J., E. M. Preston, and R. A. Lewis. A system for the experimental evaluation of the ecological effects of sulfur dioxide. Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, Washington, DC, 1978. pp. 49-53.

Legge, A. H., C. W. Harver, P. F. Lester, D. R. Jaques, H. R. Krouse, J. Mayo, A. P. Hartgerink, R. G. Amundson, and R. B. Walker. Quantitative assessment of the impact of sulfur gas emissions on a forest ecosystem. Final report submitted to Whitecourt Environmental Study Group. Environmental Sciences Centre, Kananskis, The University of Calgary, Alberta, 1976.

Leone, I. A., and E. Brennan. Modification of sulfur dioxide injury to tobacco and tomato by varying nitrogen and sulfur nutrition. J. Air Poll. Control Assoc. 22:544-547, 1972.

Lerman, S. L., and E. F. Darley. Particles. In: Responses of Plants to Air Pollution. J. B. Mudd and T. T. Kozlowski, eds., Academic Press, New York, NY, 1975. pp. 141-158.

Liebig, G. F. Arsenic. In: Diagnostic Criteria for Plants and Soils. H. D. Chapman, ed., University of California, 1966. pp. 13-23.

Likens, G. E., F. H. Bormann, R. S. Pierce, J. S. Eaton, and N. M. Johnson. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York, 1977.

Lindberg, S. E., A. C. Harriss, R. R. Turner, D. S. Shriner, and D. D. Huff. Mechanisms and rates of atmospheric deposition of selected trace elements and sulfate to a deciduous forest watershed. Pub. No. 1299, Oak Ridge National Laboratory, Oak Ridge, TN, 1979.

Linzon, S. N. The influence of smelter fumes on the growth of white pine in the Sudbury region. Canadian Department of Agriculture Publication, Ontario Dep. Lands Forests, 1958. 45 pp.

Linzon, S. N. Damage to eastern white pine by sulfur dioxide, semimature tissue needles blight and ozone. J. Air Pollut. Control Assoc. 16:140-144, 1966.

Linzon, S. N. Economic effects of sulphur dioxide on forest growth. J. Air Pollut. Control Assoc. 21:81-86, 1971.

Linzon, S. N. Effects of sulfur oxides on vegetation. Forest Chronicle 48:182-186, 1972.

Linzon, S. N. Some effects of particulate matter on vegetation. In: Ontario Proceedings of the 3rd International Clean Air Congress, Dusseldorf, West Germany, 1973. pp. A118-A120.

Linzon, S. N. Vegetation injury by airborne arsenic and sulphur dioxide emissions from gold smelters. Proceedings of the Fourth International Clean Air Congress, Tokyo, Japan, 1977.

Linzon, S. N. Effects of Airborne Sulfur Pollutants on Plants. In: Sulfur in the Environment: Part II, Ecological Impacts. J. O. Nriagu, ed., John Wiley & Sons. New York, NY, 1978. pp. 109-162.

Linzon, S. N. Acute and chronic effects of sulfur dioxide on natural vegetation. Proceedings of the Air Pollut. Control Assoc. Met., Atlanta, GA, September 1980.

Little, P. A study of heavy metal contamination of leaf surfaces. Environ. Pollut. 5:159-172, 1973.

Little, P. Deposition of 2.75, 5.0 and 8.5mm particles to plant and soil surfaces. Environ. Pollut. 12:293-305, 1977.

Little, P., and R. D. Wiffen. Emission and deposition of petrol engine exhaust Pb-1. Deposition of exhaust Pb. Atmos. Environ. 11:437-447, 1977.

Majernik, O., and T. A. Mansfield. Direct effect of So_2 pollution on the degree of opening of stomata. Nature 227:377-378, 1970.

Malhotra, S. S., and A. A. Kahn. Effects of sulfur dioxide fumigation on lipid biosynthesis in pine needles. Phytochemistry 17:241-244, 1978.

Mandl, R. H., L. H. Weinstein, and M. Keveny. Effects of hydrogen fluoride and sulfur dioxide alone and in combination on several species of plants. Environ. Pollut. 9:133-143, 1975.

Manning, W. J. Effects of limestone dust on leaf condition, foliar disease incidence, and leaf surface microflora of native plants. Environ. Pollut. 2:69-76, 1971.

Mansfield. T. A., and O. Majernik. Can stomata play a part in protecting plants against air pollution? Environ. Pollut. 1:149-154, 1970.

Markowski, A., S. Grzesiak, and M. Schramel. Indexes of susceptibility of various species of cultivated plants to sulfur dioxide action. Bulletin de L'Academie Polanaise des Sciences 23(9):637-646, 1975.

Masaru, N., F. Syozo, and K. Saburo. Effects of exposure to various injurious gases on germination of lily pollen. Environ. Pollut. 11:181-187, 1976.

Materna, J., J. Jirgle, and J. Kucera. Vysledky merceni koncentraci lyclicniky siricitheo v. lesich krusnych hor. (Measurement results of sulfur dioxide concentrations in the Ore Mountain Forests.) Ochrana Oyzdusi. 1:84-92, 1969.

Matsushima, J., and R. R. Brewer. Influence of sulfur dioxide and hydrogen fluoride as a mix or reciprocal exposure on citrus growth and development. J. Air Pollut. Control Assoc. 22:710-713, 1972.

May, P. F., A. R. Till, and M. J. Cumming. Systems analysis of ^{35}sulfur kinetics in pastures grazed by sheep. J. Appl. Ecol. 9:25-49, 1972.

McLaughlin, S. B., and N. T. Lee. Botanical Studies in the Vicinity of the Widows Creek Steam Plant. Review of Air Pollution Effects Studies, 1952-1972, and Results of 1973 Surveys. Internal Report I-EB-74-1, TVA, 1974.

McLaughlin et al., 1976

McLaughlin, S. B., D. S. Shriner, R. L. M'Coutley, and L. K. Mann. The effects of SO_2 dosage kinetics and exposure frequency on photosynthesis and transpiration of kidney beans (Phaseolus vulgaris L). Env. Exp. Bot. 19:179-191, 1979.

McLaughlin, S. B. SO_2 vegetation effects and the air quality standard: Limits of interpretation and application. Proceedings of the Air Pollut. Control Assoc. Mtg., Atlanta, GA, September 1980.

McLaughlin, S. B., and D. S. Shriner. Allocation of Resources to Defense and Repair. Chapter in Plant Disease: An Advanced Treatise. J. G. Horsfall and E. B. Cowling, eds., Academic Press, 1980.

McLaughlin, S. B., and Taylor. Relative humidity: Important modifier of pollutant uptake by plants. Science 211:167-169, 1981.

Meidner, H., and T. A. Mansfield. Physiology of stomata. McGraw-Hill, Great Britian, 1968. 128 pp.

Menser, H. A., and H. E. Heggestad. Ozone and sulfur dioxide synergism: injury to tobacco plants. Science 153:424-425, 1966.

Meszaros, E., G. Varhelyi, and L. Haszpra. On the atmospheric sulfur budget over Europe. Atmos. Environ. 12:2273-2277, 1978.

Miller, P., and J. R. McBride. Effects of Air Pollutants on Forest. In: Response of Plants to Air Pollution. J. B. Mudd and T. T. Kozlowski, eds., Academic Press, New York, NY, 1975. pp. 195-235.

Miller, J. E., H. J. Smith, P. G. Sprugel, and P. B. Xerikos. Yield response of field-grown soybeans to an acute SO_2 exposure. Radiol. Environ. Res. Div. Annu. Rep., Argonne National Laboratory, ANL-78-65, Part III, 1979.

Miller, J. E., D. G. Sprugel, R. N. Muller, H. J. Smith, and P. B. Xerikas. Open-air fumigation system for investigating sulfur dioxide effects on crops. Phytopathology 70, 1980 (in press).

Moss, M. R. Biogeochemical cycles as integrative and spatial modes for the study of environmental pollution (the example of the sulphur cycle). Int. J. Environ. Studies 9:209-216, 1976.

Mudd, J. B. Sulfur Dioxide. In: Responses of Plants to Air Pollution. J. B. Mudd and T. T. Kozlowski, eds., Physiological Ecol. Mono. Series, Academic Press, Inc., New York, NY, 1975. pp. 9-22.

Murray, J. J., R. K. Howell, and A. C. Wilton. Differential response of 17 Poa pratensis cultivars to ozone and sulfur dioxide. Plan Dis. Rep. 59:852-854, 1975.

National Academy of Science. Series on Medical and Biological Effects of Environmental Pollutants. National Academy of Sciences, Washington, DC, 1973. 191 pp.

National Academy of Science. Principles for Evaluating Chemicals in the Environment. National Academy of Sciences, Washington, DC, 1975.

National Academy of Sciences. Sulfur oxides. Board on Toxicology and Environ. Health Hazards. U.S. Environmental Protection Agency Contract, Report No. 68-01-4655, 1978.

National Air Quality, Monitoring and Emissions Trends Report, 1977. 1978. U. S. Environmental Protection Agency, Research Triangle Park, NC.

Neely, G. E., D. T. Tingey, and R. G. Wilhour. Effects of ozone and sulfur dioxide singly and in combination on yield, quality and N-fixation of alfalfa. Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control. EPA-600/3-77-001b, 1977. pp. 663-673.

Neely, G., R. G. Wilhour, D. Weber, and L. Grothaus. The Response of Selected Small Grains, Range Grasses, and Alfalfa to SO_2. Bioenvironmental Impact of a Coal-fired Power Plant: An Interm Report. E. M. Preston and T. L. Gallett, eds., EPA-600/3-79-044, U.S. Environmental Protection Agency, Ecol. Res. Ser., Colstrip, MT, 1980.

Neely, G. E., and R. G. Wilhour. Yield response of Yamhill and Hyslop winter wheat cultivars to chronic SO_2 exposures. J. Air Pollut. Control Assoc., 1981. (in press)

Neilson, D. G., L. E. Terrell, and T. C. Weidensaul. Phytotoxicity of ozone and sulfur dioxide to laboratory fumigated Scots pine. Plant Dis. Rep. 61:699-703, 1977.

Noggle, J. C., and H. C. Jones. Accumulation of Atmospheric Sulfur by Plants and Sulfur-supplying Capacity of Soils. EPA-600/7-79-109, U.S. Environmental Protection Agency, 1979.

Noland, T. L., and T. T. Kozlowski. Effect of SO_2 on stomatal aperature and sulfur uptake of woody angiosperm seedlings. Can. J. For. Res. 9:57-62, 1979.

O'Connor, J. A., D. G. Parbery, and W. Strauss. The effect of phytotoxic gases on native Australian plant species: Part I. Acute effects of sulfur dioxide. Environ. Pollut. 7:7-23, 1974.

Odum, E. P. Fundamentals of Ecology, 3rd ed. W. B. Saunders, Co., Philadelphia, PA, 1971. 570 pp.

O'Gara, P. J. Sulfur dioxide and fume problems and their solutions. In: 14th Semiannual Meeting of the American Institute of Chemical Engineers. J. Ind. Eng. Chem. 14:744, 1922.

Oshima, R. J. The impact of sulfur dioxide on vegetation: a sulfur dioxide-ozone response model. Final Report of the Cal. Air Res. Board Agree. No. A6-162-30, 1978.

Pahlich, E. Allosterische Regulation der Aktivitat der Glutamat-dehydrogenase aus Erbsenkeimlingen durch das Substrat L-Ketoglutarsaure. Planta (Berline) 100:222-227, 1971.

Pahlich, E. Uber den Hemm-Mechanismus mitochondriater Glutamat-Oxalacetat-transaminase in SO_2-begaster Erbsen. Planta 110:267-278, 1973.

Pahlich, E. Effect of SO_2-pollution on cellular regulation. A general concept of the mode of action of gaseous air contamination. Atmos. Environ. 9:261-263, 1975.

Parish, S. B. The effect of cement dust on citrus trees. Plant World 13:288-291, 1910.

Pelz, E. The individual smoke resistance of spruce. Wiss. 2. Tech Univ., Dresden II:3:595-600, 1962.

Preston, E. M., and R. A. Lewis. The Bioenvironmental Impact of a Coal Fired Power Plant, Colstrip, Montana, December, 1977. EPA-600/3-78-021, U.S. Environmental Protection Agency, 1978.

Preston, E. M. The ecological implications of chronic sulfur dioxide exposure for native grasslands. Presented at the 72nd Annual Meeting Air Pollution Control Association, Cincinnati, OH, 1979.

Rajput, C. B. S., D. P. Ormrod, and D. W. Evans. The resistance of strawberry to ozone and sulfur dioxide. Plant Dis. Rep. 61:76-79, 1977.

Rao, D. N., and F. LeBlanc. Effect of sulfur dioxide on the lichen algae with special reference to chlorophyll. Bryologist 69:69-75, 1965.

Reinert, R. A. Pollutant interactions and their effects on plants. Environ. Pollut. 9:115-116, 1975.

Reinert, R. A., A. S. Heagle, and W. W. Heck. Plant Response to Pollutant Combinations. In: Responses of Plants to Air Pollution. J. B. Mudd and T. T. Koslowski, eds., Academic Press Inc., 1975. pp. 159-177.

Reinert, R. A., and D. E. Weber. Ozone and sulfur dioxide-induced changes in soybean growth. Phytopathology 70:914-916, 1980.

Reinert, R. A., and P. V. Nelson. Sensitivity and growth of five Elation Begonia cultivars to SO_2 and O_3, alone and in combination. J. Amer. Soc. Hort. Sci. 105:721-723, 1980.

Reinert, R. A., and T. N. Gray. The response of radish to nitrogen dioxide, sulfur dioxide, and ozone alone and in combination. J. Environ. Qual., 1981. (in press)

Rennie, P. J., and R. L. Halstead. The Effects of Sulfur on Plants in Canada. In: Sulfur and its Inorganic Derivatives in the Canadian Environment. National Research Council Canada, NRCC No. 15015:69-180, 1977.

Reuther, W., and C. K. Labanauskas. Copper. In: Diagnostic Criteria for Plants and Soils. H. D. Chapman, ed., University of California, 1966. pp. 157-179.

Ricks, G. R., and J. H. Williams. Effects of atmospheric pollution on deciduous woodland. Part 2: Effects of particulate matter upon stomatal diffusion resistance in leaves of Quercus petraea (Mattuschka) Liebl. Environ. Pollut. 6:87-109, 1974.

Rist, D. L., and D. D. Davis. The influence of exposure temperature and relative humidity on the response of pinto bean foliage to SO_2. Phytopathology 69:231-235, 1979.

Rosenberg, C. R., R. J. Hutnik, and D. D. David. Forest composition of varying distances from a coal-burning power plant. Environ. Pollut. 14:307-317, 1979.

Saunders, P. J. W. Effects of atmospheric pollution of leaf surface microflora. Pestic Sci. 4:589-594, 1973.

Schoenbeck, H. Beobachtungen zur Frage des einflusses von industriellen immissionen auf die drankheit bereitschaft der Pflanze. Benchte der Landesanstalt fur Bodennutzungschertz. 1:89-98, 1960.

Schoenbeck, H. Detection of heavy metal-containing air pollutants by selected plant indicators. Ver. Dtsch. Ing. 203:75-85, 1973.

Sehmel, G. A., and W. A. Hodgson. Predicted dry deposition velocities. In: Atmosphere-surface exchange of particulate and gaseous pollutants symposium. Conf-74092. Richland, WA, 1974. pp. 399-422.

Setterstrom, C., and P. W. Zimmerman. Factors influencing susceptibility of plants to sulfur dioxide injury. Contrib. Boyce Tompson Inst. 10:155-186, 1939.

Sharp, E. L. Atmospheric ions and germination of uredospores of Purcinia striiformis. Science 156:1359-1360, 1967.

Sharp, E. L. Relation of air ions to air pollution and some biological effects. Environ. Pollut. 3:227-239, 1972.

Sheridan, R. P. Impact of emissions from a coal-fired electricity generating facilties on N_2-fixing in lichens. Bryologist 82:54-58, 1979.

Shin, J. H. A critical survey of measurements of foliar deposition of airborne sulfates and nitrates. Ann. Air Pollut. Control Assoc. 78:1-16, 1978.

Shinn, J. H., and S. Lynn. Do manmade sources affect the sulfur cycle of northeastern states? Environ. Sci. Technol. 13:1062-1067, 1979.

Showman, R. E. Linchens as indicators of air quality around a coal-fired power generating plant. Bryologist 78:1-6, 1975.

Shriner, D. S., and G. S. Henderson. Sulfur distribution and cycling in a deciduous forest watershed. J. Environ. Qual. 7:392-397, 1978.

Shugart, H. H., and D. C. West. Development of an Appalachian deciduous forest succession model and its application to assessment of the impact of the Chestnut Blight. J. Environ. Manag. 5:161-179, 1977.

Sij, J. W., E. T. Kanemasu, and S. M. Goltz. Some preliminary results of sulfur dioxide effects on phytosynthesis and yield in field-grown wheat. Tans Kans. Acad. Sci. 76:199-297, 1974.

Smith, W. H. Metal contamination of urban woody plants. Environ. Sci. Technol. 7:631-636, 1973.

Smith, H. J., and D. D. Davis. The influence of needle age on sensitivity of Scotch pine to acute doses of SO_2. Plant Dis. Reptr. 61:870-874, 1977.

Smith, H. J., and D. D. Davis. Susceptibility of conifer cotyledons and primary needles to acute doses of sulfur dioxide. Hortic. Sci. 13:703-704, 1978.

Smith, R. L. Ecology and Field Biology, 2rd ed., p. 170. New York, Harper and Row, 1980. pp 11-199.

Spedding, D. J. Uptake of sulfur dioxide by barley leaves at low sulfur dioxide concentrations. Nature 224:1229-1231, 1969.

Spinka, J. Effects of polluted air on fruit trees and legumes. Ziva 19:13-15, 1971.

Sprugel, D. G., J. E. Miller, R. N. Muller, H. J. Smith, and P. B. Xerikos. Sulfur dioxide effects on yield and seed quality in field-grown soybeans. Phytopathology 70, 1980 (in press).

Stewart, D., M. Treshow, and F. M. Harner. Sulfur dioxide and hydrogen fluoride emissions in regard to phytopathology. Can. J. Bot. 51:983-988, 1973.

Sulphur Institute. Crop Responses to Sulphur in North America. Vol. 18. The Sulphur Institute, Washington, DC, 1971. 38 pp.

Sulphur Institute. Sulphur in Agriculture Series. Vol. 3. J. S. Platu, ed., The Sulphur Institute, Washington, DC, 1979.

Temple, P. J. Dose-response of urban trees to sulfur dioxide. J. Air Pollut. Control Assoc. 22:271-274, 1972.

Thomas, M. D., and G. R. Hill, Jr. Absorption of sulfur dioxide by alfalfa and its relation to lead injury. Plant Physiol. 10:291-307, 1935.

Thomas, M. D., R. H. Hendrick, T. R. Collier, and G. R. Hill. The utilization of sulphate and sulphur dioxide for the sulphur nutrition of alfalfa. Plant Physiology 18:345-371, 1943.

Thomas, M. D. Gas damage to plants. Ann. Rev. Plant Physiol. 2:293-322, 1951.

Thomas, M. D., and R. H. Hendricks. Effect of air pollution on plants in Air Pollution. World Health Organization Monograph Ser. No. 46., Columbia University Press, New York, NY, 1951. pp. 233-278.

Thomas, M. D., and R. H. Hendricks. Effect of Air Pollution on Plants. In: Air Pollution Handbook. P. L. Magill et al. eds., New York, NY, 1956. pp. 9:1-44.

Thompson, L. K., S. S. Sidhu, and B. A. Roberts. Fluoride accumulations in soil and vegetation in the vicinity of a phosphorus plant. Environ. Pollut. 18:221-234, 1979.

Tingey, D. T., R. A. Reinert, J. A. Dunning, and W. W. Heck. Vegetation injury from the interaction of nitrogen dioxide and sulfur dioxide. Phytopathology 61:1506-1511, 1971a.

Tingey, D. T., W. W. Heck, and R. A. Reinert. Effect of low concentrations of ozone and sulfur dioxide on foliage, growth, and yield of radish. J. Am. Soc. Hort. Sci. 96:369-371, 1971b.

Tingey, D. T., R. A. Reinert, J. A. Dunning, and W. E. Heck. Foliar injury responses of 11 plant species to ozone/ sulfur dioxide mixtures. Atmos. Environ. 7:201-208, 1973a.

Tingey, D. T., R. A. Reinert, C. Wickliff, and W. W. Heck. Chronic ozone or sulfur dioxide exposures or both affect the early vegetative growth of soybean. Can. J. Plant Sci. 53:875-879, 1973b.

Tingey, D. T., and R. A. Reinert. Effect of ozone and sulfur dioxide singly and in combination on plant growth. Environ. Pollut. 9:117-125, 1975.

Tingey, D. T., and G. E. Taylor, Jr. Variation in plant response to ozone. Proceedings of the 32nd Conference of the School of Agriculture, University of Nottingham, England, 1980. 45 pp.

Treshow, M. Environment and Plant Response. McGraw-Hill Book Co., New York, NY, 1970. 422 pp.

Tyler, G. Heavy metals pollute nature, may reduce productivity. Ambio 1:53-59, 1972.

U.S. Department of Health, Education, and Welfare. Air Quality Criteria for Particulate Matter. Public Health Service, EHS, National Air Pollution Control Administration, Washington, DC, 1969.

U.S. Environmental Protection Agency. Mount Storm, West Virginia -Gorman, Maryland, and Luke, Maryland - Keyser, West Virginia Air Pollution Abatement Activity, 1971. 67 pp.

U.S. Environmental Protection Agency. Effects of Sulfur Oxides in the Atmosphere on Vegetation. EPA-R3-73-030, National Environmental Research Center, U.S. Environmental Protection Agency, Raleigh, NC, 1973. 43 pp.

U.S. Environmental Protection Agency. The Bioenvironmental Impact of Fine Particulates: A Critical Review and Summary. USEPA/CERL Report, 1975. Mimeo, 49 pp.

U.S. Environmental Protection Agency. Diagnosing Vegetation Injury Caused by Air Pollution. D. R. Hicks, ed., EPA Cont. Pub. No. 68-02-1344, 1976.

U.S. Environmental Protection Agency. Airborne Particles. Environmental Health Effects Series, Report No. EPA-600/1-77-053, 1977.

U.S. Environmental Protection Agency. Airborne Particles. EPA-600/1-77-053, Environmental Health Effect Series, 1977a. 555 pp.

U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. National Air Quality, Monitoring and Emissions Trends Report, 1977, Research Triangle Park, NC, Publ. No. EPA-450/2-78-052, 1978.

U.S. Environmental Protection Agency. Emission of Sulfur-Bearing Compounds from Motor Vehicle and Aircraft Engines. A Report to Congress. EMSL Report EPA-600/9-78-028, 1978. 437 pp.

Ulrich, A., and K. Ohki. Potassium. In: Diagnostic Criteria for Plants and Soils. H. D. Chapman, ed., University of California, 1966. pp. 157-179.

Unzicker, H. J., H. J. Jager, and L. Steubing. Influence of SO_2 on von Pfanzen. Agnew. Bot. 49:131-139, 1975.

Van Haut, H., and H. Stratmann. Farbtfelatlas uber Schwefeldioxidwirkugen and Pflanzen. (Color-Plate Atlas of the Effects of Sulfur Dioxide on Plants.) Verlag W. Girardet, Essen, West Germany, 1970. 206 pp.

Vanselow, A. P. Nickel. In: Diagnostic Criteria for Plants and Soil. H. D. Chapman, ed., University of California, 1966. pp. 302-309.

Vins, B., and R. Mrkva. Thr diameter increment losses of pine stands as a result of injurious emissions. Acta Univ. Agric-Brno Ser. C 42:25-46, 1973.

Vogl, M., S. Bortitz, and H. Polster. Physiological and biochemical contributions to research of fume damage. 6th report. Definitions of degrees of damage and forms of resistance against the SO_2 Component of injurious fumes. Biol. Zentralb. 84:763-777, 1965.

Wainwright, M. Microbial S-oxidation in soils exposed to heavy atmospheric pollution. Soil Biol. Biochem. 11:95-98, 1979.

Webb, R. A. Use of the boundary line in analysis of biological data. J. Hort. Sci. 47:309-319, 1972.

West, D. C., S. B. Mclaughlin, and H. H. Shugart. Simulated forest response to chronic air pollution stress. J. Environ. Qual. 9:43-49, 1980.

White, K. L., A. C. Hill, and J. H. Bennett. Synergistic inhibition of apparent photosynthesis rate of alfalfa by combinations of sulfur dioxide and nitrogen dioxide. Environ. Sci. Technol. 8:574-576, 1974.

Wilhour, R. G. Growth response of selected small grain and foliage crops to sulfur dioxide. U.S. Environmental Protection Agency-CERL Report, 1978. Mimeo. 4 pp.

Winner, W. E., J. D. Bewley, H. R. Krouse, and H. M. Brown. Stable sulfur isotope analysis of SO_2 pollution impact on vegetation. Oecologia 36:351-361, 1978.

Winner, W. E., and J. D. Bewley. Terrestrial mosses as bioindicators of SO_2 pollution stress. Synecological analysis and the index of atmospheric purity. Oecologia 35:221-230, 1978a.

Winner, W. E., and J. D. Bewley. Contrasts between bryophyte and vascular plant synecological responses in an SO_2-stressed white pine association in central Alberta. Oecologia 33:311-325, 1978b.

Wu, L., and A. D. Bradshaw. Aerial pollution and the rapid evolution of copper tolerance. Nature 238:167-169, 1972.

Yopp, J. H., W. E. Schmid, and R. W. Holst. Determination of maximum permissible levels of selected chemicals that exert toxic effects on plants of economic importance in Illinois. Illinois Institute for Environmental Quality, 1974. 272 pp.

Zahn, R. Effects of sulfur-dioxide on vegetation: results of gas exposure experiments. Staub 21:56-60, 1961.

Zahn, R. Uber den Einfluss verschiedener Umweltfaktoren auf die Pflanzenempfindlich-keit gegenuber Schwefeldioxyd. Z. Pflanzenkr. (Pflanzenpathol.) Pflanzenschutz 70:81-95, 1963a.

Zahn, R. Utersuchungen uber die Bedeutung Kontinuierlicher and intermittierender Schwefeldioxideinwirkung fuer die Pflanzenreaktion. (Investigations on plant reaction to continuous and/or intermittent sulfur dioxide exposure.) Stub. 23:334-352, 1963b.

Zahn, R. The effect on plants of a combination of subacute and toxic sulfur dioxide doses. Staub 30:20-23, 1970.

Ziegler, I. The effect of SO_3^{2-} on the ability of ribulose-1,5-disphosphate carboxylase in insulated spinach chloroplasts. Planta (Berlin) 103:155-163, 1972.

Ziegler. The effect of air polluting gases on plant metabolism. Environ. Qual. Safety 2:182-208, 1975.

Zimmerman, P. W., and W. Crocker. Toxicity of air containing sulfur dioxide gas. Contrib. Boyce Thompson Inst. 6:445-470, 1954.