



# The Acidic Deposition Phenomenon and Its Effects

## Critical Assessment Document



## CRITICAL ASSESSMENT DOCUMENT

The Critical Assessment Document (CAD) is a summary, integration, and interpretation of information, by the three authors identified on the title page, of information on acid deposition. It is based on a compendium of information on acid deposition, called the Critical Assessment Review Papers (CARP), based on literature published through 1982 and prepared for EPA by some 60 scientists. It was published after exhaustive review in 1984. In some areas CAD authors updated scientific references through early 1985.

The CAD is a reference document, intended primarily for Agency use although it is available through the National Technical Information Service. It is one in a series of increasingly sophisticated assessment documents produced by the National Acid Precipitation Assessment Program (NAPAP), the Federal Interagency Acid Deposition Research Program. The CAD will be superseded by the more complete 1985 Assessment, to be published late in 1985.

The CAD is organized in a question and answer format. Questions on effects are raised and answered in Chapter II, those on atmospheric sciences, in Chapter III, and in Chapter IV, linkages between atmospheric sciences and effects are made. The questions raised in the CAD are in most cases based on the original issues identified in 1980 by an EPA Steering Committee. In the intervening years, research and assessment activities have raised new questions or dramatically altered the frame of reference in which a question must be answered. The rapid expansion of research efforts has led to much better questions, but has not always provided definitive answers. This is the natural evolution of research--the quality of questions rapidly improves, and, after a period of time appropriate to the individual study, the answers follow.

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# **The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document**

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U.S. Environmental Protection Agency



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## PREFACE

### A. What is this document?

This document, The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document, hereafter referred to as CAD, is a summary, integration, and interpretation of the current scientific understanding of acidic deposition. It is firmly based upon The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers described below, augmented by additional scientific references listed at the end. The interpretations in the CAD are solely the responsibility of its authors, although much of the basic information is taken from Critical Assessment Review Papers, whose authors and steering committee have provided valuable comments and guidance.

The Critical Assessment Review Papers (CARP) is a multi-authored, comprehensive, critical review of the published scientific literature of the atmospheric phenomena and effects of acidic deposition. Literature published later than December 1982 generally is not cited. References published as recently as early 1984 may have been reviewed by individual authors, however, as the authors responded to public comments received in July and August 1983.

The original charge to the editors was to produce "a comprehensive document which lays out the state of our knowledge with regard to precursor emissions, pollutant transformation to acidic compounds, pollutant transport, pollutant deposition and the effects (both measured and potential) of acidic deposition." This charge is met upon completion of final drafts of both the Critical Assessment Document and the Critical Assessment Review Papers. To secure success in meeting the charge, the authors and editors of the Critical Assessment Review Papers have adhered to the following guidelines:

1. Contributions are to be written for scientists and informed lay persons.
2. Statements are to be explained and supported by references; i.e., a textbook type of approach, in an objective style.
3. Literature referenced is to be of high quality and not every reference available is to be included.
4. Emphasis is to be placed on North American systems with concentrated effort on U.S. data.
5. Overlap between this document and the SO<sub>x</sub> Criteria Document is to be minimized.
6. Potential vs known processes or effects are to be clearly noted to avoid misinterpretation.

7. The certainty of our knowledge should be quantified, when possible.
8. Conclusions are to be drawn from scientific evidence only.
9. Extrapolation beyond the available data should be avoided.
10. Scientific knowledge is to be included without regard to policy implications.
11. Policy-related options or recommendations are beyond the scope of this document and are not to be included.

The authors of this integrative summary have also attempted to follow these guidelines, consciously trying to write for the informed lay person, and to draw together and interpret evidence from disparate sections of the CARP. Reference is made, where possible, to CARP sections providing information for the CAD analyses; citations are made to additional references. Quotations and paraphrases of conclusions and observations from the CARP provide much of the material in the CAD. As such, they represent the conclusions of the CARP authors interpreted by the CAD authors. Some additional evidence has been developed by the CAD authors, and the conclusions drawn from this information are solely those of the CAD authors. Several of the authors of the CARP commented on earlier drafts of the CAD.

The documents have been designed to present the status of knowledge of the acidic deposition phenomenon and its effects. Neither CAD nor CARP is a criteria document. Neither document was designed to set standards or to suggest regulatory policies or recommendations. The literature is reviewed and conclusions are drawn based on the best available evidence. Both CAD and CARP are authored documents, and as such, the conclusions are those of the authors after their review of the literature. Both documents strive to provide an accurate, comprehensive, and impartial evaluation of the science of acidic deposition.

The authors of the Critical Assessment Document are indebted to the approximately sixty authors of the CARP, the editors, and the members of the Steering Committee identified in Appendix A for their dedication and patience in meeting the demanding objectives for these documents.

## B. History of the Documents

The idea of preparing a Critical Assessment Document was first suggested formally in August 1980 in a letter from Dr. Sheldon Friedlander, Chairman of the U.S. Environmental Protection Agency's Clean Air Scientific Advisory (CASAC), to the EPA Administrator recommending "a separate document that can recognize and incorporate the new information on causes, effects and data bases for all of the various pollutants relevant to acidic deposition ... addressing 'Acidic Deposition' in a complete sense ..."

Soon thereafter, the Federal Interagency Task Force on Acid Precipitation in its draft National Assessment Plan called for an assessment document to aid in setting the national research agenda. The CAD was designated to satisfy

that need. By the end of 1980 a steering committee was formed and began identifying issues for analysis in the document. Editorial and production responsibility for the document was awarded to the Acid Precipitation Program at North Carolina State University in February 1981. It was soon determined that a comprehensive critical review of the scientific literature (the CARP) was needed before an assessment (the CAD) could be written. Since that time, authors with the desired technical expertise have been identified; chapters written, reviewed, and revised; public reviews held (11/82); public comment periods called (6/83 to 7/83); and revisions of the CARP written. In short, every chapter has been exhaustively reviewed, and improved, several times. The final version of the CARP is available from the National Technical Information Service (NTIS) in two volumes: Volume I Atmospheric Sciences (PB85-100030) and Volume II Effects Sciences (PB85-100048). The Critical Assessment Document is based upon the final revision of the CARP and has been reviewed by a small number of scientists and the Steering Committee.

### C. The Future

These documents are the first of a succession of increasingly sophisticated assessment documents to be produced by the National Acid Precipitation Assessment Program (NAPAP). The next document, a NAPAP report, will be the 1985 Assessment, an analysis of the impacts of acidic deposition, atmospheric source-receptor relationships, emissions and deposition data, and control technologies, to be published late in 1985. Succeeding assessments in 1987 and 1989 will seek to integrate knowledge within a framework of source-receptor, cause-and-effect, cost-benefit, and control-mitigation analyses.

## I. INTRODUCTION

### Organization:

The acidic deposition phenomenon, although often cited for its complexity, is represented in a straightforward manner in Figure I.1. Substances emitted to the atmosphere by human activities or by natural processes are transported, transformed, and deposited from the atmosphere in precipitation or as dry gases or particles. The deposited materials then act, directly or after additional transformations, on various components of aquatic or terrestrial ecosystems. The emitted substances of interest are those, or their precursors, that may beneficially or adversely affect ecosystems. If impacts can be quantitatively related to the depositional 'loading', a 'dose-response relationship' may be determined. Such a relationship may be difficult to separate from the effects of other natural processes occurring in the ecosystem.

The atmospheric components of the picture must be considered in order to apportion the sources of deposition (the 'source-receptor relationship') or, more importantly, to predict the impact of changes in emission sources. Causality must run from emission to deposition to impacts, but attribution of effects proceeds from identifying effects to identifying amounts of deposition to identifying sources. The latter approach, upon which this document's organization is based, allows the reader to ignore parts of the greater complexity by focusing only on those steps important in determining a given impact in a specific region. Later chapters will expand on this approach.

The Critical Assessment Document (CAD), is organized in a question and answer format. Questions on effects are raised and answered in Chapter II and those on atmospheric sciences, in Chapter III. Linkages between atmospheric sciences and effects are made in Chapter IV. Chapters II and III are each organized into two sections, A and B. Section A in each of these chapters has subsections corresponding to chapters in the Critical Assessment Review Papers (CARP), upon which the CAD is based. Section B in each chapter, in answering the questions raised, integrates information found in more than one CARP chapter. Section B of Chapter II considers interactions among ecosystem components, selecting for discussion only impacts or potential impacts on the chemistry of aquatic ecosystems and forests. This very substantial narrowing of focus from the discussion in Section A results from the following logic:

- These are the sensitive ecosystems where significant impacts may be occurring.
- Understanding impacts in these ecosystems requires information from several effects chapters in the CAD and corresponding sections of the CARP.
- Direct (pre-depositional) effects on human health from inhalation of acid precursors or sulfate particulates are not discussed in the CARP and have been dealt with previously in U.S. EPA criteria documents. Indirect

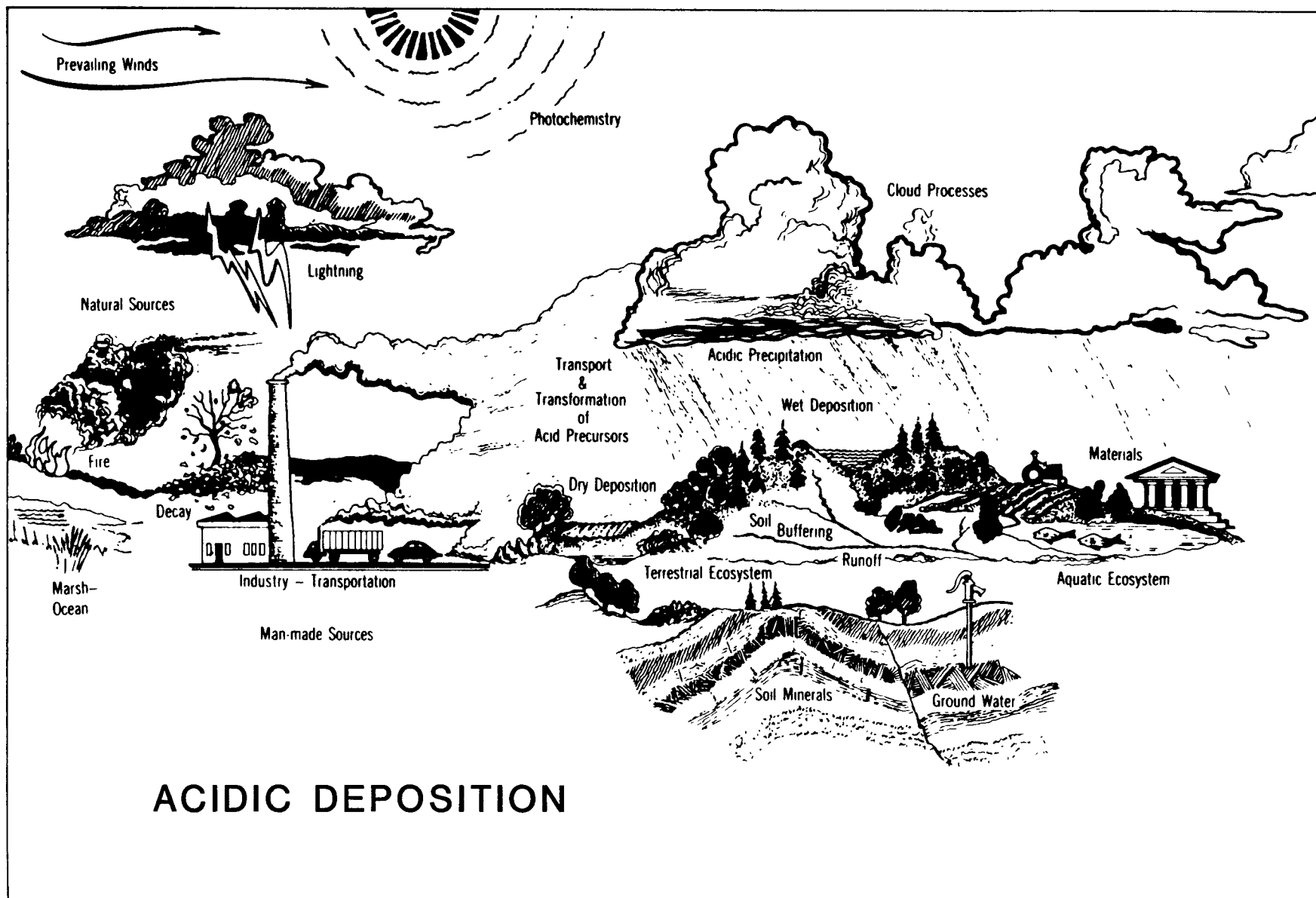


Figure I.1 A schematic representation of the acidic deposition phenomenon and its consequences. Adapted from The Interagency Task Force on Acid Precipitation (1982).

(post-depositional) effects from ingestion of food or drinking water have not been documented.

- Impacts on aquatic biota (e.g., fish) follow directly and immediately from changes in aquatic chemistry.
- Impacts of acidic deposition on agricultural crops appear small and are not manifested through the soil. Sufficient discussion of this is found in Section A. Impacts of gaseous pollutants (ozone, sulfur dioxide, nitrogen oxides) are significant, but are extensively discussed in EPA Criteria Documents.
- Effects on materials, found mostly in urban areas, are significant, but they are at this time inextricably entwined with ambient air quality, which in urban areas is determined largely by emissions from nearby sources.

The questions raised in the CAD are in most cases based on the original issues identified by the Steering Committee and peer reviewers late in 1980. In the intervening four years, research and assessment activities have raised new questions or dramatically altered the frame of reference in which a question must be answered. The rapid expansion of research efforts has led to much better questions, but has not always provided definitive answers. This is the natural evolution of research--the quality of questions rapidly improves and, after a period of time appropriate to the individual study, the answers follow. Certain physical and chemical principles are often cited or assumed in discussions in this document and are introduced in the 'chemical primer' below.

#### A chemical primer:

The emissions shown in Figure I.1 include sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ); respectively, they may be oxidized to sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) either in the atmosphere or after deposition. In the atmosphere, the oxidizing agents include hydrogen peroxide and ozone, whose concentrations are in turn affected by emissions of hydrocarbons. Reactions that generate  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  also produce hydrogen ion ( $\text{H}^+$ ), a component present in or generated by all acids.

- All pure substances are electrically neutral.

Whether in a rain droplet, as a solid material, or in soils, vegetation or a lake, a charged species (an ion) must be accompanied by species of equal and opposite charge; i.e.,  $\text{SO}_4^{2-}$  cannot be isolated by itself. In solution  $\text{SO}_4^{2-}$  may be accompanied by  $\text{H}^+$  (sulfuric acid,  $\text{H}_2\text{SO}_4$ ), or some other positive ion. Neutralization of the sulfuric acid by a base such as calcium carbonate ( $\text{CaCO}_3$ ) would result in a neutral product,  $\text{CaSO}_4$  in this case. The ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are referred to as 'base cations' because of reactions such as this. In Chapter II the association of  $\text{SO}_4^{2-}$  with aluminum ( $\text{Al}^{3+}$ ) will be shown to be of great importance. Ions of positive charge are called cations; those of negative charge, anions.

- All acids may donate  $H^+$  to a suitable receptor.

Those acids that donate  $H^+$  (hydrogen ion) most readily are called 'strong acids', the strongest being the 'mineral acids',  $H_2SO_4$ ,  $HNO_3$ , and  $HCl$ . Some organic compounds and  $Al^{3+}$  hydrated in aqueous solution act as weak acids; that is, they incompletely dissociate giving  $H^+$ .

- The concentration of  $H^+$  in aqueous solution may range from very large to very small.

A neutral aqueous solution at  $20^\circ C$  contains  $10^{-7}$  g hydrogen ion per liter, which is one ten-millionth mole. Acidic solutions have more  $H^+$  per liter; basic solutions have less. Because natural waters may have hydrogen ion concentrations that vary by at least a factor of  $10^8$  (one hundred million) a more convenient measure of  $H^+$  concentration,  $[H^+]$ , has been developed. This measure is "pH."

$$pH = -\log [H^+]$$

The range of  $10^{-2}$  to  $10^{-10}$  moles per liter, for example, is simply expressed as pH 2 to pH 10. Basic solutions (low acidity) have  $pH > 7$ . A change in pH of one unit (e.g., pH 5.5 to 4.5) corresponds to a change in  $[H^+]$  by a factor of ten. Small changes in pH represent large changes in concentration;  $H^+$  is the important factor in solution.

#### The evolving point of view:

The acidic deposition phenomenon has been recognized in some form for over a century, and research to understand the many aspects of the phenomenon accelerated beginning in the 1950's (Cowling 1982). By the early 1970's the phenomenon had become an issue of much public debate. In this temporal context the authors of the CAD, with a mean experience in acidic deposition of five years, are neophytes. None the less, we feel that there existed a characterization of acidic deposition, part scientific and part popular public perception, when this document was begun in 1980. The scientific basis for this view can readily be found in papers presented at the international conference in Sandefjord, Norway, in 1980 (Drabløs and Tollan 1980) and in other important reports (Likens 1976, NAS 1981). Significant aspects of the characterization include:

- A focus on hydrogen ion concentration or pH of rain and 'acid' rain of pH less than 5.6
- The prospect of a continuing 'titration' and acidification of lakes, and loss of fish, in locations receiving acid rain
- A concern for accelerated leaching of nutrients from soils because of acid rain with adverse effects on forest and crop plant nutrition
- A view of sources of acidity to the atmosphere hundreds of kilometers from affected receptors.



This characterization is admittedly an extreme oversimplification. There was much healthy scientific debate and a much broader scientific view. [See, for example, Rosenqvist's view of acidification of surface water (1978) and Hepting's discussions of the occurrence and large number of potential causes of widespread forest declines (1971).] The local air pollution episodes such as that in Donora, Pennsylvania, had not been forgotten.

We further feel that the research of hundreds of scientists over the last several years has resulted in a rapid evolution of the questions, and the definition of the acidic deposition 'problem'. We attempt below to give the reader our sense of this evolution.

The focus has shifted from hydrogen ion concentration (or pH) as the "culprit" to hydrogen ion as an indicator. This reflects an attention to biological activity and soil chemistry, the flows of sulfur and nitrogen through soils and their biological or physical storage. Important conclusions include:

- The sensitivity of a component of the terrestrial ecosystem (e.g., soil or soil water) to acidification is determined both by concentrations of chemical substances entering or within the system (intensity factors) and by the amounts of substances or storage of substances (capacity factors).
- Capacity can be regenerated by chemical or physical processes; the rate of regeneration is thus very important.
- The effects on ecosystems from deposited substances other than hydrogen (e.g., sulfur and nitrogen compounds) may be more significant than those of hydrogen.
- The deposited material's form seldom makes a difference; dry deposited sulfur and nitrogen compounds may be as important in quantity and effect as those deposited in precipitation.
- Nitrogen, usually a beneficial nutrient to unmanaged ecosystems, may create adverse effects at high amounts of deposition--ecosystems become saturated; nitrogen concentrations in water following snowmelt may also be large.
- The past history of an ecosystem, even over 'geological time' is very important in determining effects of current deposition and the potential for future effects. Thus, regional analyses (e.g., of the glaciated Northeast or the unglaciated Southeast) are both necessary and appropriate.
- Future increases in aquatic acidity in the northeastern United States and Canada may be less than was predicted; future acidification may be greater in the Southeast.

- Lakes are not acidifying rapidly; rates of change in aquatic chemistry and fish populations are unknown, but dramatic acidification over a period of just a few years has not been observed; some reductions in acidity may have been observed.
- Soil pH's are not likely to change rapidly, even in unmanaged ecosystems. Acidic soils become acidic over centuries of weathering.
- Acidity production within the aquatic/terrestrial ecosystem is a natural process. One must not look solely to atmospheric deposition for sources of acids. Nitrification, the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , is one example of a major natural source of acids in most soils in humid regions.

The above conclusions take into account the importance of knowing total deposition, particularly of sulfur, and perhaps of nitrogen. In addition:

- Dry materials collected in buckets or in most air quality samplers represent an unknown proportion of materials deposited on trees, grasses, etc.
- Concentrations of substances other than hydrogen ion in solution will determine the pH. These concentrations must be known both to understand the causes of acidity and to evaluate the quality of measurements. Depending on the substances present, the 'natural' pH of rainwater in pristine areas remote from man's activities may be greater or less than 5.6, perhaps ranging from 4.8 to 6.5.

The observations about effects above have implications for what information is needed about atmospheric phenomena:

- Knowing the specific chemical or physical forms of deposited materials may be less critical than was previously thought.
- Pollutants deposited from both distant and relatively nearby sources are important. Understanding both long-range and short- to intermediate-range transport, therefore, is necessary. This requires knowledge of specific chemical or physical forms in the atmosphere.

Certain observations on effects on ecosystem components may also be made:

- Loss of fish populations may often be from reproductive failure (lack of 'recruitment') rather than deaths of adult fish.
- Adverse effects of acidic deposition on crops are small to none; impacts of other air pollutants are greater.
- Widespread sustained decreases in the growth of certain coniferous trees have been observed in the eastern United States, but the cause is unknown. To attribute decline to acidic deposition is premature, perhaps unwarranted; symptoms are similar to those reported for declines in many different species and regions over the years.

- Dramatic changes in soil chemistry, although requisite only a few years ago in models of effects of acidic deposition on forests, are not always found where dieback is occurring. Soil-mediated change is not ruled out, however.

The statements above represent the authors' perspective and are elaborated in the following chapters.

## II. EFFECTS SCIENCES SUMMARY

### SECTION A. ECOSYSTEM COMPONENTS

#### A.1 INTRODUCTION

The acidic deposition phenomenon is complex and our understanding of it and its effects is limited. This complexity, plus the uncertainties in our knowledge of natural processes and cycles, makes difficult the definition of effects of acidic deposition, isolated from other manmade or naturally-induced stresses. In addition, understanding the behavior of precursor gases that contribute to acidic deposition, their reactions, transport, and ultimate fate, and determining which deposited chemicals are of concern to receptor systems are not any simpler. Therefore, answers to acidic deposition related issues are likely to be equally complex, somewhat uncertain, and subject to change as the quality of available evidence improves. There is no doubt, however, that effects have occurred and are occurring due to acidic deposition. Future research will better quantify the magnitude and extent of these effects.

##### A.1.1 WHAT EFFECTS OF ACIDIC DEPOSITION HAVE BEEN STUDIED?

Effects research has focused on soils, vegetation, aquatic chemistry, aquatic biota, structural and cultural materials, and human health. Effects are described by changes in these components and are determined by interactions in the ecosystems in which the components are found.

##### A.1.2 WHAT COMPONENTS OF ECOSYSTEMS MUST BE CONSIDERED TO UNDERSTAND THE EFFECTS OF ACIDIC DEPOSITION?

Since the number of possible interactions in ecosystems staggers the human mind, one direct approach is to track the individual chemical components throughout the ecosystem, a type of bookkeeping. The cycling of sulfur and nitrogen is of particular interest in understanding the effects of acidic deposition. The sulfur and nitrogen cycles, Figures II.1 and II.2 respectively, are comprised of interdependent pathways; alterations of any part of the cycle will effect change in other parts of the cycle. Since one component depends on another, and nitrogen and sulfur compounds interact in air, soil, and water, any attempt to quantify effects on the cycles and ecosystems, or to predict subsequent changes adequately, is difficult.

##### A.1.3 HOW DO THESE ECOSYSTEM COMPONENTS INTERACT?

Reviewing the sulfur and nitrogen cycles reveals that the vegetation, soils, animals, water, and air all interact. While the acidic deposition phenomenon begins with an alteration of air chemistry, it is the deposition of substances on the land, water, and vegetation that causes effects. Acidic deposition, in wet form, is a dilute solution of acid, i.e., hydrogen ions and associated anions. This solution is easily altered, chemically, upon contact with any exposed surface. If the interacting surface is basic, the

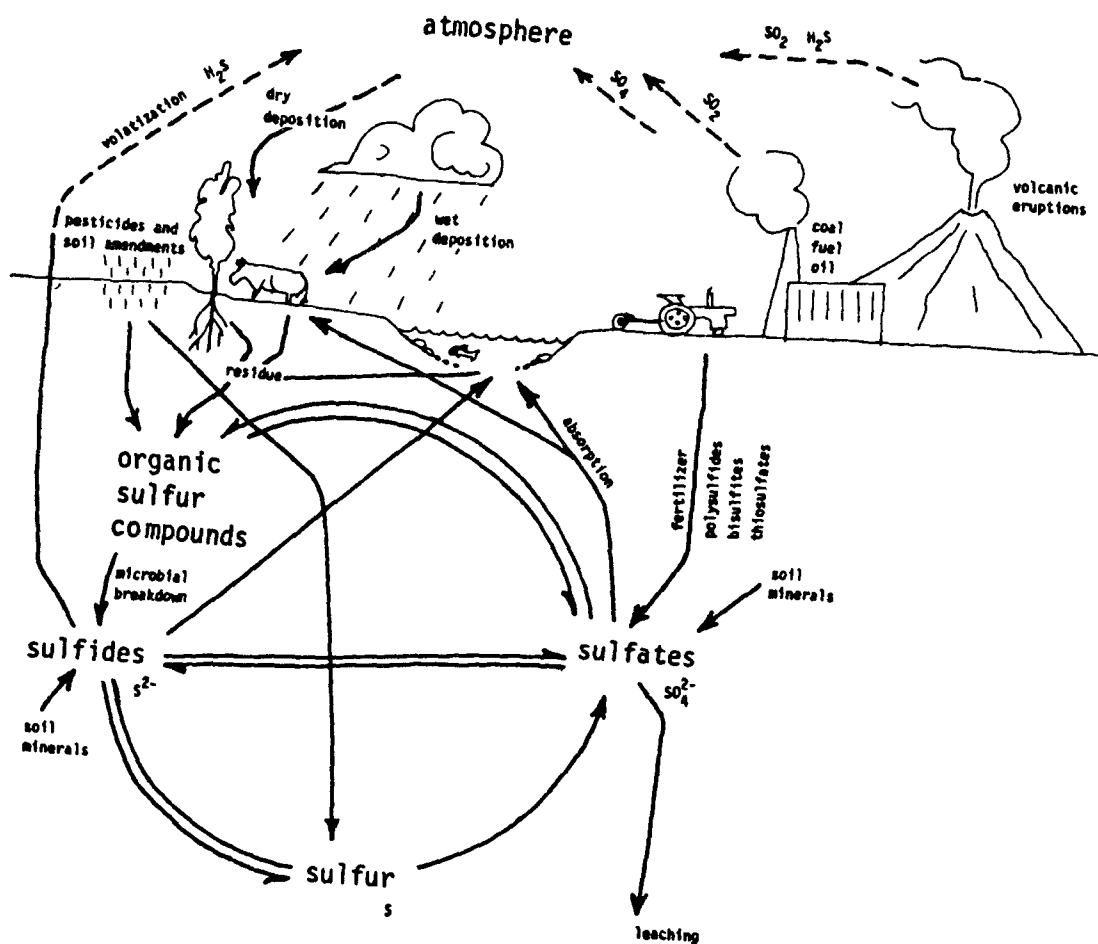


Figure II.1 The sulfur cycle.

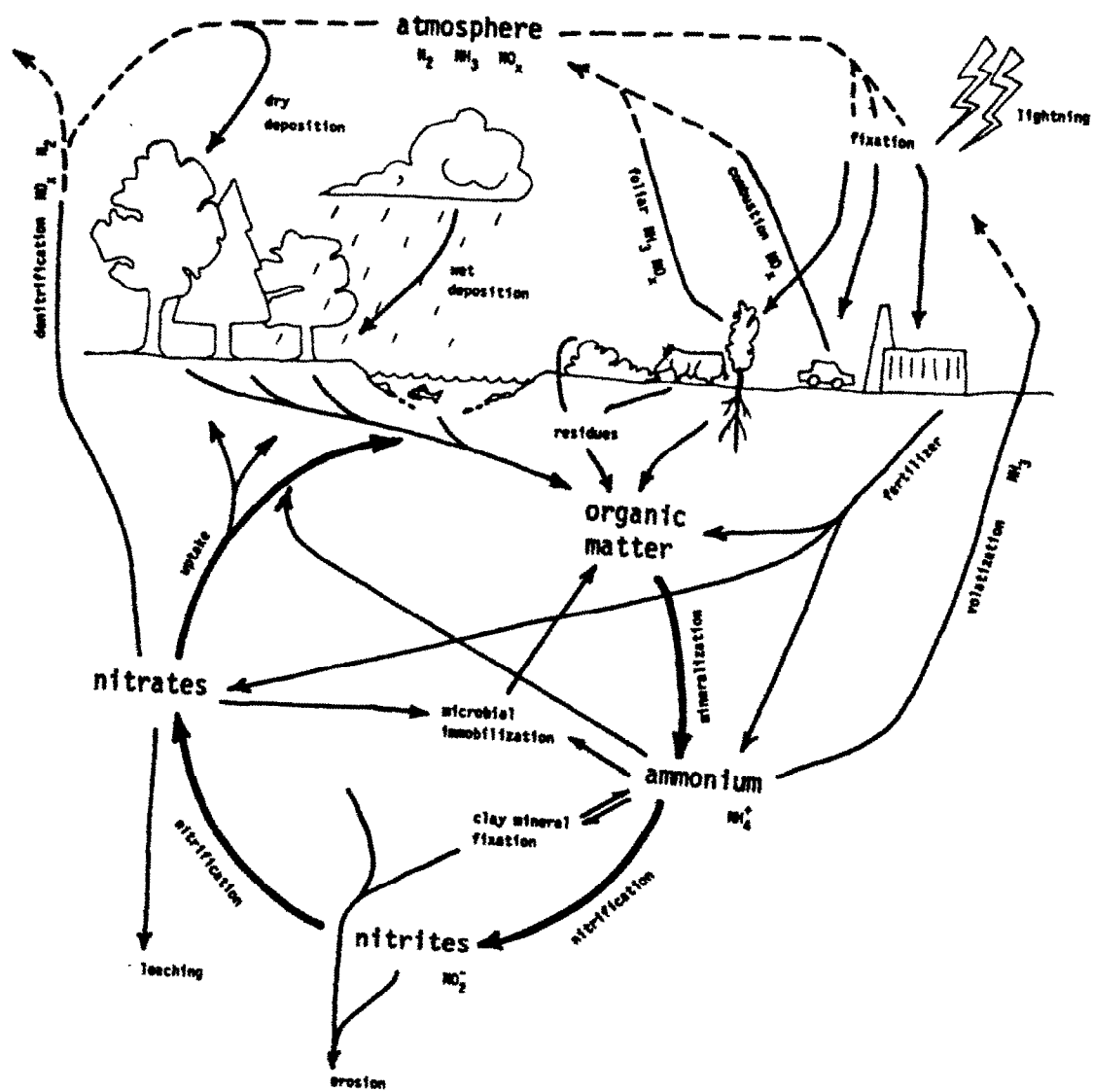


Figure II.2 The nitrogen cycle.

pH increases. If the surface is acidic, the pH may decrease. The anions may exchange with other anions at the surface. The same surfaces that come in contact with precipitation also collect dry-deposited substances, including those dry substances that are nitrogen and sulfur rich. Therefore, when precipitation, which falls an average of less than 10 percent of the time in the eastern United States, contacts a surface, it dissolves the dry-deposited nitrogen and sulfur compounds (in addition to those compounds already in the precipitation), often making the total of these substances in the aqueous solution quite high. Because basic substances are also deposited in dry form, the pH of the precipitation may or may not change. Undisputably, however, cumulative loading of sulfur and nitrogen compounds to the surfaces below continues to increase.

Figure II.3 is a representation of a stream ecosystem, the stream and its watershed, including soil and vegetation. The material from the atmosphere is deposited on soil, vegetation, or stream. The deposited substances may remain for some time within soil and on vegetation before entering the stream. At any point along the pathway the materials can change chemically and/or have an effect on another ecosystem component.

#### A.1.4 WHAT LEVEL OF UNDERSTANDING WILL BE NECESSARY TO DEFINE INTERACTIONS AMONG ECOSYSTEM STRUCTURE, FUNCTION, AND ACIDIC DEPOSITION INFLUENCE?

The level of understanding ultimately needed to attribute effects to acidic deposition will be determined by the purpose for which the understanding is needed. If society perceives that acidic deposition is a highly detrimental phenomenon, correlative evidence is likely to be sufficient for recommending change. From a purely scientific perspective, the data base required for determining cause-and-effect relationships will be quite detailed.

The information needed to suggest that acidic deposition is, in fact, affecting ecosystems comes in two pieces. The first is correlations between observed ecosystem changes and deposition levels. Such correlative evidence has driven the recent concerns and such evidence continues to accumulate. These correlations are not sufficient to prove that acidic deposition causes effects; statistical correlation is never sufficient proof of causality. The second piece of evidence to determine the effects of acidic deposition is controlled experiments that demonstrate ambient levels of acidic deposition cause changes not expected if the chemistry of deposition were less 'polluted'.

Evidence of both sorts is accumulating. The evidence is as yet insufficient to provide a complete picture of the effects of acidic deposition. The correlations are confounded by changes in several anthropogenic pollutants that have occurred simultaneously with suspected changes in acidic deposition. These changes include increases in ozone, metals deposition, and sulfate aerosols. All have been linked to the burning of fossil fuels. Research has demonstrated that these pollutants, as well as precursors of acidic deposition (sulfur and nitrogen oxides), can cause effects. Definitive results from controlled experiments are few. Laboratory experiments may lack important ecosystem components; ecosystem experiments are difficult to control.

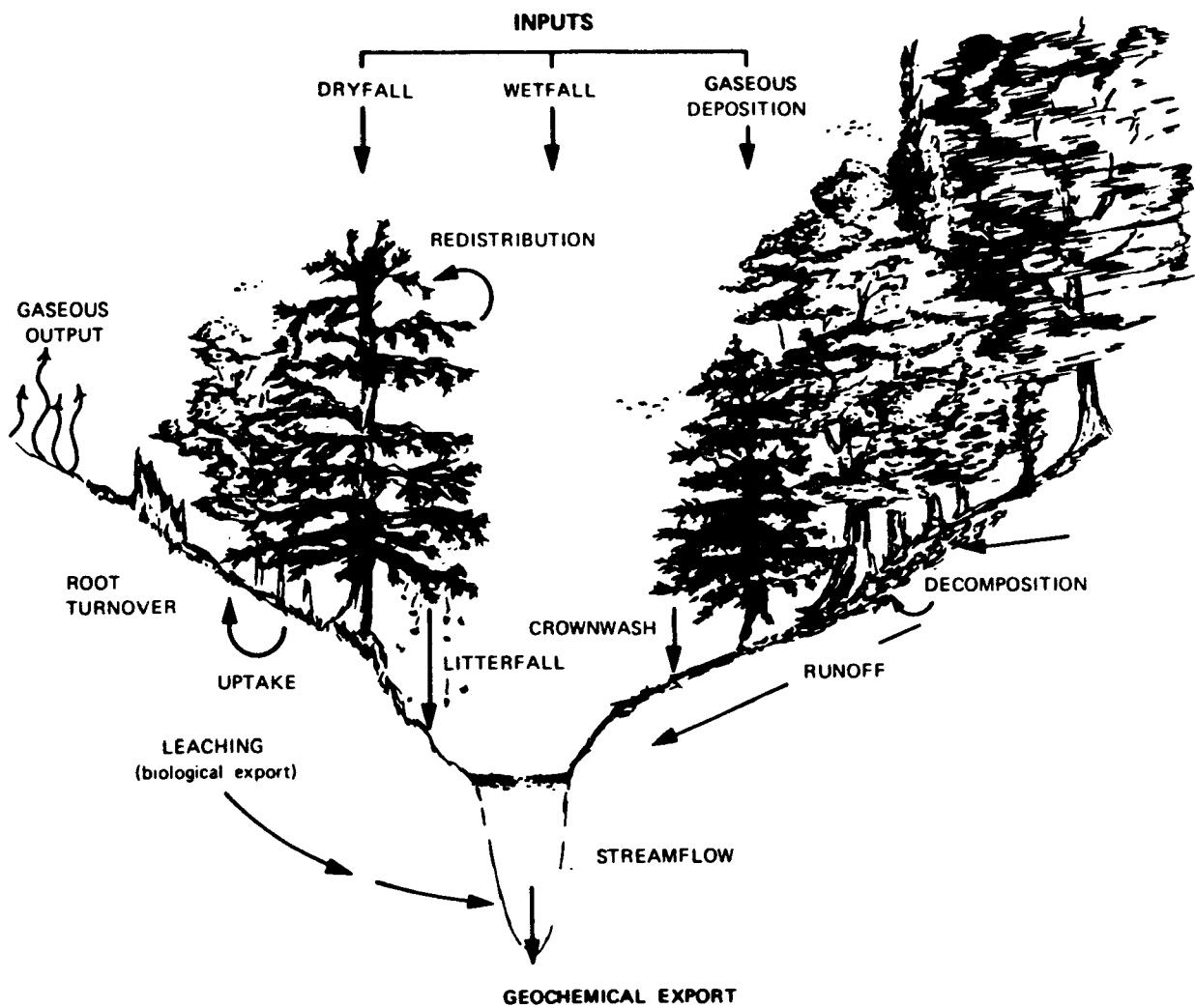


Figure II.3 A conceptual diagram of wet and dry deposition pathways in an ecosystem context. From Johnson et al. (1982).



## A.2 WHAT IS KNOWN ABOUT THE INFLUENCE OF ACIDIC DEPOSITION ON ECOSYSTEMS?

This section reviews the state of scientific knowledge described in the Critical Assessment Review Papers about effects on each ecosystem component and materials. We will follow a progression beginning with terrestrial effects (soils and vegetation) through aquatic effects (chemistry and biology) to indirect effects on human health and effects on materials.

### A.2.1 WHAT ARE THE EFFECTS ON SOIL SYSTEMS? [CARP E-2]

#### A.2.1.1. WHY IS KNOWLEDGE OF SOILS IMPORTANT FOR UNDERSTANDING THE EFFECTS OF ACIDIC DEPOSITION? [CARP E-2.1]

Soils play a key role in ecosystems. They are one of the most stable ecosystem components and, together with climate, they determine a terrestrial system's productivity. Because much of the water that enters streams and lakes flows first through soils, soil properties, particularly soil chemistry and pore structure, can greatly influence aquatic systems. Thus, significant changes in soils could have serious ecosystem implications.

As soils change so do associated aquatic ecosystems. Acidic deposition may directly influence the transfer of substances from terrestrial to aquatic systems, as when material deposited from the atmosphere flows rapidly over or through the soil with little interaction, or it may act indirectly, as when deposited materials cause changes in soil processes such as weathering, leaching, and/or organic matter decomposition. In either case, substances produced and/or deposited in soils are transported to the aquatic system. [CARP E-2.1.1]

"Soil provides the physical support and most of the water, nutrients, and oxygen needed by plant roots for normal growth and development. Well over 95 percent of our food and much of our fiber come directly or indirectly from terrestrial plants" [CARP E-2.1.2]. Soil properties limit the productivity of terrestrial ecosystems and changes in the soil properties, whether natural or man-induced, may alter the productivity of the terrestrial system. [CARP E-2.1.2]

#### A.2.1.2 WHY IS UNDERSTANDING/QUANTIFYING THE EFFECTS OF ACIDIC DEPOSITION ON SOILS DIFFICULT? [CARP E-2.1]

Soils in the United States can be divided into approximately 12,000 soil series, each with a unique combination of properties (see Figure II.4). Because of this diversity, generalizations about the effects of acidic deposition on soils are difficult. Furthermore, changes in soils are normally measured in decades, not days, weeks, or years.

Hydrogen ion deposition is expected to have a minor influence on most soils. Sulfate and nitrate deposition are potentially more significant. Soils are complex chemical, physical, and biological systems; thoroughly assessing effects of atmospheric deposition on elements transferred from terrestrial to aquatic systems requires extensive measurement and quantification of soils' inputs, internal processes, and outflows. Our knowledge of these various

Figure II.4 Generalized soil map of the United States (Soil Survey Staff 1975) showing regions dominated by suborders or groups of suborders. The most common suborder is named. Many other suborders exist within the boundaries of each area.

#### Alfisols

- A1 Aqualfs
- A2 Boralfs
- A3 Udalfs
- A4 Ustalfs
- A5 Xeralfs

#### Aridisols

- D1 Argids
- D2 Orthids

#### Entisols

- E1 Aquents
- E2 Orthents
- E3 Psamments

#### Histosols

- H1 Hemists
- H2 Hemists and Saprists
- H3 Fibrists, Hemists, and Saprists

#### Inceptisols

- I1 Andepts
- I2 Aquepts
- I3 Ochrepts
- I4 Umbrepts

#### Mollisols

- M1 Aquolls
- M2 Borolls
- M3 Udolls
- M4 Ustolls
- M5 Xerolls

#### Spodosols

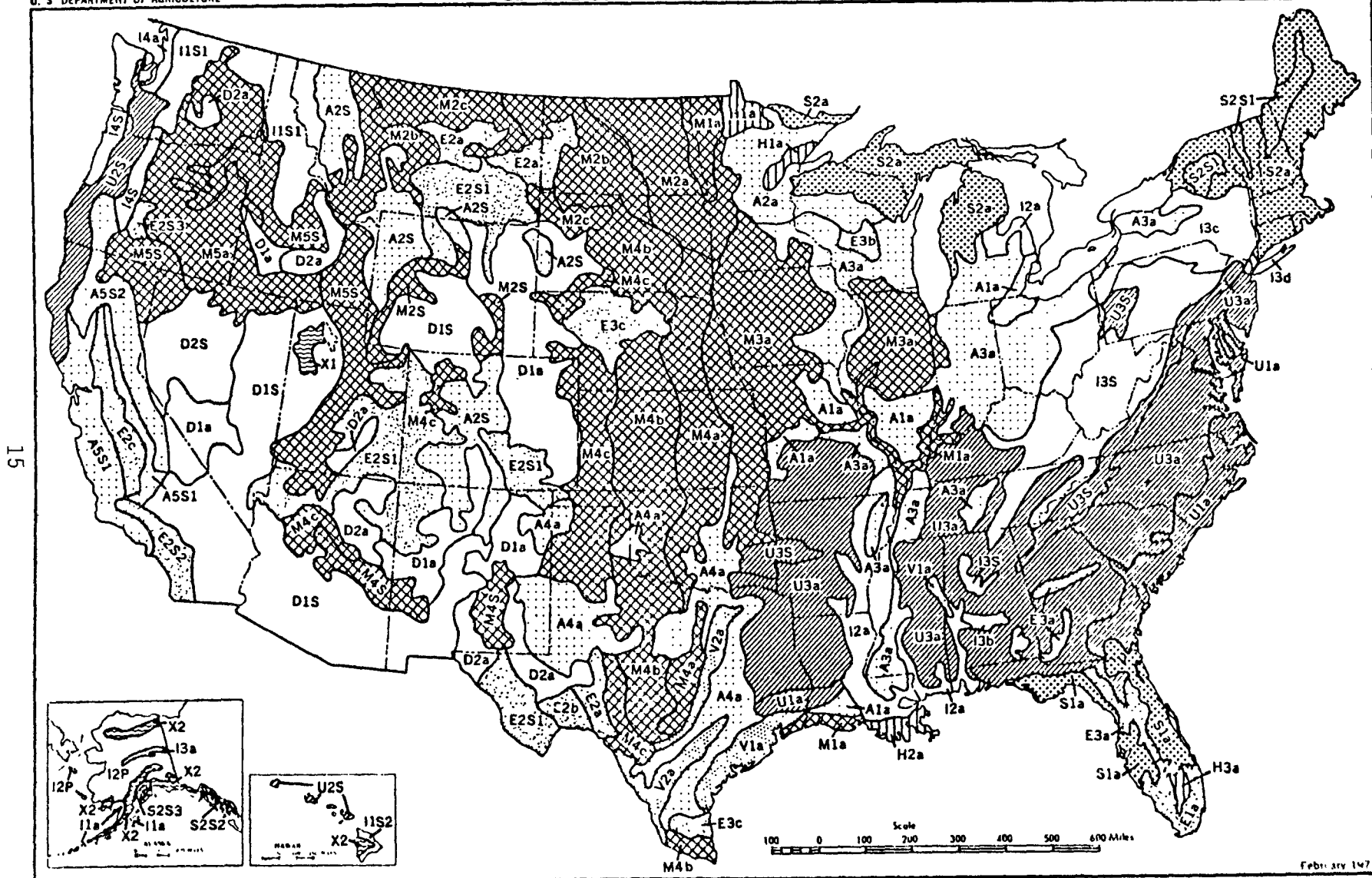
- S1 Aquods
- S2 Orthods

#### Ultisols

- U1 Aquults
- U2 Humults
- U3 Udults

#### Vertisols

- V1 Uderts
- V2 Usterts



processes is incomplete, even in unperturbed systems. As a result, understanding the effect of acidic deposition on soils is an ongoing challenge. The changes that may occur within days, weeks, or years are likely small, and their quantification nearly impossible.

Chemical, physical, and microbial properties are some of the major factors making one soil distinct from another. Soil chemical properties may provide the protective mechanisms to prevent alterations in soil water chemistry resulting from acidic deposition. A soil's resistance to chemical changes is measured by its buffering capacity, nitrogen status, carbon to nitrogen ratio, initial pH, sulfate adsorption capacity, and amount and type of weatherable minerals. The physical properties control water flow, the most important variable determining the potential for deposition and soil to interact. Soils having high surface runoff rates, such as those with low porosities on steep slopes, allow precipitation to flow through rapidly without changing its chemical composition. Such systems would provide little protection for aquatic systems, which would receive the precipitation unbuffered by the terrestrial system. The biological component of the soil contributes some of the means of resistance and/or recovery. Microbial processes in the soil may consume or generate acidity. [CARP E-2.1.3]

Each of the above factors must be considered when one attempts to determine whether acidic deposition is influencing soils, vegetation, and associated surface water chemistry.

#### A.2.1.3 WHAT ARE THE SOURCES AND FATES OF SULFUR, NITROGEN, AND HYDROGEN IONS IN SOILS? [CARP E-2.2.1]

The sources of these ions are site specific. Sulfur in ecosystems comes from either sulfur-bearing minerals or deposition (natural and anthropogenic). The primary sources of nitrogen are the atmosphere, biological fixation, and deposition. The sources of hydrogen are biological processes and deposition. Deposited sulfur, nitrogen, and hydrogen ions may be retained in, or passed through, the soil component of an ecosystem.

In the soils, the ions may be chemically transformed through physical or biological processes, physically adsorbed to soil particles, or removed by leaching into surface or groundwaters, uptake by plants, or conversion to gases. These processes and their names are illustrated in Figures II.1 and II.2.

#### A.2.1.4 WHAT SOIL PROCESSES COULD BE AFFECTED BY ACIDIC DEPOSITION? [CARP E-2.3]

Five types of soil processes could be affected by the deposition of acidic and acidifying substances:

1. Leaching of cations (base cations or aluminum)
2. Weathering (solubilization) of minerals
3. Adsorption of anions
4. Mobilization of metals
5. Microbial processes

Any of these processes may result in impacts on the productivity of vegetation or on surface and groundwater chemistry.

A.2.1.5 WHAT EVIDENCE IS THERE THAT SOIL PROCESSES HAVE BEEN AFFECTED?  
[CARP E-2.3]

Historical field data in the United States are not available to indicate definitively that soils are changing at rates faster than expected from natural processes. Both field and laboratory studies using simulated acidic precipitation suggest pH changes do occur in soils, aluminum is more rapidly mobilized, basic cations are lost at a more rapid rate, and microbial processes are affected by simulated acid precipitation. In all instances, however, these studies involve either application rates far exceeding natural precipitation or application of concentrated acid. Neither of these techniques allows for the normal influences of mineral weathering and vegetative interaction associated with natural nutrient cycling. "Soils exposed to concentrated acids over short periods undergo reactions and changes that would never occur with more dilute acid inputs over longer periods" [CARP E-2.3.1]. Therefore, our understanding of effects of acidic deposition on soils must rely heavily on basic soil chemistry and theoretical calculations, rather than on experimental results.

A.2.1.5.1 IS SOIL pH LIKELY TO CHANGE AS A RESULT OF PRESENT LOADINGS OF  
ACIDIC DEPOSITION? [CARP E-2.3]

No. Changes in soil pH, at current amounts of acidic deposition observed regionally in the United States, are unlikely. "Soil acidification is a natural process in humid regions. It is obvious that atmospheric deposition contributes to this process; however, at current levels it is a minor contribution" [CARP E-2.7]. Most soils that are easily acidified are already acid, having changed over the centuries. Soils likely to become perceptibly more acid due to current levels of deposition are limited in number and geographic extent. In fact, very few soils in the United States meet the acidification criteria discussed in Section A.2.1.6.1 below.

A.2.1.5.2 ARE NUTRIENTS LOST FROM SOILS AT AN INCREASED RATE AS A RESULT OF  
ACIDIC DEPOSITION? [CARP E-2.3.3]

Yes. "There is little doubt that acid deposition can accelerate cation leaching rates, but the magnitudes of these increases must be evaluated within the context of natural internal leaching processes" [CARP E-2.3.3.1]. Data on basic cation leaching due to acidic inputs are inconsistent. The long-term effect (decades or centuries) of acidic deposition, however, is likely to be increased removal of cations from soils. Unfortunately, it is not clear whether this will reduce available cations and enhance the acidification of soils. Cation leaching rates, although increased by acidic deposition, may remain insignificant relative to total soil cation supplies and plant growth requirements.

A.2.1.5.3 IS NUTRIENT RENEWAL IN SOILS FROM MINERAL WEATHERING OCCURRING AT RATES SIMILAR TO THE LOSSES OF NUTRIENTS? [CARP E-2.3.3]

Maybe. Exchangeable cations lost as a result of leaching and uptake by vegetation are replenished by the weathering of primary minerals. Acidic deposition is expected to increase the weathering rates of minerals. If this replenishment rate were equivalent to the rate at which cations are lost, no change in soil nutrient status would be expected. Studies of the most acid lake waters (Wright in Johnson et al. in press) indicate that base cation neutralization inputs may not have kept up with acid sulfate inputs, at least along the major water flow-paths through soils.

The rate at which minerals weather naturally can be estimated from the amount of hydrogen ion that can be assimilated by soils without a decrease in soil pH. It is expected that mineral weathering rates for soils in the United States naturally range from 20 to 2000 meq m<sup>-2</sup>. Most soils have weathering rates in excess of 200 meq m<sup>-2</sup>. Even in those soils thought to have the lowest mineral weathering rates (Spodosols), 20 to 200 meq m<sup>-2</sup> of H<sup>+</sup> could be assimilated. Therefore, only in areas where H<sup>+</sup> inputs exceed this range would a loss of nutrients be expected to be significant. In the northeastern quadrant of the United States, H<sup>+</sup> deposition is approximately 40 to 160 meq m<sup>-2</sup> (estimated wet plus dry). The soils in this region that have H<sup>+</sup> assimilation rates below 40 to 160 meq m<sup>-2</sup>, assuming no increase in mineral weathering, would be vulnerable to change. However, if mineral weathering rates were to double (hypothetical, actual unknown-see below) as a result of acidic deposition in this same region, no significant change in base cation status would be anticipated, even in soils with the lowest weathering rates. [CARP E-2.3.3.1, Table 2-5; Seip in Johnson et al. in press]

At present, no changes in mineral weathering rates due to acidic deposition inputs have been computed from field or laboratory research. Studies are presently underway to quantify these rates as influenced by acidic deposition. Until these studies are complete, it is not possible to evaluate accurately the influence of mineral weathering in preventing soil acidification or significant base cation losses in natural systems. The lack of this necessary data base is one of the most obvious deficiencies in our present knowledge about current or future effects of acidic deposition on soils or surface and groundwaters. As is pointed out by Johnson, "soil weathering rate remains one of the least understood of the master variables controlling soil acidification even after many years' recognition of its great importance" (Johnson et al. in press).

A.2.1.5.4 ARE MICROBIALLY-CONTROLLED SOIL PROCESSES LIKELY TO BE AFFECTED BY PRESENT LOADINGS OF ACIDIC DEPOSITION? [CARP E-2.4, E-2.5]

Not significantly. No evidence exists that suggests current rates of acidic deposition in the United States will cause a decrease in microcrobial activity over the long term. Although alterations in microbial processes have been documented in short-term simulated exposures, longer-term exposures have demonstrated that such processes can recover. It is recognized that certain microbial species are quite sensitive to changes in pH, changes

similar to those that might occur during a single rain event. However, microbial populations in soils are quite adaptable; species shifts occur and processes continue when microbial populations are impacted. Possible effects of acidic deposition on soil microbial activity in natural systems have not been ruled out, but important effects have not been demonstrated at ambient levels under field conditions. [CARP E-2.4]

An important biologically-mediated process that has been extensively studied is organic matter decomposition. It appears this process in forests will be only slightly inhibited over the long-term by acidic deposition, i.e., a less than 2 percent decrease in decomposition rates at pH above 3.0. Thus, unless average precipitation pH falls to 3.0 or below, significant impacts of acidic deposition on litter decomposition in natural systems are not expected. [CARP E-2.5]

#### A.2.1.5.5 ARE METALS MORE LIKELY TO BE MOBILIZED AS A RESULT OF ACIDIC DEPOSITION? [CARP E-2.3.3.3, E-2.6]

Yes. Metals are more readily mobilized with increased soil water acidity. The increased mobility of aluminum in uncultivated, unamended acid soils has the greatest potential for adverse impacts on both terrestrial plant growth and surface water chemistry. Aluminum is the third most abundant element on Earth and a major structural component of soils. When pH drops below 5.0, because of either natural or anthropogenic influences, aluminum becomes soluble in soil water solution. The presence of dissolved organic matter in solution may reduce aluminum solubility. Caution must be exercised, however, in attributing all aluminum movement into soil water solution to acidic deposition. Naturally acid soils with high free aluminum concentrations will likely contribute aluminum to soil water independent of rainfall pH.

The introduction of a mobile anion to an acid soil will lower the pH of a soil solution. A cation-anion balance in solution is required, and most of the exchangeable cations in acid soils are hydrogen ion and aluminum. Due to cation exchange processes in the maintenance of cation-anion balance, increased concentration of an anion such as sulfate in an acid soil solution causes increased hydrogen ion and aluminum concentration regardless of whether the anion is introduced as a neutral salt or an acid. Field studies have confirmed that this mechanism operates in many soil systems. Thus, there remains some question whether, in the eastern United States where soils are already acid, acidity of deposition, per se, is an influential factor in aluminum mobility. It is important to recognize, however, that introducing sulfur, in any form, can increase the potential for aluminum movement in highly acid soils ( $\text{pH} \leq 4.0$ ).

#### A.2.1.6 WHAT IS A SENSITIVE SOIL? [CARP E-2.3.5]

Two views of sensitivity must be considered. Until recently, a sensitive soil was thought of as one whose pH was likely to change due to acidic deposition. Soil sensitivity, or potential effects of acidic deposition, can be separated into two categories: "1) changes related to soil pH/basic cation changes, which include any direct losses of nutrients or changes in processes or availability, and 2) changes in soil solution and/or leachate chemistry that might affect aquatic systems or be toxic to plant roots, for

which the primary concern is change in (available) aluminum concentration" [CARP E-2.3.5.2]. Within each of these sensitivity categories are distinctly different soils. Therefore, the term 'sensitivity' must be used carefully to express sensitivity of the soil to one or the other of the above potential effects.

#### A.2.1.6.1 WHAT ARE THE CHARACTERISTICS OF A SENSITIVE SOIL? [CARP E-2.2.8, E-2.3.5]

Many soil classification schemes have been proposed. Each has serious weaknesses when studied in detail, but all generally agree when viewed on a national scale. Soils in which pH changes and basic cation losses might occur have the following characteristics: 1) the cation status of the soils is not renewed by flooding, 2) they have no buffering carbonates to depths in excess of 1.0 m, 3) they have a low cation exchange capacity, but presently have a pH greater than 5.5, and 4) they have a low sulfate adsorption capacity. There are very few soils in the United States with high enough pH and low enough reserves of exchangeable cations that they could be acidified by current amounts of acidic deposition.

The soils in which acidic deposition is likely to increase aluminum in soil solution are those that are already extremely acid, i.e., pH less than 4.0. The buffering capacity of these soils is largely controlled by aluminum mineral chemistry. Increased acidic inputs can therefore increase the rate of aluminum release and the aluminum concentration in soil solution or leachate. This is most likely to occur in coarse-textured acid soils, again, where the cation exchange capacity is not renewed by flooding, and the soils are free of buffering carbonates and have a low sulfate adsorption capacity (SAC). Most soils of the eastern United States meet all but the low SAC criterion.

Knowledge of sulfate adsorption capacity of soils is a primary missing link to understanding the acidic deposition effects. The presence of a mobile anion is necessary for leaching of cations to occur. The dominant anion in atmospheric deposition is sulfate. Therefore, the reaction of sulfate, especially its adsorption or free movement, is an important soil characteristic. Soils containing large quantities of iron and aluminum oxides have the capacity to adsorb sulfate. These metals are common to all soils. Aluminum is a major structural component of soils, but the oxide form is common only in highly-weathered, acid soils, similar to the soils found in the eastern United States. Sulfate-adsorbing soils are believed to delay cation leaching effects of dilute sulfuric acid inputs until a point when the adsorption capacity is exceeded down through the soil zones of interest. Thus, SAC determines the rate or time of release of metals to soil water solution and/or aquatic systems but does not necessarily prevent it. [CARP E-2.2.8]

#### A.2.1.6.2 WHERE ARE THE SENSITIVE SOILS IN THE UNITED STATES? [CARP E-2.3.3, E-2.3.5]

Figure II.5 identifies regions of the United States where acidic deposition is most likely to have an impact on soil or surface waters. It should first be noted that it is unlikely that acidic deposition will adversely affect



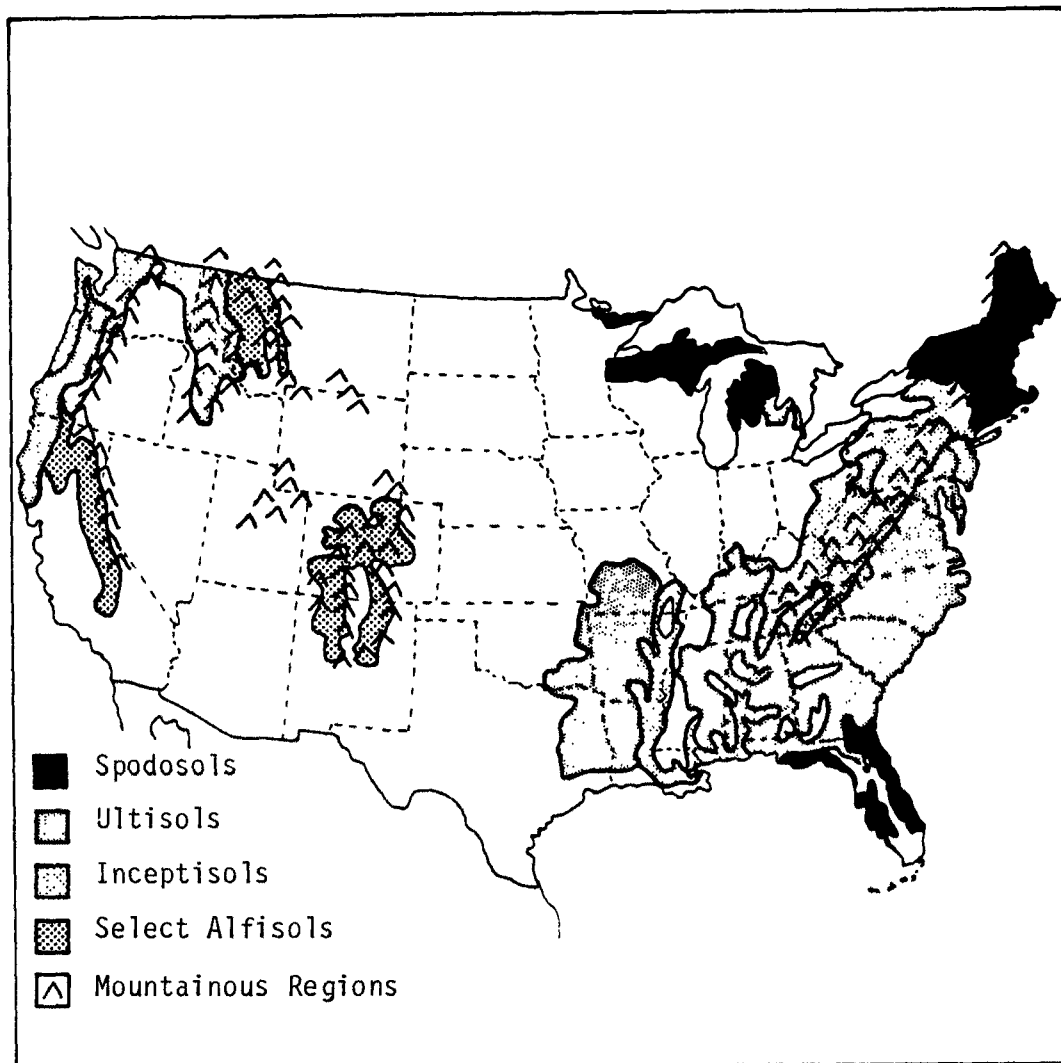


Figure II.5 Regions with soils potentially sensitive to mobilization of aluminum or with limited hydrogen ion neutralization capacity. Areas in black, Spodosols are of immediate concern, due to their potential to contribute aluminum to the soil water solution. Ultisols and Inceptisols may contribute aluminum after saturation of sulfate adsorption capacity. Mountain regions with thin soils and steep slopes have limited hydrogen ion neutralizing capacity.

cultivated soils. Not only do many management practices result in acid production much greater than that expected from acidic deposition, but good agricultural practice also requires controlling pH within a range that is favorable for plant growth. Routine additions of nitrogen fertilizers may result in the release of between one and two orders of magnitude more hydrogen ion than will be derived annually from acidic deposition. Because impacts of these additions are routinely counteracted by liming, soil scientists have little interest in the negative effects of acidic deposition on cultivated soils. Deposition of sulfur has helped alleviate sulfur deficiencies in soils in the Southeast and Midwest. As a result, the concern over acidic deposition effects is focused primarily on uncultivated, unamended soils, which are found mostly in forested and grassland regions of the United States.

Those regions of the United States dominated by Ultisol, Spodosol, and some of the Inceptisol soil orders are predicted to be sensitive to the mobilization of aluminum by acidic deposition. Because Ultisols and Inceptisols have a relatively high SAC, soil or surface waters in regions dominated by these soil orders should respond slowly to changes in sulfate deposition. Only the Spodosol regions of the United States are expected to respond quickly to changes in sulfate deposition. In the regions of the United States that have very thin soils, in particular, steeply sloped, mountainous regions, surface water quality will respond quickly to changes in acid deposition. Rapid transfer of precipitation directly to the aquatic system in regions of very thin soils prevents neutralization.

It must be recognized that mapping efforts at any scale above the most detailed (e.g., county soil maps) will by necessity include a wide range of conditions within any map unit. For this reason, the associated maps should be used with some caution.

#### A.2.1.7 COULD OBSERVED/POTENTIAL CHANGES IN SOILS AS A RESULT OF ACIDIC DEPOSITION BE REVERSED? [CARP E-2.3.4]

The natural trend in soil pH is toward greater acidity, independent of acidic deposition. Decreasing the loading of acidic deposition will not change this process. However, decreasing anion deposition, sulfate for example, would likely decrease the rate at which aluminum will be mobilized. The time required to observe a significant change in aluminum mobility after decreased sulfate deposition is unknown.

#### A.2.1.8 WHAT IS THE TIME FRAME IN WHICH CHANGES IN SOIL CHEMISTRY COULD RESULT FROM ACIDIC DEPOSITION? [CARP E-2.3]

Decades or centuries are the most likely time frames in which soil chemistry changes could result from acidic deposition. The time frame is soil and site dependent.

## A.2.2 WHAT ARE THE EFFECTS OF ACIDIC DEPOSITION ON FORESTS AND CROPS? [CARP E-3]

### A.2.2.1 WHAT CONSTITUENTS OF PRECIPITATION AND THE ATMOSPHERE INFLUENCE VEGETATION?

Plants need 16 elements or essential nutrients, in appropriate proportions, for optimal growth. Precipitation supplies all of these nutrients in various quantities and for some elements, provides enough to replenish that taken up by the plants during a growing season.

Plant growth can be limited by the scarcity or absence of any element. Nitrogen is usually the limiting nutrient in unmanaged systems. Infrequently, sulfur is a limiting nutrient. The amount of sulfur or nitrogen needed for optimal plant growth is species specific. The constituents of precipitation that are most important in determining plant response are nitrogen, sulfur, and trace metals. Hydrogen ion is also important because it influences the availability of nutrients to the plant. Many of the trace metals, along with sulfur, nitrogen, and hydrogen, are essential elements. The concern, however, is related to the quantities of these elements, particularly quantities sufficiently large to induce phytotoxicity.

### A.2.2.2 WHAT ARE THE PRIMARY MECHANISMS BY WHICH VEGETATION MIGHT BE AFFECTED BY ACIDIC DEPOSITION? [CARP E-3.2, E-3.4]

Both indirect and direct mechanisms are known. Changes in soils, and resultant changes in productivity, are the potential indirect effects of acidic deposition on vegetation. The discussion of soils in the previous section recognized that soil properties play a major role in controlling plant growth. Soil pH, per se, is unlikely to change and nutrient cycling and biologically-mediated processes in soils should remain relatively stable at current regional average amounts of acidic deposition. However, nutrient and aluminum concentrations can change in soil water solution and eventually be taken up by plants or delivered to ground or surface waters.

The following potential direct effects of acidic deposition on vegetation are hypothesized: leaching of nutrients from foliage; increased permeability of leaf surfaces to toxic substances, water, and disease agents; altered reproductive processes; altered rhizosphere relationships; erosion of protective wax surfaces; chlorophyll degradation; premature senescence; and general physiological alterations. Only the first of these direct effects has been observed in the field under ambient conditions [CARP E-3.4.1.1], but all six have been reported in simulated rain experiments.

### A.2.2.3. WHY ARE THE EFFECTS OF ACIDIC DEPOSITION ON VEGETATION DIFFICULT TO DISCERN? [CARP E-3.3, E-3.4]

Because plants exist in a complex, often stressful, environment and are themselves complex biological systems, acidic deposition is only one factor that may alter their response. Isolating acidic deposition's effects from the effects due to other stresses and natural variability is quite difficult. As a result, our knowledge and ability to discern the effects of acidic

deposition on plants is developing slowly. The effect of acidic deposition or any other anthropogenic stress, on plants depends upon the concentration, duration, frequency, and combination of stresses to which the plant is exposed. In addition, many natural environmental factors influence plant performance. These include the availability of nutrients, proper soil pH, light, temperature, adequate water, etc. Each factor alone, if dramatically altered, can induce both positive and negative plant effects. Furthermore, a plant must interact with its biological environment--disease, competition between plants, insects, and other organism interactions. Finally, the genetic makeup, species, and/or life stage of the plant must be considered in determining the effects of any given pollutant on plant response. The response to combined effects of these natural factors and of anthropogenic stresses determines how well a plant will fare in a particular environment.

#### A.2.2.4 WHAT DO WE KNOW ABOUT ACIDIC DEPOSITION'S EFFECTS ON CROPS? [CARP E-3.4.2]

A number of studies on the effects of acidic deposition on crops have been published in the last five years. Limitations in research designs, however, restrict the usefulness and applicability of many of the experimental conclusions. In most of these studies, only large differences in crop yields would be considered statistically significant. Results from different studies are often inconsistent and difficult to compare because of important differences in methodologies. Consequently, we currently know little about the effects of acidic deposition on agricultural crops.

##### A.2.2.4.1 WHAT TIME FRAME IS IMPORTANT IN DEFINING EFFECTS OF ACIDIC DEPOSITION ON CROPS? [CARP E-3.4.2]

The time frame in which acidic deposition might affect crops depends on the crop, the acidity of deposition, and the frequency of exposure. A crop likely responds to every rain event. It is not known, however, whether a single rain event is sufficient to induce a beneficial or detrimental longer-term response, e.g., an increase or decrease in productivity.

At present, weighted mean pH during the growing season has been used as the dose parameter for annual crop effects. Perennial plants are exposed to acidic deposition for years; longer-term average and/or total exposures are considered most important, primarily because no data indicate significant effects resulting from a few extreme exposures.

Any conclusions drawn relative to the important time frame need to be plant family, if not species or cultivar, specific.

##### A.2.2.4.2 IS THERE EVIDENCE TO SUGGEST THAT CROPS ARE RESPONDING TO ACIDIC DEPOSITION? [CARP E-3.4.2.2.1]

Yes. Thirty-four crop varieties (28 species) have been exposed to simulated acidic precipitation in controlled-environment experiments. Of the 34, six exhibited a decreased yield, eight exhibited increased yield, 17 showed no effect, and three species exhibited both increased and decreased yield depending on the hydrogen ion concentration or conditions of exposure.

Fourteen crop cultivars (nine species) have been exposed in field studies and only one (garden beet) showed consistently decreased yield at all experimental acidity levels. Three cultivars were negatively affected and six were positively affected by at least one of the acidity levels. Most of the cultivars studied in the field and in controlled environments exhibited no effect on growth or yield as a result of exposure to simulated acidic precipitation.

A.2.2.4.3 IS THERE EVIDENCE TO SUGGEST THAT CROP PRODUCTIVITY HAS BEEN SIGNIFICANTLY AFFECTED BY ACIDIC DEPOSITION? [CARP E-3.4.2.3]

There is very little evidence. Field studies are the most appropriate means of estimating effects because the experimental plants are grown under normal environmental conditions, especially when common agricultural practices are used. Only 'Amsoy' soybeans have consistently shown significant decreased productivity as a result of exposure to simulated acidic precipitation at the ambient loadings currently observed in the eastern United States. Studies on this soybean variety have provided the most convincing evidence that crop productivity might be affected by acidic deposition.

"Available experimental results do not appear to indicate that the negative effects of acidic precipitation outweigh the positive effects; however, many crops and agricultural systems have not been properly or adequately studied" [CARP E-3.5]. In comparison to the effects of natural stresses and of other gaseous pollutants, the effects of acidic deposition on crop productivity are likely to be small.

A.2.2.4.4 WHAT HAS PREVENTED A CLEAR QUANTIFICATION OF THE EFFECTS OF ACIDIC DEPOSITION ON CROPS? [CARP E-3.4.2.3]

Crop response to acidic deposition is measured by changes in growth and yield, or productivity. This productivity is influenced by all other environmental conditions and cultivation practices, as well as by the positive effects of sulfur and nitrogen fertilization and the negative effects of acidity. Quantifying the net effects of one specific factor, acidic deposition, is complicated by interactions among all of these variables.

A.2.2.5 WHAT DO WE KNOW ABOUT THE EFFECTS OF ACIDIC DEPOSITION ON FORESTS? [CARP E-3.4.1]

We know that within the last 25 years changes without obvious natural cause have taken place in the growth and development of forests especially in Europe but also in the eastern United States. We also know that changes are occurring in the amounts and patterns of emissions of atmospheric pollutants and the exposure of forests in Europe and North America to gaseous pollutants, toxic metals, and acidic deposition. But we do not know if the latter have caused the former. The complex chemical nature of combined pollutant exposures, the fact that both sulfur and nitrogen are essential nutrients, and the potential of these pollutants to have both direct effects on vegetation and indirect effects (through soil-mediated impacts) makes quantifying effects on forests particularly challenging.

A.2.2.5.1 IS THERE EVIDENCE TO SUGGEST THAT ACIDIC DEPOSITION IS AFFECTING FOREST GROWTH? [CARP E-3.4.1]

- No. Although we cannot yet conclude that acidic deposition has not, and will not, affect forest growth, we have no direct evidence that acidic deposition per se currently limits, or has limited forest growth in North America or Europe. Experimental data from irrigation studies on seedlings and young trees have not shown cause for immediate alarm but the data are difficult to interpret because of treatment artifacts. Growth response of forest trees is influenced by many variables such as genetic diversity, competition, climate, and site factors. The additional possible effects of acidic deposition, gaseous pollutants, trace metals, and interactions between pollutants, and the lack of appropriate control sites for comparison increase further the problem of detecting responses to any one factor.

"Although the task of assessing potential impacts on forest productivity is assuredly difficult, the potential economic and ecological consequences of even subtle changes in forest growth over large regions dictates that it should be attempted" [CARP E-3.4.1.7]. Such studies are now under way.

A.2.2.5.2 IS THERE EVIDENCE TO SUGGEST THAT A REGIONAL DECLINE OF FORESTS IS OCCURRING IN EUROPE OR NORTH AMERICA? [CARP E-3.4.1]

Yes. Researchers in Europe, particularly in the Federal Republic of Germany, have observed obvious, but unexplained, large-scale regional changes in the growth and behavior of forests containing Norway spruce, silver fir, Scots pine, European beech and certain other broad-leaved and needle-bearing trees. These decline phenomena, called 'Waldsterben', include three types of symptoms: growth decreases, abnormal growth, and water stress (Schutt and Cowling 1984). In the United States, a decline of red spruce at high elevations has been observed in New York and New Hampshire and has been quantitatively documented in the Green Mountains of Vermont, where widespread mortality was preceded by decreased annual growth. Between 1965 and 1979, an overall reduction of approximately 50 percent in tree basal area and forest density was observed in the Green Mountains (Johnson and Siccama 1984). In the pine barrens of New Jersey, pitch, short-leaf, and loblolly pines have shown decreased diameter growth.

A.2.2.5.3 WHAT HYPOTHESES HAVE BEEN PROPOSED TO EXPLAIN RECENT REGIONAL FOREST DECLINES?

Forest scientists have proposed several major hypotheses to explain one or more parts of the declines. These hypotheses have been developed largely to explain observations in the German forest environment. Since decline symptoms in high-elevation spruce forests in the United States resemble some of those found in Germany, the hypotheses deserve careful consideration. A report expected from a joint U.S.-German scientific group that carefully studied German and U.S. forests in the spring and summer of 1984 should provide an excellent comparison of symptoms and evaluation of damage hypotheses. One classification of 'Waldsterben' hypotheses has recently been provided by Schutt and Cowling (1984):

- Acidification - aluminum toxicity: changes in soil from acidic deposition
- Gaseous pollutants causing direct damage to foliage
- Magnesium-deficiency resulting from leaching by materials deposited on foliage
- Excess-nutrient, especially excess nitrogen, introduced to the soil system
- Air transport of growth-altering organic substances which may be taken up either through foliage or from the soil.

These five hypotheses include both direct effects on foliage and indirect effects, changes in soil which cause changes in growth. All of these assume further that the trees are subject to

- General stress resulting from climatic effects (fluctuation in rainfall and temperature), and exposure to biotic pathogens such as viruses, fungi, or insects.

#### A.2.3 WHAT ARE THE EFFECTS ON AQUATIC CHEMISTRY? [E-4]

##### A.2.3.1 WHY ARE SURFACE AND GROUNDWATERS AN IMPORTANT CONSIDERATION IN STUDIES OF ACIDIC DEPOSITION EFFECTS?

Surface waters are important for human consumption, recreation and wildlife habitat. The most critical use of surface and groundwater is as drinking water. Detrimental effects on drinking water would have serious ramifications. To date, there is no evidence to warrant concern about groundwaters in the United States being affected by acidic deposition. However, evidence that some surface waters are being acidified, for whatever reason, has resulted in focusing research on these systems. The discussions to follow are limited to changes in lakes and streams.

##### A.2.3.2 WHAT SURFACE WATER CHEMICAL CHARACTERISTICS MAY BE INFLUENCED BY ACIDIC DEPOSITION? [CARP E-4.2, E-4.3]

The status of hydrogen ions, sulfate, base cations, aluminum, nitrate, and organic carbon in aquatic systems may be affected by acidic deposition. Acid neutralizing capacity (ANC), ion exchange and mineral weathering rates, nutrient and organic carbon availability in the watershed may all be affected, depending on the aquatic system and the amount and composition of deposition it receives.

##### A.2.3.3 WHAT ATMOSPHERIC CHEMICAL INPUTS INFLUENCE CHEMICAL CHARACTERISTICS OF AQUATIC SYSTEMS? [CARP E-4.3.1]

Hydrogen ion additions in aquatic systems were originally the focus of most concern because increases in hydrogen ion, by definition, increases the acidity of surface waters. Whether the hydrogen enters the aquatic system

from the terrestrial system or directly from acidic deposition makes little difference.

More recently, however, other deposition components have been recognized as being important. In addition to  $H^+$  deposition, atmospheric deposition of sulfur ( $SO_4^{2-}$  and  $SO_2$ ), nitrogen (as  $NO_3^-$  and  $NH_4^+$ ), and base cations (e.g.,  $Ca^{2+}$  and  $Mg^{2+}$ ) can greatly influence the chemistry of a system. Phosphorus and organic carbon deposition may also be important in some systems.

Significant internal production of ANC may occur due to chemical and biological transformations of  $NO_3^-$  in either the terrestrial or aquatic system. Under conditions where nitrate is not rapidly immobilized and metabolized, it may serve as a mobile anion, carrying base or acidic cations from the terrestrial to the aquatic system. Nitrate mobility is not often observed, however, except during periods of rapid snowmelt.

Because sulfur is especially problematic, its influence will be treated separately in the following Sections A.2.3.4 and A.2.3.5.

Deposited ammonium ion,  $NH_4^+$  is consumed chemically or biologically, often resulting in decreased ANC.  $NH_4^+$  deposition can be a major source of the net acid input to some systems, e.g., about 25 percent at Harp Lake, Ontario. Clearly, the impacts of acidic deposition cannot be assessed based upon free acid ( $H^+$ ) measurements alone. [CARP E-4.3.1.1]

Deposition of base cations must also be considered in calculating ion exchange, mineral weathering, acid neutralization and net loss of base cations from the system. The total deposition of other cations and anions, particularly nitrogen and phosphorus, may contribute substantially to the available nutrients of inland freshwaters. These atmospheric inputs may be an important nutrient source for aquatic organisms in nutrient-poor systems, e.g., watersheds with granitic substrates and a large water surface area to drainage area ratio. Gaseous exchange of nitrogenous compounds may also be an important influence on lake chemistry but it is poorly understood.

Precipitation inputs of phosphorus and nitrogen may account for about half of the concentration of these elements in oligotrophic lakes. This input becomes much less influential on the total budget of an aquatic ecosystem when runoff from land-use activities increases (i.e., agriculture, urbanization). Systems dominated by terrestrial inputs of phosphorus and nitrogen are usually much more biologically productive, if not eutrophic. [CARP E-4.3.1.5.1]

Precipitation inputs of organic carbon may be ecologically significant for some aquatic ecosystems, particularly oligotrophic lakes, based on preliminary data. Mean concentrations in precipitation averaged about  $6 \text{ mg C } \ell^{-1}$  and accounted for 28 percent of the total organic carbon inputs for a small oligotrophic lake in New Hampshire. Data are not sufficient, however, to extrapolate the importance of atmospheric inputs of organic carbon to oligotrophic lakes in general. [CARP E-4.3.1.5.1]



#### A.2.3.4. WHY IS DEPOSITION OF SULFUR COMPOUNDS PARTICULARLY IMPORTANT TO AQUATIC CHEMISTRY? [CARP E-4.3.1.5]

Increased sulfate deposition has a great effect on aquatic chemistry because, on an equivalent basis, the sulfate increase in the waterbody must be matched by an increase in cations, either protolytic (proton-donating, e.g.,  $H^+$ ,  $Al^{n+}$ ) or non-protolytic (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$ , etc.). Increasing the former will result in loss of alkalinity (acidification) of the waterbody. Increasing the latter will result in basic cation loss from the terrestrial system but no alkalinity loss in the aquatic system. The proportion of these two processes in any given watershed is a matter of research investigation.

Sulfate may be stored in watersheds through sulfate adsorption, a process that may also generate ANC if the sulfate is reduced or if strong acid is neutralized. Sulfate reduction in lakes will also generate ANC although only the net production of ANC, i.e., net reduction of nitrate or sulfate, on an annual basis is important. In some systems, sulfate moves through the watershed as a conservative substance.

Sulfur dioxide and sulfate, whether wet or dry deposited, move along similar pathways through terrestrial and aquatic systems; therefore, sulfur's effect on aquatic systems does not depend on the chemical form or physical form of deposition.

#### A.2.3.5. HOW DEPENDENT ON ATMOSPHERIC DEPOSITION ARE SURFACE WATER SULFATE VALUES? [CARP E-4.3.1.5.2]

As with soils, rock weathering and atmospheric deposition provide sulfur for surface waters. In the absence of reactive sulfur sources in bedrock or in decaying organic matter, atmospheric deposition is the primary source of sulfur. This is especially true in areas that receive acidic deposition but do not have significant sources of reactive sulfur in the watershed. In such areas sulfate still can become the dominant anion in low alkalinity waters.

Plotting the mean and range of excess sulfate (above that supplied by sea salt cycling) export from watersheds across northern North America on a line that transects the region of large atmospheric deposition of sulfate (Figure II.6) shows a positive relationship between excess sulfate deposition and sulfate in the runoff, although sulfate export exceeds deposition in the areas of highest deposition. The wet deposition of excess sulfate is shown at each location, with estimated total sulfate deposition shown at four locations. Dry deposition of sulfate and  $SO_2$  may account for most of the greater sulfate export from watersheds compared to wet-deposited sulfate entering watersheds. In areas still accumulating sulfate in watersheds, this positive relationship will not hold.

The influence of atmospheric sulfate deposition on surface water sulfate values is also suggested by statistically significant correlation between sulfate concentrations in surface waters and sulfate concentrations in precipitation, over a wide range of concentrations, as illustrated in Figure II.7. Southeastern Canada and the northeastern United States receive precipitation with high concentrations of sulfate and also have surface

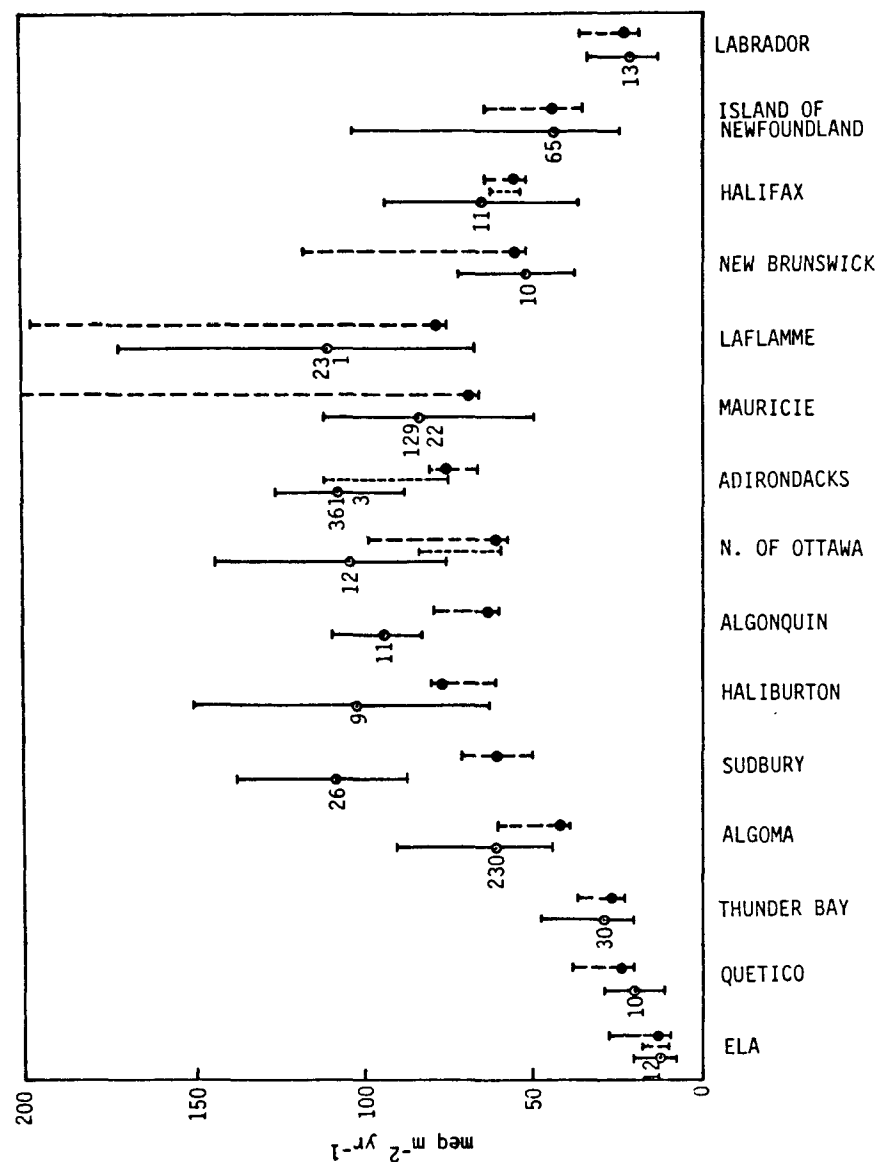


Figure II.6 Mean and range of basin specific yield of excess sulfate ( $\circ$ ) compared with atmospheric excess sulfate deposition ( $\bullet$ ) in precipitation for 1980 (Thompson and Hutton 1981, 1982) and the range of estimated wet deposition for 1977-80 from the CANSAP precipitation network (Barrie and Sirois 1982). Also shown are the ranges of wet plus dry deposition of sulfate (---) calculated from the 1980 measurements of  $\text{SO}_x$  in the atmosphere at 4 Canadian Acid Precipitation Network Stations (Barrie 1982). Adapted from U.S./Canada (1983).

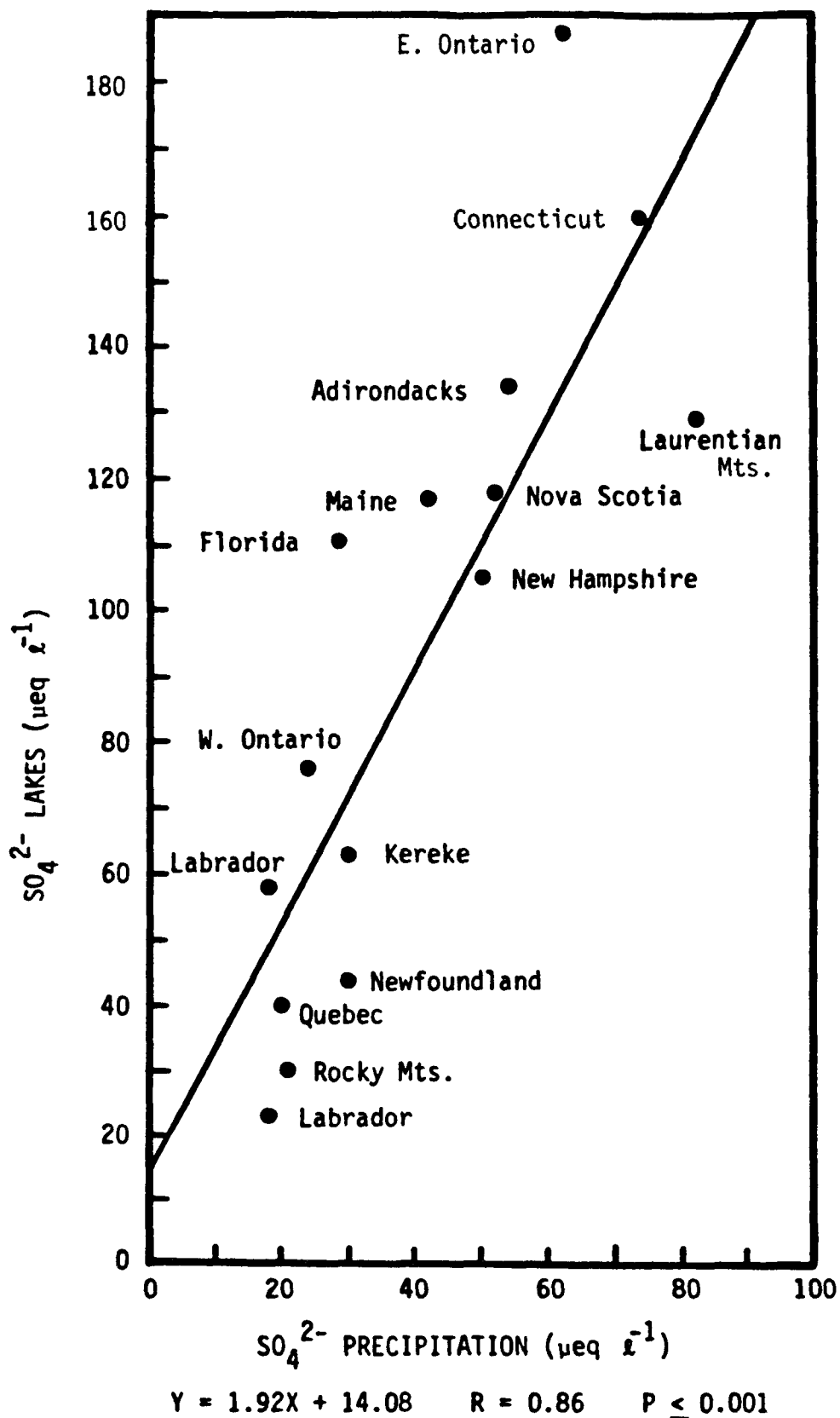


Figure II.7 Mean concentration of SO<sub>4</sub><sup>\*</sup> (excess SO<sub>4</sub><sup>2-</sup>, over and above that supplied by sea salt cycling) for 15 lake groups in North America and mean SO<sub>4</sub><sup>\*</sup> in wet deposition at nearby deposition monitoring stations. Adapted from Wright (1983).

waters with high concentrations of sulfate. Similarly, the areas receiving precipitation with low concentrations of sulfate are also those with low concentrations of sulfate in surface waters (northern Quebec, Labrador, Colorado, Rocky Mountains). Based on this data, background sulfate concentrations are estimated at 20 to 40  $\mu\text{eq l}^{-1}$  for North American lakes. Sulfate concentration values of 100 to 160  $\mu\text{eq l}^{-1}$  in lakes in areas of eastern North America receiving acidic deposition suggest that anthropogenic atmospheric deposition accounts for 80 to 120  $\mu\text{eq l}^{-1}$  (average 100  $\mu\text{eq l}^{-1}$ ) of sulfate. A relatively large region of eastern North America is included in this estimate, with some areas relatively distant from sulfate sources.

"Those waterbodies in areas closer to sulfur emission sources will have larger increases in sulfate concentrations. For example, lakes near Sudbury, Ontario have  $\sim 400 \mu\text{eq l}^{-1}$  of sulfate from atmospheric deposition while lakes east of the Rhine-Ruhr industrial region of Germany can have  $> 1000 \mu\text{eq l}^{-1}$  of sulfate from atmospheric deposition" [CARP E-4.3.1.5.2].

#### A.2.3.6 WHAT FACTORS "CONTROL" SURFACE WATER CHEMISTRY? [CARP E-4.3.2]

Each of the following may play a significant role in contributing to or neutralizing system acidity: vegetative canopy, soils, bedrock, hydrology/residence time of water, presence of and processes in wetlands, and the surface water system itself. Each of several components of aquatic or terrestrial systems may assimilate some or all acidic deposition falling on a watershed, depending on the site. On a regional basis, some variables play a much more important role than others. The components are linked; atmospheric deposition may affect one component directly with effects subsequently propagated to others. The pathways of water, and its chemical constituents, through the system from first interception of precipitation to final appearance in surface waters determine which components are affected.

Water that flows through the vegetative canopy contains higher concentrations of most elements than incident precipitation because the chemical content of precipitation changes as it washes off deposited particles and collects leachates from the vegetation. Particle washdown by precipitation is independent of any ability of the canopy to assimilate deposited chemical constituents. However, cation leaching from the canopy may represent significant acid-neutralizing capacity. The relative importance of each of these processes is not well understood. [CARP E-4.3.2.1]

Soils assimilate acidic deposition through mineral weathering, cation exchange, sulfate adsorption, and biologic processes. Generally, soils containing carbonate materials can assimilate acidic deposition to an almost unlimited extent because of abundant exchangeable bases. Soils that do not contain carbonate materials can also assimilate some acidic deposition because of cation exchange reactions and mineral weathering. Assimilation ability is affected by the soil chemical properties (especially cation exchange capacity, base saturation, and sulfate adsorption capacity), the permeability at each layer, the surface area of the soil particles, and the depth of soil in the watershed. [CARP E-4.3.2.2]

The effective surface area of massive, impermeable silicate bedrock for chemical reaction is minimal. Bedrock that is jointed or fractured has greater surface area for reaction, but complete assimilation will occur only at considerable depth, potentially affecting the groundwater chemistry but having little effect on stream and lake chemistry. Silicate bedrock having a porous nature, e.g., weakly cemented sandstone and bedrock of carbonate minerals, will have the greatest capacity for surface reactions. [CARP E-4.3.2.3]

✓ Hydrology, specifically flow paths through terrestrial systems and residence times of water in lakes, can determine the extent of reactions between strong acid components of deposition and each component the water contacts. Soil physical properties are major determinants of water flow and thus, of the interaction of soil with acid rain. Water running rapidly through soils (e.g., on steep slopes with low porosities or well-drained, highly porous soils) may have little opportunity to interact and may be changed only slightly in composition [CARP E-2.1.3.1]. A generalized view of the flow of water through a terrestrial ecosystem is shown in Figure II.8. Water striking the surface may infiltrate the soil or flow across the surface. About 75 percent of precipitation enters the soil in temperate climates. The type of forest floor or its disturbance, the presence of large channels ('macropores') from burrowing animals and decomposition of tree roots, and the degree of water saturation of the soil at the time of precipitation are examples of the many factors affecting soil hydrology. Considerable scientific debate has arisen from the suggestion that during heavy rain or rapid snowmelt a greater proportion of flowing water will contact the most acid, humus-rich soils high up in the watershed, resulting in 'natural' acidification. [CARP E-2.1.4, E-4.3.2.4]

The role of wetlands in assimilating acidic deposition is generally unknown. Alkalinity present in the aqueous component of the wetland can neutralize acidity, and other processes including reduction and ion exchange reactions may contribute to assimilation. The biogeochemistry of wetlands is poorly understood; these systems are considered by some to be extremely vulnerable to acid deposition while others view them as potential contributors to acidity and acidification because of their often natural low pH. [CARP E-4.3.2.5]

Whatever the factors controlling surface water chemistry, it appears that alkalinity in the surface water is the best single measure of the combined acid-neutralizing processes in the watershed. Although alkalinity represents only one component, it is a result of continuing terrestrial and aquatic interactions. Undisturbed surface waters of high alkalinity are likely to be contained within watersheds with high neutralizing capacity. [CARP E-4.3.2.6.1]

"Alkalinity or acid-neutralizing capacity (ANC) determines a lake's instantaneous ability to assimilate acidic deposition, but the ANC renewal rate depends upon the ANC supply rate from the watershed. In addition, internal production of alkalinity is important, especially in lakes with low alkalinity. Because biological processes can alter the relative amounts of acidity and alkalinity within a body of water, nutrient status is important in determining the sensitivity of a lake to acidification" [CARP E-4.8].

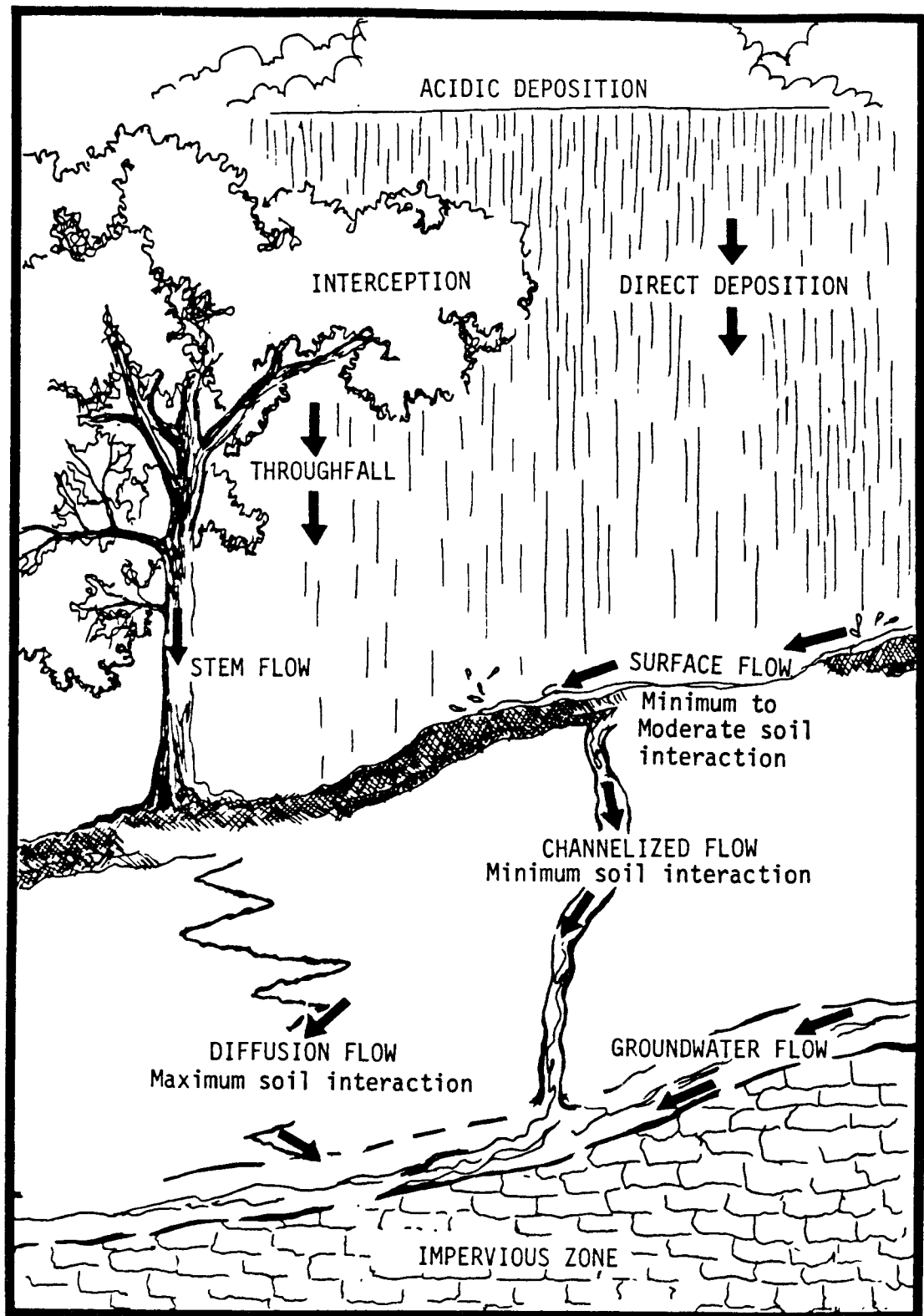


Figure 11.8 Flow paths of precipitation through a terrestrial system.

A.2.3.7 IS THERE EVIDENCE TO SUGGEST THAT ACIDIC DEPOSITION HAS ALTERED SURFACE WATER CHEMISTRY? [CARP E-4.4.3]

Yes. Many studies have been conducted to examine temporal changes in stream and lake chemistry in relation to the chemical composition of precipitation. A consistent drawback of studies of trends is a lack of clear documentation of the "historic" data used. Often these crucial data have not been proven unbiased, either in the sampling or analytical procedures used.

In each case listed below, viewed by the authors of the CARP as being 'most reliable', the scientists who performed the studies concluded that pH and/or alkalinity decreased in at least some of the surface waters studied. [CARP E-4.4.3.1.3]

- La Cloche Mt. region, Ontario
- Halifax, Nova Scotia
- New England; Maine, New Hampshire, Vermont
- Adirondack region, New York
- New Jersey, Pine Barrens
- Sierra Nevada Mts., California
- USGS Hydrologic Bench-Mark Stations

"In every case reviewed the scientists who performed these studies concluded that changes in surface water chemistry reflected, at least partly, either (1) trends in regional emissions of SO<sub>2</sub>, or (2) changes in chemical composition of incident precipitation. This reviewer finds the body of evidence presented ... convincing. Particularly noteworthy by its absence is any body of data indicating consistent decreases in alkalinity or pH of surface waters at otherwise undisturbed sites not receiving acidic deposition. Furthermore, this reviewer is unaware of any natural process that would cause decreases in pH and/or alkalinity at the rates indicated by these studies. Until appropriate evidence is presented in support of some such natural process or until some better explanation of the data presented ... is put forth, the only logical conclusion is that acidic deposition (of either remot or local origin) at these sites has caused, or is now causing, acidification of some surface waters. It is only reasonable to assume that other surface waters of similar sensitivity that receive similar levels of acidic deposition have become, or are now being, acidified." [CARP E-4.4.3.1.3]

The concentration of sulfate in clearwater lakes and streams has increased due to atmospheric deposition in some systems and may be decreasing in some regions with decreasing acidic components in deposition [CARP E-4.4.3.1.2.3]. Measures of sulfate, bicarbonate, hydrogen ion, and base cations are an appropriate means to evaluate site-by-site changes.

In addition to examining available historical records, scientists have begun to analyze the record contained in lake sediments. Paleolimnological techniques, including the dating of sediments, have been used to reconstruct chronological sequences of pollution inputs to lakes (e.g., lead) and responses of the lake biota (e.g., plankton). Knowledge of pH relationships between water and diatoms for present-day diatom assemblages allows researchers to calibrate the sedimentary diatom record and estimate past pH

of lake waters to produce a dated record of lake acidification. [CARP E-4.4.3.2]

Detailed paleolimnological analyses for pH change over the past 300 years have been completed for 15 acidic lakes in the northeastern United States. Analysis of diatoms in the sediment cores indicated that nine of the lakes have experienced pH decreases in recent years (9 to 80 years); at least three of these declines may represent, in part, recovery from earlier pH increases caused by disturbances such as lumbering in the watershed. [CARP E-4.4.3.2]

#### A.2.3.8 WHAT TIME FRAME IS IMPORTANT IN ACIDIC DEPOSITION'S EFFECTS ON AQUATIC CHEMISTRY? [CARP E-4.4.2, E-4.4.3]

Both long-term acidification (over years or decades) and short-term (days or weeks; episodic) acidification from release of accumulated chemicals during snowmelt or deposition from heavy rains are of concern to the extent that biota, particularly fish, may be affected. Evidence for long-term acidification has been cited above, but little evidence of the time course of acidification is available. The sediment records cited above indicate that there may be a lag of decades between the first evidence of increased deposition and significant increase in acidity of the lake. The acidity change of the lake may then occur over a period of a few years. (Davis et al. 1983). Section B of this chapter further discusses rates of aquatic response.

To predict the importance of episodic events to aquatic ecosystems, one must be able to evaluate the probability of chemical (pH, alkalinity, aluminum, etc.) change of specific magnitude in a lake or stream for a specified duration.

Episodic events have resulted in pH decreases of more than one pH unit. Not all aquatic systems within areas receiving acidic deposition experience significant pH decreases, however, and even simple dilution by 'non-acidic' rainwater can result in decreased pH and alkalinity. Studies to date indicate that pH during spring snowmelt or heavy rain may reach 4.5 to 5.0, the same range observed in long-term acidification (see Table II.1.). During episodic acidification, aquatic systems with pH's as high as 7.0 can reach pH < 5.0; long-term acidification to pH < 5.0 is generally not observed in aquatic systems with apparent initial pH's > 6.5. Much of the water reaching a stream during a storm event may pass through the upper layers of soils that are often dominated by organic acidity. Nitrification in the soils, during drought periods in the summer or under the snowpack, may generate acidity, resulting in pH depression and increased nitrate flux during episodes. [CARP E-4.4.2]

#### A.2.3.9 WHAT OPTIONS ARE AVAILABLE TO COUNTERACT SURFACE WATER ACIDIFICATION? [CARP E-4.7]

Although the most effective control of acidification is to control the acidic and acidifying inputs, another option involves treating acidic waters with acid-neutralizing chemicals. Lime [ $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ] and limestone ( $\text{CaO}_3$ ) are two such neutralizing agents that have been added to aquatic



TABLE II.1 MAGNITUDE OF pH AND ALKALINITY ( $\mu\text{eq } \ell^{-1}$ ) DECREASES IN LAKES AND STREAMS DURING SPRING SNOWMELT OR HEAVY RAINFALL. SURFACE ALKALINITIES IN THESE AREAS ARE GENERALLY  $< 200 \mu\text{eq } \ell^{-1}$ .

Location	Approximate annual sulfate loading ( $\text{kg ha}^{-1} \text{ yr}^{-1}$ )	Water Chemistry					
		Prior to episode		During episode		Change	
		pH	Alkalinity	pH	Alkalinity	$\Delta$ pH	$\Delta$ Alkalinity
Adirondacks, NY	38						
Panther Lake, 1979 <sup>a</sup>		6.6	162	4.8	-18	1.8	180
Sagamore Lake, 1979 <sup>a</sup>		6.1	29	4.9	-17	1.2	46
Woods Lake, 1979 <sup>a</sup>		4.8	-39	4.5	-42	0.3	4
Little Moose Lake, outlet, 1977 <sup>b</sup>		7.0		4.9		2.1	
New Hampshire	38						
The Bowl-upstream, 1973 <sup>c</sup>		5.6		5.0		0.6	
The Bowl-downstream, 1973 <sup>c</sup>		6.2		5.8		0.4	
South-Central Ontario <sup>d</sup>	30						
Harp Lake #4, 1978		6.6	108	5.4	8	1.2	100
Paint Lake #1, 1978		5.5	61	5.0	8	0.5	53
Dickie Lake #10, 1978		4.8	-16	4.5	-32	0.3	16
Southern Blue Ridge Province	27						
White Oak Run, VA, 1980 <sup>e</sup>		6.0		5.7		0.3	
Raven Fork, NC, 1981 <sup>f</sup>		5.7	20	4.4	<20	1.3	
Enloe Creek, NC, 1981 <sup>f</sup>		5.9	60	5.5	<20	0.4	
West Prong of the Little Pigeon River, 1978 <sup>g</sup>		6.3	40	5.8	10	0.5	30
Southwestern Ontario <sup>h</sup>	25						
Speckled Trout Creek, 1981		6.7		5.1		1.6	
Barrett River, 1981		6.6		5.0		1.6	
Quebec <sup>i</sup>	22						
Ste.-Marguerite River, 1981		6.7	76	5.9	70	0.7	6
Minnesota <sup>j</sup>	17						
Filson Creek, 1977		6.6		5.5		1.1	
Washington	<20						
Ben Canyon Creek <sup>k</sup>		7.0		5.8		1.2	
Idaho	<20						
Silver Creek <sup>k</sup>		6.1		5.7		0.4	

<sup>a</sup>Galloway et al. 1980

<sup>b</sup>Schofield 1977

<sup>c</sup>Martin 1979

<sup>d</sup>Jeffries et al. 1979

<sup>e</sup>Shaffer and Galloway 1982

<sup>f</sup>Jones et al. 1983

<sup>g</sup>Silsbee and Larson 1982

<sup>h</sup>Keller 1983

<sup>i</sup>Brouard et al. 1982

<sup>j</sup>Siegel 1981

<sup>k</sup>Lefohn and Klock 1983

systems. Base additions have been made both directly to lakes and to watersheds or streams, but the relative effectiveness and total consequences of each of these approaches have not been fully evaluated.

Base additions are intended to change the chemistry (e.g., pH and calcium levels, trace metal concentrations) of the aquatic system to produce a more hospitable environment for certain aquatic biota, particularly fish. Negative consequences may include pH shock associated with dramatic increases in pH, the problems associated with aluminum hydrolysis at the stream-neutralized lake interface, and the potential for lake reacidification.

An alternative option is fertilization of surface waters by adding phosphorus to increase algal productivity and generate acid neutralizing capacity. While the chemical costs associated with phosphorus addition are low, applications may not be efficient, particularly in view of potential interactions with aluminum. In the few studies conducted, the benefits to the ecosystem have not been evaluated. [CARP E-4.7.2]

Mitigative options as described above have several major drawbacks:

- ° The costs are generally unknown.
- ° The applications must continue over time.
- ° The area of coverage would need to be large to be regionally effective.
- ° Effects of mitigative options are not fully understood.

#### A.2.4 WHAT ARE THE EFFECTS ON AQUATIC BIOTA? [CARP E-5]

##### A.2.4.1 WHAT POTENTIAL EFFECTS OF ACIDIC DEPOSITION ARE OF CONCERN? [CARP E-5.5, E-5.6]

The potential effects of acidic deposition on aquatic biota include changes in plankton and algal populations and productivity, and losses of fish populations. Acidification results in a shift in the structure and function of the plankton community. However, the many chemical, biological, and physical interactions involved make it difficult to predict potential changes in phytoplankton and zooplankton communities and the subsequent impact on higher trophic levels. Acidification eliminates sensitive algal species, may decrease phosphorus and inorganic carbon concentrations, and may depress nutrient cycling rates. These changes tend to decrease phytoplankton biomass and productivity. Acidification also may increase water clarity, allowing light to penetrate into deeper waters, where nutrient levels are generally higher. This would tend to increase productivity. Evidence for both productivity changes has been gained in field studies. Productivity may not be affected despite changes in the community structure: plankton biomass was unaffected in one field experiment. [CARP E-5.5]

Aluminum and hydrogen ions interact to cause fish mortality. This interaction may be most important during short time periods (e.g., spring snowmelt). Results of laboratory experiments suggest that fish growth rates decrease in acidified waters [CARP E-5.6.4.1.3], yet increased fish growth has often been observed in the field. The reason for this apparent

inconsistency may be that the greater abundance of forage organisms available to a dwindling fish population outweighs increased metabolic demands at low pH.

Recruitment failure evident by reduced or missing age groups in fish populations--not decreased growth, loss of food items, or adult mortality --appears responsible for many fish extinctions. This failure may result either from acid-induced mortality of fish eggs and/or larvae or from reductions in the number of eggs spawned. [CARP E-5.6.2.2]

#### A.2.4.2 HOW MAY CHANGING WATER CHEMISTRY INFLUENCE THE FISH POPULATIONS OF SURFACE WATERS? [CARP E-5.6]

Fish reproduction and survival depends on water chemistry, both pH and the concentrations of metal ions. Increases in certain metal concentrations are associated with decreasing pH levels in acidified surface waters [CARP E-4.6]. Declines in fish populations as a result of acidification may, therefore, be a function of both low pH levels and elevated concentrations of some metals, especially aluminum.

Critical values for fish survival, if developed only on the basis of water quality in laboratory experiments or at one location in a lake, may be misleading. Water quality may vary substantially in different areas of an aquatic system. Behavioral responses, such as avoidance of low pH regions, may offset, in part, the effects of acidification. The presence of 'refuge' areas and behavioral adaptations must be considered in our assessment of the impacts of acidification.

Physiological toxicity of low pH waters is generally believed to be the result of impaired body salt regulation, due to the interference of elevated hydrogen ion levels with osmoregulatory mechanisms. Through the gill epithelium, freshwater fish normally actively exchange sodium from the water for hydrogen or aluminum ions, and chloride for bicarbonate, in order to maintain higher salt concentrations in their tissues than is in the water. This active uptake of sodium may be disrupted by increased hydrogen ion concentrations in the water. "Brown trout surviving in the Tovdal River, Norway, collected immediately following a fish kill (apparently resulting from an acid episode), had significantly reduced plasma chloride and sodium levels (Leivestad and Muniz 1976; CARP E-5.6.2.4). The plasma content of potassium, calcium, and magnesium was not affected. Therefore, impairment of the active transport mechanism for sodium and/or chloride ions through the gill epithelium was suggested as the primary cause of fish death. Severe internal ionic imbalance would affect fundamental physiological processes such as nerve conductions and enzymatic reactions" [CARP E-5.6.4.1.5].

High metal concentrations can also be toxic to fish and are associated with decreased pH levels in waters. Aluminum, manganese, and zinc concentrations increase in acidic surface waters apparently as a result of increased solubility at lower pH levels. Concentrations of cadmium, copper, lead, nickel, and other metals can also increase due to direct atmospheric deposition, and acidification may increase their availability and subsequent toxicity. At present, measurements of zinc, manganese, cadmium, copper,

lead, and nickel in surface waters of eastern North America and Scandinavia are below toxic concentrations (and/or maximum acceptable limits), unless a local emissions source exists. [CARP E-5.6.4.2]

Aluminum, however, has been found to be toxic to fish at a level within the range of concentrations measured in acidic surface waters, i.e., concentrations as low as 0.1 to 0.2 mg  $\ell^{-1}$ . "Total aluminum levels measured range up to 1.4 mg  $\ell^{-1}$  in the Adirondack region, New York (Schofield 1976), 0.76 mg  $\ell^{-1}$  in southwestern Sweden (Dickson 1975, Wenblad and Johansson 1980), 0.6 mg  $\ell^{-1}$  in southern Norway (Wright et al. 1980), and 0.8 mg  $\ell^{-1}$  in the Pine Barrens of New Jersey (Budd et al. 1981)" [CARP E-5.6.4.2]. In addition, for brook trout stocked in 53 Adirondack lakes, aluminum was found to be the primary chemical factor, of 12 water quality parameters measured, most highly correlated with trout survival.

Aluminum toxicity in fish appears to result from the combined effect of impaired ion exchange and of respiratory distress caused by mucous clogging of the gills. Brown trout exposed to aluminum concentrations as low as 0.19 mg  $\ell^{-1}$  at pH 5.0 rapidly lost sodium and chloride from the blood. Moderate to severe gill damage was noted at aluminum levels of 0.5 and 1.0 mg  $\ell^{-1}$  at pH 4.4 and higher. At pH levels 5.2 to 5.4, aluminum was particularly toxic in supersaturated solutions. Complexation of aluminum by organic chemicals appears to reduce toxicity and enhance fish survival. [CARP E-5.6.4.2]

A recent study using controlled experiments in a continuously monitored Norwegian river illustrates a relationship between fish mortality and river chemistry and hydrology (Henriksen et al. 1984). During a two-week period in the winter of 1983, four episodes of pH-drops from pH 5.9 to 5.1 coincided with increased water flow from rainfall and snowmelt, dilution of calcium ion, and increase of aluminum species. Concurrent observations of health and behavior of Atlantic salmon at three stages of development (eggs, summer old, one-year old) during the episodes showed changes in behavior indicative of physiological stress in both ages of fish and death of four one-year old fish; stress and mortality were not found in a chemically protected control group.

"It should be kept in mind that acidification of freshwaters is a complex process that involves more than merely increases in acidity. Other well-documented changes include increased concentrations of metal ions, increased water clarity the accumulation of periphyton (microflora attached to bottom substrates) and detritus, and changes in trophic interactions (e.g., loss of fish as top predators). The response of aquatic systems to acidic deposition must be viewed in terms of all these changes that together constitute the acidification process" [CARP E-5.1].

#### A.2.4.3 WHAT ARE THE CHARACTERISTICS OF THOSE SURFACE WATERS WHERE CHANGES IN FISH POPULATIONS MIGHT OCCUR? [CARP E-5.2, E-5.6]

Fish population changes attributable to acidic deposition are most likely to occur in those surface waters that would exhibit long-term changes in aquatic

chemistry or substantial short-term fluctuations. Either fish mortality or recruitment failure could occur. Chemical changes can also alter an ecosystem's habitat suitability for some fish species. Ultra-oligotrophic (nutrient poor) lakes and streams are the most likely to be affected. Lakes and streams of this type occur in large areas of eastern Canada and the northeastern United States, as well as in some sections of the western United States and northern Florida.

Ultra-oligotrophic waters are especially common where glaciation removed younger calcareous deposits and exposed weather-resistant granitic and siliceous bedrock. The absence of carbonate rocks in the drainage basin results in lakes with little carbonate-bicarbonate buffering capacity; hence, such lakes are very vulnerable to pH changes. In areas of low acidic deposition, such lakes often have pH's in the 5.5 to 6.5 range (thus they are naturally acidic) with most of the acidity due to carbonic acid ( $H_2CO_3$ ). These lakes tend to be small and have low concentrations of dissolved ions. [CARP E-5.2.1]

Simply stated, the characteristics of the surface waters where changes in fish populations might occur are those characteristics which cause an aquatic system to be susceptible to chemistry changes. The extent of effects on fish populations is largely determined by the system's capacity to assimilate increased chemical inputs. The more severe the changes in aquatic chemistry as a result of those inputs, the more likely the aquatic biota, particularly fish, will be subsequently affected. The determining factors are part of the specific system itself; the same deposition amount has the potential to cause different degrees of change, ranging from no change to acidification, in different systems.

#### A.2.4.4 WHAT EVIDENCE IS THERE THAT CHANGING WATER CHEMISTRY HAS AFFECTED FISH POPULATIONS? [CARP E-5.6]

Effects of acidification on aquatic biota, independent of cause, are reasonably well documented. Evidence is clear from field, laboratory, and whole system studies that acidification of sufficient magnitude affects fish, other aquatic organisms, and aquatic system structure. Having demonstrated that change in the acidity of waters is, in some areas, a result of acidic deposition is sufficient evidence to suggest that concomitant changes in biota followed. Observation of mortality of individual fish is not sufficient to explain population loss. The absence of fish in an acidic aquatic system is not sufficient evidence that such loss is the result of acidification. Attribution of fish population loss to acidification requires records of changes in both aquatic chemistry and fish populations.

Few reliable long-term records of changes in fish populations exist in the United States. The best evidence for concomitant acidification and loss of fish populations is for the Adirondack region of New York State. The presence today of fish in Adirondack lakes and streams is inversely correlated with pH levels. Loss of fish populations since the 1930's has been documented for about 180 Adirondack lakes (out of approximately 2877). Historical records are not available, however, to relate each loss specifically to acidification. In other regions of the United States, no

adverse effects of acidic deposition or acidification on fish have been definitively identified. [CARP E-5.6.2.1.1]

#### A.2.4.6 WHAT OPTIONS ARE AVAILABLE TO MAINTAIN FISH POPULATIONS? [CARP E-5.9]

Selection for tolerance to acidity is the only general strategy, other than direct alteration of the water chemistry, that might maintain fish populations. Genetic screening, selective breeding, and acclimation are all potential mechanisms to maintain fish resources in acidified systems. Although each has merit, it is doubtful that they could be used to reestablish naturally-reproducing fish populations, and they do not address the problem of restoring other biotic components. Because metal concentrations will remain high in acidified waters, any tolerant fish species introduced would need to be monitored for metal concentrations that might harm the health of those who consume the fish.

Regular restocking of some acidic systems is also an option. Acidification appears first to affect recruitment of fish. Adult fish can tolerate lower pH's than fish fry. Thus, although the population might not be able to maintain itself, restocking would be a viable strategy in some systems.

#### A.2.5 WHAT ARE THE EFFECTS OF ACIDIC DEPOSITION ON HUMAN HEALTH? [CARP E-6]

##### A.2.5.1 HOW COULD ACIDIC DEPOSITION AFFECT HUMAN HEALTH? [CARP E-6]

Acidic deposition or its precursors could affect human health either directly by inhalation or indirectly by ingestion of affected food or drinking water. Direct effects on human health have been studied extensively in U.S. EPA criteria documents and will not be discussed here.

Indirect (post-depositional) effects on human health causally related to acidic deposition have not been demonstrated. Human exposure to toxic substances may be influenced by acidic deposition through bioaccumulations along food chains and drinking water contamination. The substances of concern are methyl mercury, which can accumulate in aquatic food chains, and lead, a potential drinking water contaminant. In addition, high aluminum concentrations in water used in dialysis therapy are a potential cause of brain damage. Other elements and chemicals of concern include arsenic, asbestos, cadmium, copper, and nickel, but data on these elements are limited. [CARP E-6.1]

"Bioaccumulation of methyl mercury in fish is the main if not sole source of human exposure, barring episodes of accidental discharge or misuse of manmade methyl mercury compounds" [CARP E-6.2.3]. Pike and trout are among the most likely species to be affected by acidic deposition and have the highest human consumption figures and average methyl mercury concentrations. Elevated methyl mercury concentrations in fish muscle (most notably of pike and perch) have been statistically associated with higher acid concentrations in water. However, changes in acidity may also coincide with changes in a number of variables that affect mercury concentrations in fish: the available data does not establish increasing acidity as the causal factor.

Assessments of the impacts of acidic deposition on drinking water quality are tentative and based on limited data. Drinking water quality is dependent on the source and the management of the water supply. Sources of drinking water include both surface and groundwaters as well as direct precipitation. Management practices that can greatly affect water quality include storage, treatment, and distribution of water prior to use. [CARP E-6.3.1]

Increasing corrosivity due to increasing acidity is probably the most significant potential impact of acidic deposition on drinking water supplies. The risk of exposure to higher concentrations of toxicants (e.g., corrosion products such as lead and possibly cadmium) is greater where the water supply is not treated for corrosivity, and where water storage facilities are small, necessitating the direct use of raw water during storm flow periods. Water systems of concern include surface-water and roof-catchment cisterns.

Very few data on the impacts of atmospheric deposition on drinking water quality exist, however, increases in metal concentrations due to acidity are a potential adverse effect that may increase the risks to human health. Any increases in lead concentrations in drinking water are an additional burden of lead to the body, especially in children where many already have elevated blood and bone lead concentrations. [CARP E-6.3.1, E-6.3.2]

In general, the smaller the water supply, the greater the risk, with small, privately-owned surface water systems serving a single dwelling at greatest risk. Groundwaters in the United States do not appear affected by acidic deposition although reports from Scandinavia suggest there is a potential effect. [CARP E-6.3.1.3]

#### A.2.5.2 WHAT EVIDENCE EXISTS TO SUGGEST HUMAN HEALTH IS BEING AFFECTED? [CARP E-6.2, E-6.3]

No adverse human health effects, either from fish consumption or drinking water, have been documented as being a consequence of metal mobilization by acidic deposition. The extent of human exposure appears small. [CARP E-6.5]

#### A.2.5.3 WHAT OPTIONS ARE AVAILABLE TO MINIMIZE THE RISK OF INDIRECT HEALTH EFFECTS DUE TO ACIDIC DEPOSITION? [CARP E-6.3]

The primary mechanism by which health effects could be minimized is through treatment of drinking water to decrease corrosivity. This is a common practice in municipal drinking water supplies of low alkalinity and/or pH. Those populations not supplied drinking water by major water treatment facilities could be encouraged to monitor their drinking water supplies periodically to ensure the water supply is safe. Small-scale technology for mitigating corrosivity is available, if needed.

## A.2.6 WHAT ARE THE EFFECTS ON MATERIALS? [CARP E-7]

### A.2.6.1 WHAT EFFECTS ON MATERIALS MAY OCCUR AS A RESULT OF ATMOSPHERIC DEPOSITION OR ATMOSPHERIC POLLUTION? [CARP E-7.1]

Damage to materials from atmospheric deposition may include the corrosion of metals, erosion and discoloration of paints, decay of building stone, and the weakening and fading of textiles. All of these effects occur under natural environmental conditions as a result of moisture, sunlight, carbon dioxide, atmospheric oxygen, temperature fluctuations, and the action of micro-organisms. Quantifying the relative amount of damage caused by specific manmade air pollutants, and by specific pollutant transformations and contact processes (e.g., acid precipitation) is extremely difficult. Table II.2 summarizes potentially damaging effects on materials generally attributed to air pollutants and other environmental factors.

### A.2.6.2 WHAT IS THE ROLE OF ACIDIC DEPOSITION IN DEGRADATION OF MATERIALS? [CARP E-7.1.1]

The percentage of materials degradation occurring from acidic deposition, in contrast to that caused by other natural and human factors, is not known. In general, distinguishing between the effects of gaseous  $\text{SO}_2$ , sulfate aerosol, and wet deposited substances is difficult. If effects of acidic deposition are defined to include all the mechanisms by which acidic and acidifying pollutants may contact and damage surfaces, a considerable body of experimental evidence for damage to materials exists. Sulfur oxides, other acidic gases, and particulates are important, potentially damaging pollutants; moisture (atmospheric humidity and wetness of surfaces) is a very important factor.

### A.2.6.3 WHAT COMPONENTS OF ACIDIC DEPOSITION ARE MOST IMPORTANT IN MATERIALS DEGRADATION PROCESSES? [CARP E-7.1.1]

The primary factor in materials degradation due to acidic deposition is the corrosivity of the acids themselves, i.e., the nitric and sulfuric acids formed from sulfur and nitrogen oxide transformation. Although evidence suggests that acid precipitation can cause material degradation, it appears that more extensive degradation occurs from gaseous impaction of  $\text{SO}_2$  or dry deposition onto moist surfaces or in a very humid environment. Under these conditions the acids may become highly concentrated and do the most damage. Information on sulfur dioxide concentrations, duration of wetness, and oxidation-reduction rates is needed to understand this problem. [CARP E-7.1.1]



TABLE II.2 POTENTIAL EFFECTS OF AIR POLLUTION ON MATERIALS

Materials	Type of impact	Principal air pollutants	Other environmental factors	Methods of measurement	Mitigation measures
Metals	Corrosion, tarnishing	Sulfur oxides and other acid gases	Moisture, air, salt, particulate matter	Weight loss after removal of corrosion products, reduced physical strength, change in surface characteristics	Surface plating or coating, replacement with corrosion-resistant material, removal to controlled environment.
Building Stone	Surface erosion, soiling, black crust formation	Sulfur oxides and other acid gases	Mechanical erosion, particulate matter, moisture, temperature fluctuations, salt, vibration, CO <sub>2</sub> , micro-organisms	Weight loss of sample, surface reflectivity, measurement of dimensional changes, chemical analysis	Cleaning, impregnation with resins, removal to controlled environment.
Ceramics and Glass	Surface erosion, surface crust formation	Acid gases, especially fluoride-containing	Moisture	Loss in surface reflectivity and light transmission, change in thickness, chemical analysis	Protective coatings, replacement with more resistant material, removal to controlled atmosphere.
Paints and Organic Coatings	Surface erosion, discoloration, soiling	Sulfur oxides, hydrogen sulfide, ozone	Moisture, sunlight, particulate matter, mechanical erosion, microorganisms	Weight loss of exposed painted panels, surface reflectivity, thickness loss	Repainting, replacement with more resistant material
Paper	Embrittlement, discoloration	Sulfur oxides	Moisture, physical wear, acidic materials introduced in manufacture	Decreased folding endurance, pH change, molecular weight measurement, tensile strength	Synthetic coatings, storing in controlled environment, deacidification, encapsulation, impregnation with organic polymers.
Photographic Materials	Microblemishes	Sulfur oxides	Particulate matter, moisture	Visual and microscopic examination	Removal to controlled atmosphere
Textiles	Reduced tensile strength, soiling	Sulfur and nitrogen oxides	Particulate matter, moisture, light, physical wear, washing	Reduced tensile strength, chemical analysis (e.g., molecular weight) surface reflectivity	Replacement, use of substitute materials, impregnation with polymers
Textile Dyes	Fading, color change	Nitrogen oxides and ozone	Light, temperature	Reflectance and color value measurements	Replacements, use of substitute materials, removal to controlled environment.
Leather	Weakening, powdered surface	Sulfur oxides	Physical wear, residual acids introduced in manufacture	Loss in tensile strength, chemical analysis	Removal to controlled environment, consolidated with polymers, or replacement
Rubber	Cracking	Ozone	Sunlight, physical wear	Loss in elasticity and strength, measurement of crack frequency and depth	Add antioxidants to formulation, replace with more resistant materials

## SECTION B. ECOSYSTEM INTERACTIONS

### B.1 INTRODUCTION

This section of the effects summary answers questions about interactions among ecosystem components--bedrock, soils, soil water, microorganisms, vegetation, animals, surface and groundwaters. Of potential vegetative effects, only those on forests are considered. Impacts of acidic deposition on crops are most certainly overwhelmed by the additions of fertilizer, lime, and other amendments in common agronomic and horticultural practices. The impacts of the gaseous precursors of acidic deposition and ozone on crops have been discussed in criteria documents prepared for rule-making under the Clean Air Act. Analysis of impacts upon perennial vegetation other than forests is not sufficiently developed in the CARP to allow discussion here.

### B.2 WHAT EXPLANATIONS HAVE BEEN PROPOSED FOR OBSERVED REGIONAL DECLINES OF FORESTS?

Explanations proposed for forest declines in the United States and Europe can be broadly described:

1. Climatic changes such as drought have induced the declines.
2. Biotic pathogens such as viruses, fungi, or insects have induced the declines.
3. Air and precipitation quality (acidic deposition, its precursors, oxidants, or trace metals) have directly induced the declines.
4. Air and precipitation quality have indirectly induced the declines through changes in soil chemical characteristics.
5. Complex combinations of the above.

The hypotheses for the cause of 'Waldsterben' raised in Section A.2.2.5.3 are encompassed in explanations 3 and 4. Explanations 1 and 2 encompass general stress, also described earlier. Below we discuss potential direct (foliar) and indirect (soil-mediated) roles of acidic deposition or its precursors.

#### B.2.1 WHAT ROLE COULD ACIDIC DEPOSITION PLAY IN THE PROPOSED EXPLANATIONS?

Acidic deposition has been proposed by some scientists as a causal or contributing factor in forest growth declines. Two general ideas have been proposed:

1. Acidic deposition, its precursors, or both directly affect vegetation and induce decline. One hypothetical mechanism of action is as follows:

- (a) Acidic deposition, including fog or cloud water at high elevations, directly impacts the aerial portion of a tree such that increased leaching of nutrients, particularly Mg, occurs.
  - (b) The root system is unable to replenish nutrient losses at a rate sufficient to maintain optimal nutrient status and growth.
  - (c) The trees with limited nutrients support the newest, most actively growing parts of the tree; older leaves/needles prematurely die.
  - (d) Decreased aerial growth is accompanied by decreased root growth, continued leaching losses, and further decline.
  - (e) Ultimately, the tree is weakened and secondary factors begin playing a role (e.g., pathogenic organisms and environmental stress) eventually causing death.
2. Acidic deposition, its precursors, or both indirectly affect vegetation and induce decline. One hypothetical mechanism of action is as follows:
- (a) Acidic deposition directly changes the chemistry of soil systems, i.e., increases acidity and aluminum concentrations.
  - (b) The changing conditions in the soil, perhaps during changes from warm and dry to wet periods, cause a direct toxicity to the roots, reducing the uptake of water and nutrients.
  - (c) The reduced root system is no longer able to support the aerial biomass.
  - (d) Older leaves or needles prematurely die and drop from the tree as the newer growth receives most of the available water and nutrients.
  - (e) Decreased aerial and root production over time weakens the tree, making it susceptible to secondary stress factors.

Detailed studies should allow evaluation of these and other hypotheses over the next several years.

#### B.2.2 IS THERE EVIDENCE TO SUPPORT THESE TWO HYPOTHESES?

Limited evidence is available to support each of them. This evidence includes increased leaching of basic substances from foliage and soil, increased sulfate concentrations in soil, and, in at least one instance, increased aluminum concentrations in soil. Unfortunately, trees respond to stress in a limited number of ways. As a result, many factors that cause declines result in quite similar symptoms. Identifying any single factor as a causal agent in a forest system may require years of investigation using both field and laboratory data.

The recent regional declines of red spruce, pitch pine, and shortleaf pine all began in the late 1950's or early 1960's. In many areas, this was a severe drought period. Some scientists believe that the drought was sufficient to cause growth losses during that period and possibly predispose the trees to other environmental stresses. But not all areas showing declines were subjected to drought. If there was some other general, for example climatological, change during this period of sufficient magnitude to stress forests, it has not yet been identified.

Oxidants and other gaseous pollutants can cause decreases in growth similar to those expected from acidic deposition, and these pollutants cannot now be excluded as causal factors. Furthermore, it might be expected that oxidants and acidic deposition interact to cause an effect. Ozone for example is known to cause membrane damage in cells, making them more susceptible to nutrient leaching losses. Such mechanisms would be quite significant in hypothesis 1 above.

Several highly speculative relationships are described below.

Coniferous forests, such as those experiencing recent regional decline, normally are quite tolerant of acidic soil conditions, with many of the tree species growing on soils with pH's below 4.0. The dilute acidity contributed by acidic deposition probably would not have caused changes in soil pH. As will be discussed in the following aquatics section, however, sulfate deposition can increase soil water acidity in already acid soils, without accompanying changes in soil pH. This acidity is derived from the aluminum exchange process. If the soils of concern in these systems were mineral soils, the hypothesis that root damage occurs could be plausible. However, many soils being studied are organic soils, and aluminum would be complexed by organics, making biologically-toxic forms of aluminum minimally available.

A metal-induced toxicity is also plausible (Friedland et al. 1984). Measurements of heavy metals in the areas of reported decline confirm increases in metal concentrations in the soils and trees. As acidic deposition has changed over time, so has the deposition of metals, although metals deposition is rarely measured.

Organic matter often tends to accumulate in sites showing the most dramatic declines. This could indicate that microbial processes have been affected and needed nutrients are accumulating in the litter and are no longer available for plant growth. A nutrient deficiency would result, again showing symptomatology similar to that being observed.

Recently, it has been proposed that nitrogen may be playing a role in the observed declines. Nitrogen inputs can detrimentally affect the relationship between tree roots and beneficial fungi that symbiotically exist in the soil. Nitrogen, usually considered a limiting nutrient in most forest ecosystems, could now be in excess of amounts required by some tree species. Friedland et al. (1985) found a predisposition of red spruce to winter damage and suggest that it may be a component of decline. As one of three suggested causes, they propose a testable hypothesis that nitrogen alters growth processes and interferes with winter-hardening or cuticle formation.

In summary, it has been confirmed that most of the recently described decline of forests in the eastern United States began in the late 1950's and early 1960's. Drought is the one obvious climatological change that has been examined that might explain these declines, but it has not proven to be sufficient explanation. Therefore, anthropogenic causes are suspected, although other climatic factors such as early or late frost frequency and severity, or winter temperature extremes merit consideration. Decline appears to have occurred during the same period when regional emissions increases were most evident. As a result, effects of substances emitted from fossil-fuel burning are the focal point of research. Research has not demonstrated that acidic deposition, or any component of atmospheric deposition, is the primary cause of decline or that it is even playing a role. If it were, it is unclear whether sulfur or nitrogen in deposition would be implicated as the element of most concern. However, current hypotheses suggest nitrogen deserves more attention in forest growth studies.

#### B.2.3. WHAT FOREST REGIONS OF THE UNITED STATES WOULD MOST LIKELY BE AFFECTED BY ACIDIC DEPOSITION IF THE HYPOTHESES WERE CORRECT?

Because published data have shown only recent declines of coniferous tree species, those regions of the United States vegetated by such species are of primary concern. These areas are shown in Figure II.9. The areas at highest risk would be those coniferous forests at high elevations where deposition and cloud water acidity tend to be greatest, air pollution episodes may occur, and natural environmental stress is great. This includes the mountainous areas of the eastern and western United States. Since it is mainly the eastern United States that is receiving regional acidic deposition, eastern mountain regions would be considered the most susceptible areas; future surveys of western forests are not expected to demonstrate general forest decline attributable to acidic deposition except in localized areas receiving high levels of pollution.

#### B.3 WHAT HYPOTHESES HAVE BEEN PROPOSED TO EXPLAIN CHANGES IN SURFACE WATER CHEMISTRY?

Hypotheses have been proposed to explain observed changes in pH, alkalinity, or sulfate concentrations in surface waters. Each is a plausible explanation, supported by experimental evidence, for acidification at selected sites. None applies universally to all surface waters; no single explanation for change will likely ever suffice for all sites. Six hypotheses to consider for clear water lakes and streams follow:

1. A decrease in normally high, anaerobic, groundwater table levels creates high hydrogen ion production and accelerated loss of cation through oxidation of reduced chemicals.
2. Logging, fires, landslides, or other disturbances have resulted in accelerated cation leaching from watersheds, due to exposure of previously unweathered material to chemical weathering, leading to increased pH in water. As the watershed recovers from the disturbance, the pH of the system may decrease, returning to 'natural' steady state.

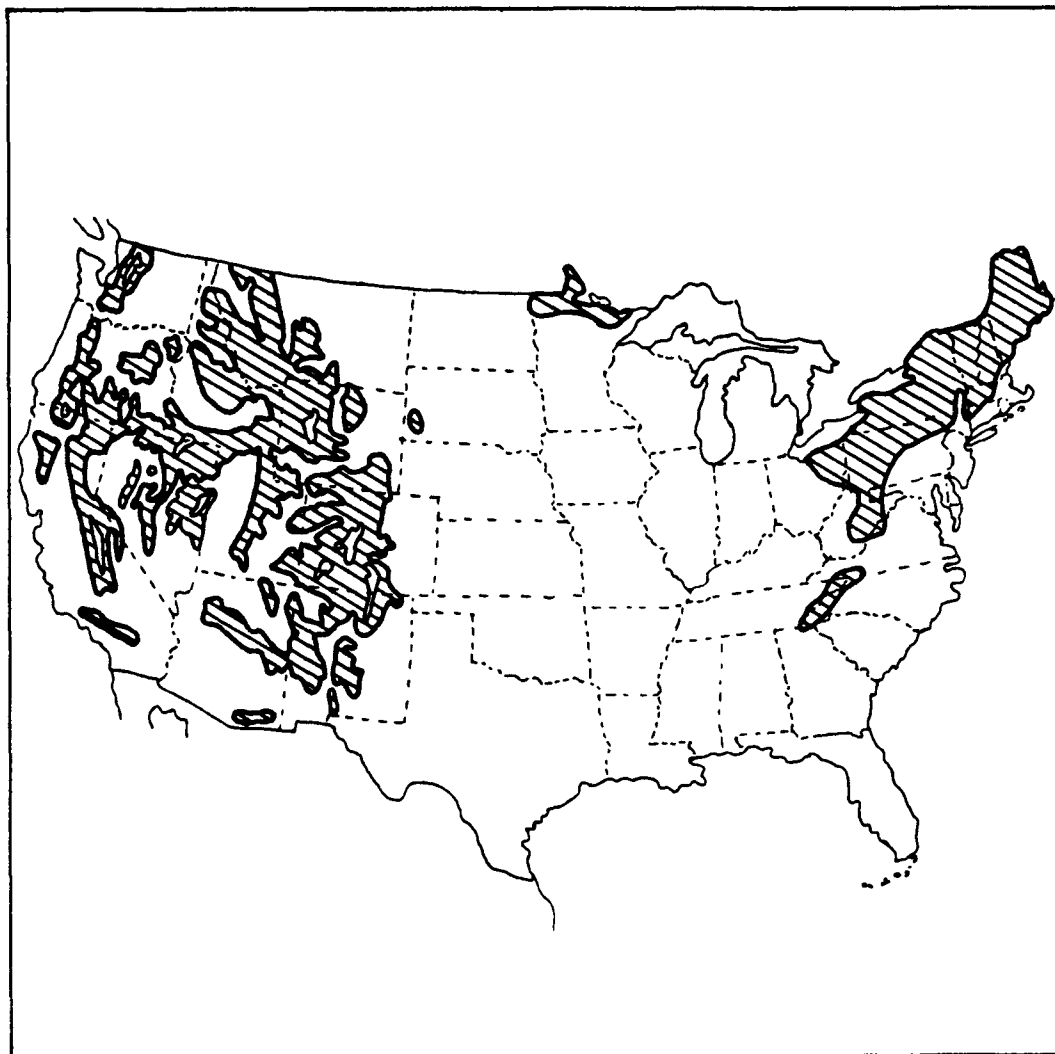


Figure II.9 Regions of the United States with high-elevation forests (boreal, sub-alpine, and montane; mixed boreal and deciduous; mixed boreal, lake, and deciduous). Adapted from Eyre (1963).

3. Long-term trends in the net production of forest biomass affect soil and soil water chemistry. A rapidly growing forest will acidify soils. A decrease in forest growth rate, such as in an aging forest, or accumulation of organic matter on the forest floor, perhaps through decreased decomposition and mineralization rates, will decrease the rate of acidification.
4. Shifts in vegetation cover type result in physical and chemical changes in soils and watersheds, and long-term changes in surface water chemistry. Reforestation can cause soil acidification. In general, coniferous forests and forest species such as red alder that support high nitrogen fixation rates increase the rate of soil acidification.
5. Acidification of agricultural soils occurs from fertilizer amendments and is usually counteracted by addition of agricultural lime. Acidification of waters could occur in regions where abandoned farmland is undergoing reforestation and basic inputs from liming have ceased.
6. Acidic deposition introduces additional hydrogen ion in excess of what is normally produced.

#### B.3.1 WHAT ROLE DOES ACIDIC DEPOSITION PLAY IN THE ACIDIFICATION OF LAKES AND STREAMS?

Acidic deposition must contribute to acidification somewhere in the ecosystem. The deposition inputs may be overwhelmed by the natural acidification processes, however, and not cause a measurable change. The magnitude of the depositional contribution is discussed in Section A.3.1.

The fate of hydrogen and nitrate ions in ecosystems is difficult to monitor; hydrogen ion exchanges are ubiquitous and nitrate is often immediately transformed in various processes as illustrated in the nitrogen cycle (Figure II.2). The effects of atmospheric deposition on surface waters are best known from the study of the transport and fate of sulfate. If sulfate increases in waters in areas where sulfur is not a dominant component of the forest soil minerals or underlying bedrock, the increases must have been derived from atmospheric deposition of sulfur: whether wet or dry, or in neutral, acidic or acidifying form. Since monitoring of surface waters in the past did not include sulfate as a water quality parameter of interest, few historical data are available to judge the significance of deposition to changes in aquatic systems or the number of systems showing increases or decreases in sulfate. Therefore, we know that sulfur is deposited on watersheds from the atmosphere, but we do not know the number of systems that have experienced changes, how frequently deposition leads to acidification, or how soon changes in sulfate in waters follow changes in sulfur deposition.

If sulfate arrives on land or water in acidic form, it unquestionably contributes to acidification. However, neutral salts of sulfur introduced into the aquatic system from either the atmosphere or the terrestrial system may not lead to acidification, although sulfate concentration would increase.

The terrestrial assimilation/retention/transformation of sulfur compounds prior to discharge into the aquatic system plays the key role. Studies of surface waters that account for changes in both the cations and anions over time are needed to assess the role of changing sulfate deposition.

#### B.3.2 WHAT CONCLUSIONS CAN BE DRAWN FROM THE AVAILABLE EVIDENCE?

All of the above hypotheses can be supported with documentation for selected ecosystems. Therefore, we conclude the following:

- Atmospheric deposition of acidic and acidifying substances contributes to acidification processes.
- Surface water acidification can occur from natural processes.
- Estimates of the magnitude and geographic distribution of acidic deposition's influence on changes in surface water acidity over the years are almost exclusively based on correlative evidence.
- Man's activities can lead to both increases and decreases in surface water pH.
- No single acidification hypothesis applies to all locations.
- Acidification occurs without concomitant land use changes.
- In those studies where land-use changes can be demonstrably ruled out as a factor, acidic deposition must be considered as a likely cause of observed surface water acidification.
- At what rate surface water chemical changes occur, with or without acidic deposition, is still the primary question to be answered.

#### B.4 WHAT HYPOTHESES HAVE BEEN PROPOSED TO SUGGEST FUTURE CHANGES IN WATER CHEMISTRY WILL OR WILL NOT OCCUR?

Acidic deposition contributes to the natural processes of acidification. Over geologic time (thousands of years), all soil systems receiving rainfall in excess of evapotranspiration will naturally become acidic. It is also clearly evident that some systems have become increasingly acidic as a result of acidic deposition. However, those areas where acidification has been documented are relatively simple systems where lakes are surrounded by little vegetation, shallow soils, steep slopes, and acidic deposition (< pH 5.0) is occurring. These systems are likely to respond relatively quickly to acidic deposition (within years to decades). At the other end of the scale are systems where soils are highly buffered and water passes slowly through the soils with a maximum opportunity to be buffered. Between these extreme cases is a continuum of systems with a multitude of possible combinations of characteristics. Thus, we can expect a continuum of responses by aquatic systems.



One scientific view, subscribed to by the authors, is that the terrestrial assimilation/retention/transformation of sulfur compounds prior to discharge into the aquatic system plays a key role in determining the rate of acidification. This view is described below but is not a scientific consensus; others believe that natural organic acidification is the determining factor. Sulfate adsorption, mineral weathering, cation exchange processes, and hydrologic retention must be insignificant in a watershed for acidification to occur quickly from acidic deposition. If any of these processes is significant, effects are delayed until the capacity for the process is reached. In a watershed where sulfate inputs and outputs are equal ('steady-state') the question of further aquatic acidification will depend primarily on the rate at which mineral weathering can replace lost cations. In watersheds where sulfate steady state has not been reached (sulfur inputs are greater than sulfur outputs), acidification will be delayed until sulfate adsorption capacity is exceeded and a steady state in sulfate input/output relationships is reached. Then, ion exchange and mineral weathering rates become the primary factors determining the onset of acidification.

For surface or groundwater acidification to occur, the concentration of hydrogen ion in the entering water must be greater than that already present. In many aquatic systems, the major input of water arrives from the terrestrial watershed system. Much acidic precipitation and dry deposition of acidic and acidifying substances passes through the vegetation canopy, through or over soils, and is subsequently delivered to aquatic systems. At any point along this pathway, processes that release base cations can lead to neutralization of the water's acidity. Other processes can produce hydrogen ion and increase acidity. In most systems, sufficient base cations in the terrestrial system prevent the acidity in precipitation from increasing the acidity of a water body.

In some ecosystems of northeastern North America, the amount of sulfur input to the watershed has been shown to approximately equal the amount of sulfate coming out of the watershed [CARP, E-4.4.1, Table 4.3]. That is, the ecosystem is saturated with sulfur. When the waterbody is also acidic under this 'steady-state' condition, and has little organic acidity, it is likely that acidic deposition increased the acidity at some time. However, in some systems where sulfur inputs equal sulfur outputs, the associated water body is not currently acidic or is not sufficiently acidic to have had obvious impact on biota. In this case, it is believed that the hydrogen ion associated with the sulfate exchanges for base cations and the sulfate enters the aquatic system largely in neutral, nonacidifying form.

How long will those watersheds where sulfate inputs and outputs are equal, and where significant acidification has not yet occurred, remain unacidified? Two rate-related hypotheses, each leading to a different future condition, address this question:

1. Continued deposition will deplete the cation reserves and acidification will follow--presently, acidification is not occurring because sulfate is moving to the aquatic systems accompanied by base

cations rather than hydrogen ion, but these cation reserves will be depleted in years to decades.

2. At present levels of deposition, most aquatic systems not now affected will not be affected because mineral weathering is replenishing base cations at a rate equal to losses--cation reserves are sufficiently large that changes would not occur in decades to centuries.

A restriction placed on the above discussion is that sulfate inputs and outputs from the watershed were equal. This steady-state condition is not universal. In watersheds where sulfate inputs are greater than the outputs, sulfate is accumulating. Most of the accumulation occurs in the soils through the process of sulfate adsorption.

Sulfate adsorption occurs primarily in acid, highly weathered soils common to the eastern and, particularly, the southeastern United States. The principal exchangeable cation in an acid soil is aluminum. Aluminum exchange provides a buffering system that prevents rapid changes in soil pH of acid soils just as base cations buffer high pH soils. An increase in anion concentrations, e.g., sulfate in an acid soil low in base cations, tends to mobilize aluminum as the accompanying cation coming into the system is scavenged by the clay and exchanges aluminum. The sulfate now forms an aluminum sulfate complex which upon hydrolysis produces acidity in water. In acid soils, whether the anion is introduced as an acid or neutral salt, the same reaction occurs and aluminum is released. However, the soil pH must be low for aluminum transport to occur readily.

In summary, sulfur deposited on acid soils mobilizes aluminum. Much of the eastern United States has soils that are acidic enough for this process to occur. Many of these soils, particularly in the Southeast, are highly weathered, however, and have a characteristically high sulfate adsorption capacity. That is, acid soils tend to adsorb sulfate to the clays so it is not easily mobilized. As a result, aluminum, a cation whose hydrolysis acidifies soil water or surface water, is not easily mobilized. There is, however, for a given concentration of sulfate input a saturation point where no additional sulfate can be adsorbed, and aluminum sulfate moves through the soil column. At this point of 'breakthrough', the receiving aquatic system could become increasingly acidic.

Several recent publications provide expanded discussions of rate-related acidification hypotheses and the terrestrial phenomena controlling surface water acidification. The authors have found the following particularly helpful: Johnson and Reuss 1984, National Academy of Sciences 1984, Schnoor and Stumm 1984, and Johnson et al. 1985.

#### B.4.1 WHAT DATA ARE NEEDED TO TEST THESE HYPOTHESES?

Data needed to test surface water acidification hypotheses must be gathered both by survey and intensive research on chemical and physical processes in watersheds.

Surveys indicate the current status of surface waters, providing a baseline for predicting future changes. Important data are aquatic chemistry (particularly alkalinity, organic acidity, and concentrations of sulfate, aluminum, base cations, and hydrogen ion) and the physical characteristics (hydrology, bedrock, and soil chemistry, depth, and texture) of the watershed. The chemical and physical data combined provide a good indication of water quality and an indication, by correlations among factors, of whether the hypotheses provide explanations of changes in the past consistent with current observations.

Surveys of greater frequency or intensity could provide better predictive information. Measurements of sulfate inputs and outputs in many watersheds would indicate the regional distribution of sulfate steady state. Extensive sampling and intensive measurements of those soil properties--cation exchange capacity, percent base saturation, sulfate adsorption capacity, sulfate and nitrate retention, organic and mineral matter--thought to be most important in determining soil and surface water chemistry would reduce uncertainty in predictions.

The predictions of greatest certainty must wait for results of detailed watershed studies over a period of years, with corroboration in the laboratory. Processes in watersheds are dynamic, and their changes over time (seasons or years, for example) will have a profound effect on water chemistry. Changes in rates of mineral weathering to produce acid neutralizing materials, the reversibility of sulfate adsorption, and the cycling of sulfur and nitrogen in biomass are particularly important. To study changes in rates may require manipulation of parts of watersheds (simulated rain or exclusion of rain) or studying the responses of materials taken from watersheds.

#### B.4.2 IF INCREASES IN SURFACE WATER ACIDITY WERE TO OCCUR, WHAT LOCATIONS IN THE UNITED STATES WOULD BE AT HIGHEST RISK?

The best single indicator of sensitivity of surface waters to increased acid inputs is alkalinity. Alkalinity in an unperturbed, surface water system reflects a watershed's characteristics. Systems with high alkalinity are likely to have high acid neutralizing capacity in the watershed and would not be sensitive to acidic deposition. Systems with low alkalinity are likely to have poor acid neutralizing capacity in the watershed. As shown in Figure II.10, areas throughout the eastern United States, the upper Midwest, and the mountainous western regions are the only areas found to have extensive low alkalinity systems<sup>1</sup>. For a system to increase in acidity, however, several conditions must be met:

1. Acidic inputs must be present.

<sup>1</sup>Regional alkalinity maps showing more detail, particularly in regions having less than 200  $\mu\text{eq l}^{-1}$  alkalinity, are in preparation. Revised maps based on the U.S. EPA National Surface Water Survey will be available at the end of 1985.

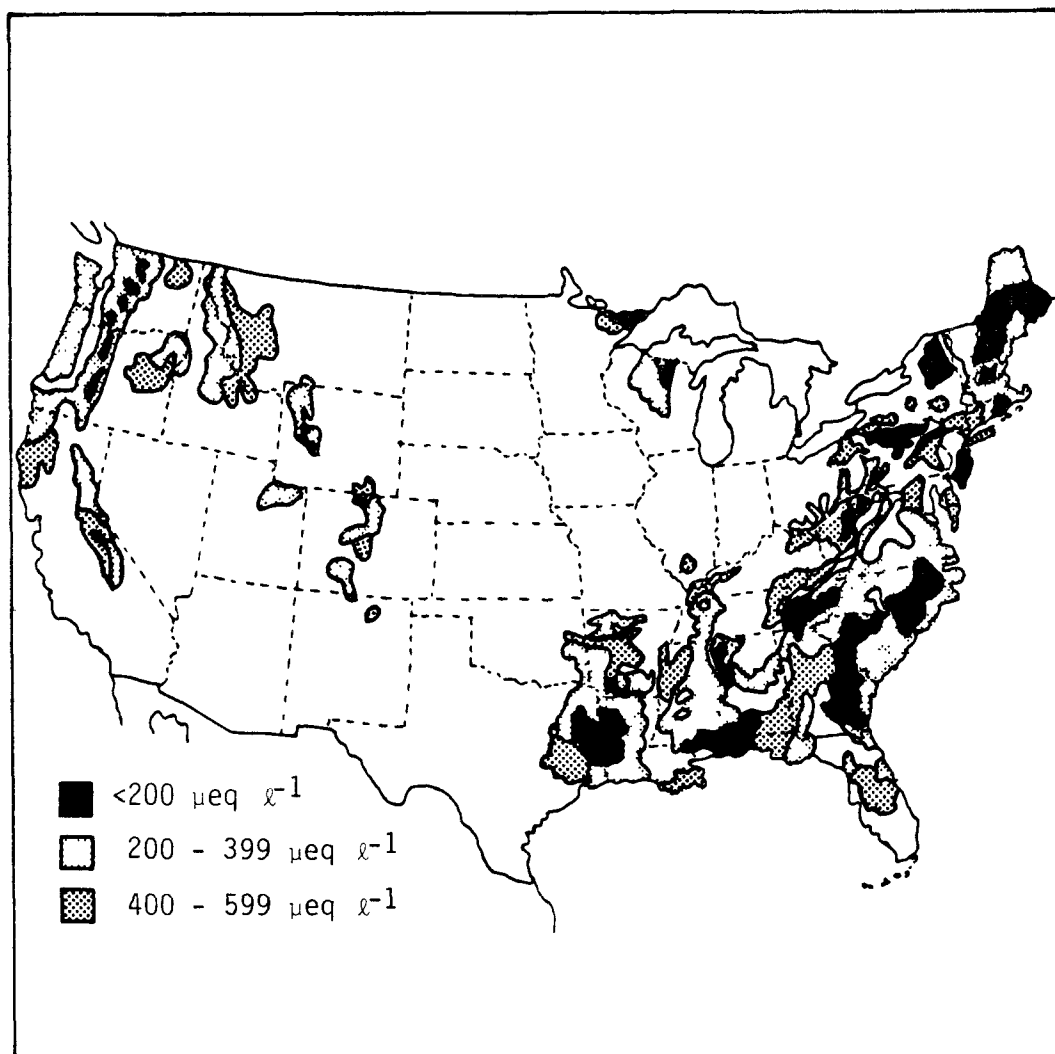


Figure II.10 Total alkalinity of surface waters. Adapted from Omernik and Powers (1982).

2. The watershed must not be able to neutralize the acid by base cation exchange processes.
3. Anions (sulfate) must be mobile.

Criterion 1 is met only in the eastern United States except for local, isolated areas. Criteria 2 and 3 are not known for most watersheds, but based on several watershed studies and geochemical theory, Criterion 3 is likely to be met often in the Northeast and seldom in the Southeast.

The region of highest risk for increasing acidity of aquatic resources in the near future is likely to be the southeastern United States. This response would be observed as sulfate adsorption capacity is exceeded. Assuming that most sensitive watersheds in the Northeast are sulfate-saturated (i.e., satisfy Criterion 3) and that deposition of acid there has been constant or decreasing over the last decade, this region would experience little increase in acidity in the near future, although changes in some watersheds could still be expected.

#### B.4.3 WHAT IS THE TIME FRAME IN WHICH CHANGES MIGHT BE OBSERVED?

The currently available database provides no way to predict exactly the time frame for changes. Additional acidification at current input amounts could be expected in decades in some systems not now satisfying Criteria 2 and 3. Aquatic systems now satisfying Criterion 3 above would respond most rapidly to changes, either increases or decreases, in acidic inputs; of these, only those meeting Criterion 2 would become more acidic.

### III. ATMOSPHERIC SCIENCES SUMMARY

#### SECTION A. ATMOSPHERIC PROCESSES

##### A.1 INTRODUCTION

###### A.1.1 WHAT ARE THE RELEVANT QUESTIONS CONCERNING THE EMISSION AND PROCESSING OF ACIDIFYING SUBSTANCES?

The processes through which acidic substances reach the environment are complex and uncertain, and it is important to ask the right questions about those processes to avoid being overwhelmed by scientific detail. Three sets of considerations determine how appropriate a question is:

- 1) the nature of the effects that are of most concern; what doses of pollutants are producing the effects occurring at present?
- 2) the causal relationships that determine what happens to an acid precursor when it is released to the environment; what have doses been in the past and what doses are projected?
- 3) the nature of the possible controls that could be instituted to reduce the deposition of harmful material; what would be the dose if emissions changed?

Although it is not the purpose of this document to evaluate the merits or feasibility of alternative control strategies, part of the document's usefulness depends on its providing a guide to the best scientific estimates and an evaluation of uncertainties in estimates of how emissions are related to deposition.

This section evaluates the present scientific capability for answering questions relating emissions to deposition of acidifying substances. The first-level questions, those asking for a broad characterization of each of the steps leading to acidic deposition, are discussed in Section A. Second-level questions, those directly concerned with the relationship between emissions and deposition, are discussed in Section B. They fall into two categories: questions about whether it is possible to identify some sources as significantly different from or more important than others, and questions about the overall material budgets and the predictability of changes in them.

###### A.1.2 WHAT ARE THE MOST IMPORTANT SUBSTANCES THAT ARE EMITTED AND DEPOSITED? WHAT SPATIAL SCALES AND TEMPORAL SCALES ARE MOST IMPORTANT? WHERE ARE THE MOST SENSITIVE AREAS? [CARP E-3, E-4]

Part II concluded that the primary material of concern to aquatic ecosystems is the sulfate ion,  $\text{SO}_4^{2-}$ , whether it is deposited as sulfuric acid,  $\text{H}_2\text{SO}_4$ , or as a neutral salt (ammonium sulfate or calcium sulfate, for instance). Harmful effects can also be attributed to nitrate,  $\text{NO}_3^-$ ,

deposition, and it is possible that some effects are associated specifically with acidity--i.e., unneutralized sulfate and nitrate deposition. Because precipitation or other moisture eventually arrives at surfaces, it does not matter for most effects of concern whether the sulfate or nitrate was dry or wet deposited. For forests, it is not yet clear whether nitrogen compounds or sulfur compounds are of most concern, or indeed whether either of them is; nor is it known whether exposure to particular compounds in the air or deposition to the soil system is more important.

Other substances play subsidiary roles. Neutralizing material, coming mostly from soils but also released in combustion, affects whether the sulfate or nitrate appears as acid or salt. It can also affect the rates of chemical transformation in the atmosphere. Oxidizing materials are important in producing chemical change.

Most effects on soils, forests, and aquatic systems appear to result from the long-term accumulation of sulfates and nitrates. For that reason average deposition rates over one or more years are the most important quantities. The magnitude of effects may depend on time of year, whether the material accumulates during the growing season, for instance. Some evidence suggests that acid deposition episodes, sudden introduction of high concentrations of acidic materials, may produce shocks to aquatic systems. These shocks may occur from heavy rains. In the North these generally result, however, from snowmelts releasing the material accumulated over an entire winter season.

Areas sensitive to acidic deposition are broadly distributed over North America; those receiving the highest inputs from deposition are found in northeastern North America, while the southeastern United States has experienced the largest recent increase in deposition. Sensitive watersheds tend to be small and widely distributed. Sensitive soil areas and forest tracts are larger and widely distributed. For all three systems only a limited amount of detailed survey information exists.

#### A.1.3 WHAT IS THE CAUSAL STRUCTURE RELATING EMISSION TO DEPOSITION?

The Atmospheric Sciences volume of the Critical Assessment Review Papers (CARP) is organized by chapter (A-1 through A-9) according to the sequence of events from emission of acid precursor (sulfur oxides and nitrogen oxides) to deposition. Burning of fuel produces sulfur dioxide, sulfate, nitrogen oxides, and other materials (A-2). The pollutants are transported, sometimes for long distances, by a variety of atmospheric processes (A-3); during transport some of the  $\text{SO}_2$  is oxidized to sulfate and some of the  $\text{NO}_2$  to  $\text{NO}_3^-$  (A-4). If the polluted air encounters a storm system, some  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2$ , and  $\text{NO}_3^-$  will be scavenged and wet deposited (A-6). Otherwise the material is dry deposited (A-7) or leaves the continent. The result is flows of compounds in the air (A-5) and in dry and wet deposits (A-8). These deposits may affect soils (E-2), forests and crops (E-3), water chemistry (E-4), fish and other aquatic life (E-5), human health (E-6), and materials (E-7). The current capability for modeling the atmospheric sequence is discussed in Chapter A-9. The sequence is illustrated in Figure III.1 (Goble 1982).

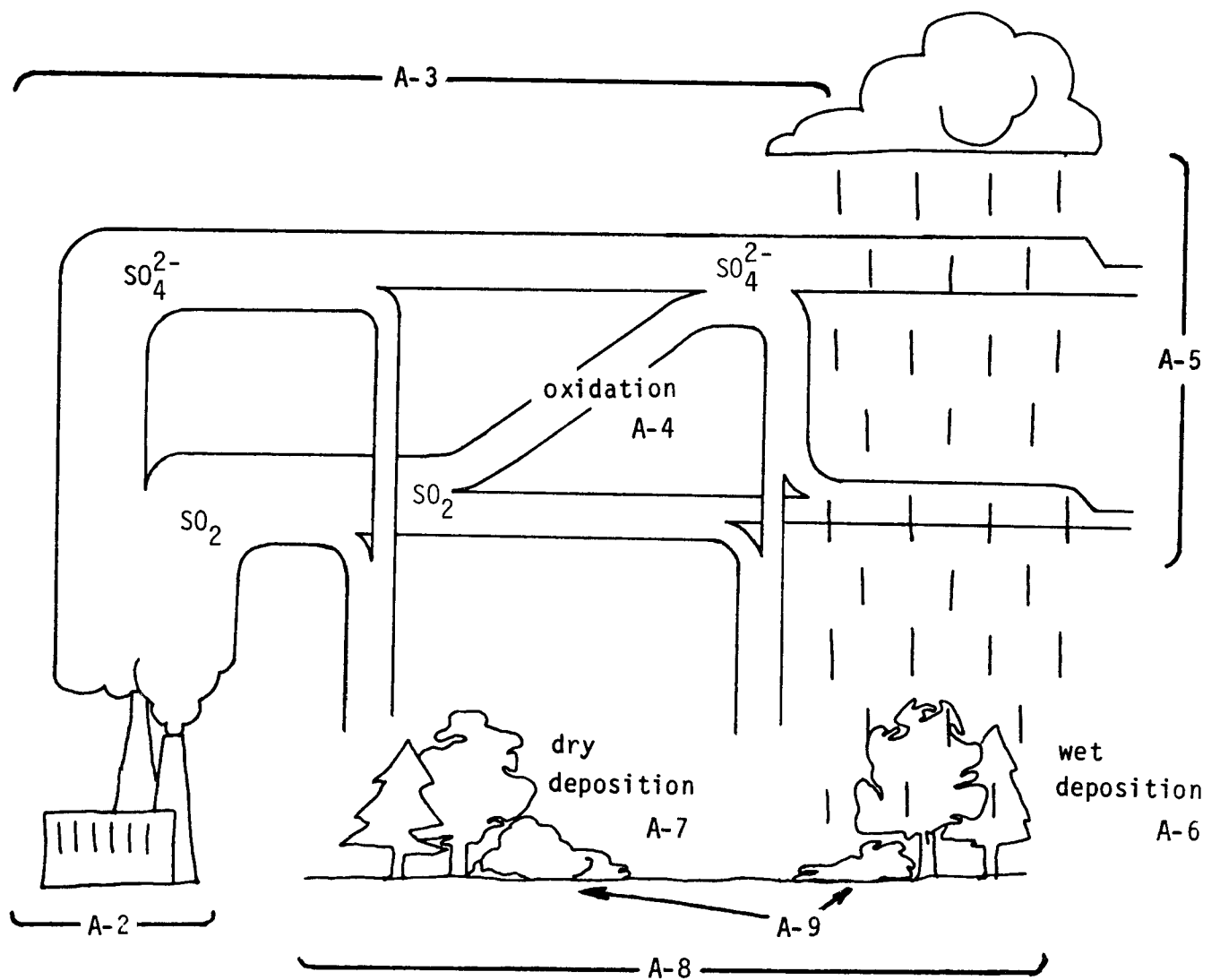


Figure III.1 Atmospheric processes in acidic deposition. Each stage is labeled by the chapter in CARP, Vol. I.



The transformation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  can take place directly in the gas phase, in solution with water vapor, or on particles. In each case numerous potential contributing chemical reactions occur. Such a breakdown is illustrated in Figure III.2, which shows only the primary chemical interactions with  $\text{SO}_2$ ; along with each interaction comes a whole cycle of chemical reactions. Thus, when the acidic deposition problem is considered in scientific detail, Figure III.1 begins to look something like the artist's sketch given in Figure II.3, where each line represents an alternative process (Goble 1982).

#### A.1.4 WHAT ARE THE ISSUES IN RELATING EMISSIONS TO DEPOSITION?

From the perspective of the public, planners, or regulators, the purpose of this document must be to provide a basis for evaluating the current state of affairs regarding acid deposition and for anticipating future trends in deposition with or without the implementation of control policies. Opportunities for control are limited. Controls on sulfur and nitrogen oxide emissions from various sources have most frequently been considered; controls on the production of oxidizing material, possibly by controlling hydrocarbon emissions, and attempts to treat effects directly have also been proposed. Future emissions trends are tied directly to economic activity and to control policies and, thus, are somewhat easier to gauge than trends in deposition. For that reason, the important question is how will changes over a spectrum of emissions alter flows and effects? If we attempt to answer such a question by tracing in detail through all of the branches of Figure III.3 we will learn nothing; uncertainties and errors accumulate rapidly because of the large number of branches and stages. Instead, we need summary information that represents averages over many processes.

#### A.2 WHAT IS KNOWN ABOUT THE STEPS IN THE SOURCE-RECEPTOR PATH?

This section reviews the state of scientific knowledge described in the Critical Assessment Review Papers (CARP) for each stage in the path from emission to deposition. Just as we reversed the causal order, treating effects first and atmospheric processes second, we will begin with deposition and work backward, in Figure III.1, to emissions. The justification is similar: what happens in later stages determines what information is needed about earlier stages.

##### A.2.1 WHAT AMOUNTS OF ACIDIFYING SUBSTANCES ARE WET AND DRY DEPOSITED? [CARP A-8]

##### A.2.1.1. HOW IS WET DEPOSITION OF SULFUR AND NITROGEN COMPOUNDS AND HYDROGEN IONS MEASURED? [CARP A-8.2.3]

The idea behind wet deposition measurements is simple enough. You put a bucket out in the rain and then perform chemical analyses of the rainwater. Obtaining measurements that are both reliable and representative, however, requires considerable care. Five characteristics of data collection can be distinguished; all must be considered in comparing data from different sites (or networks).

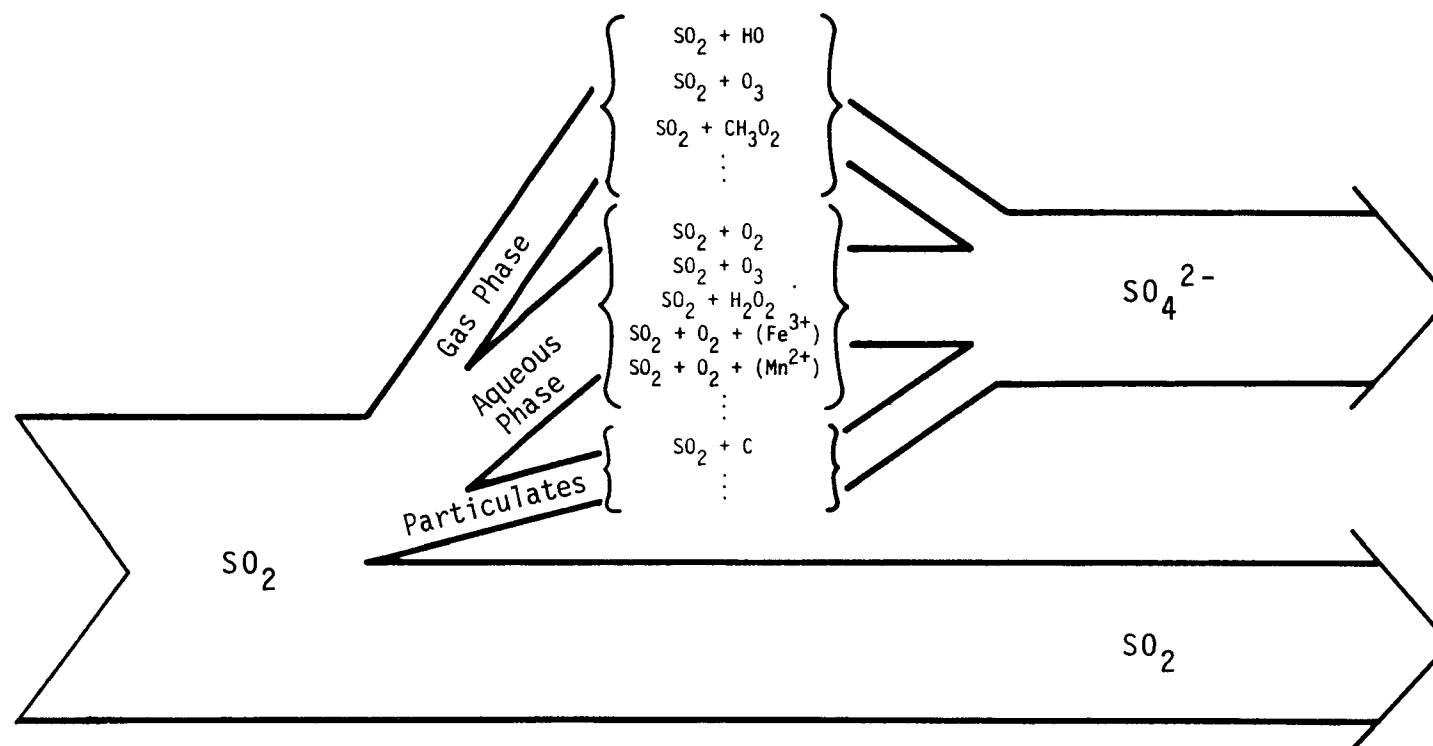


Figure III.2 Sample processes in  $\text{SO}_2$  oxidation. This figure illustrates how complex each of the steps in Figure III.1 is when examined in detail.

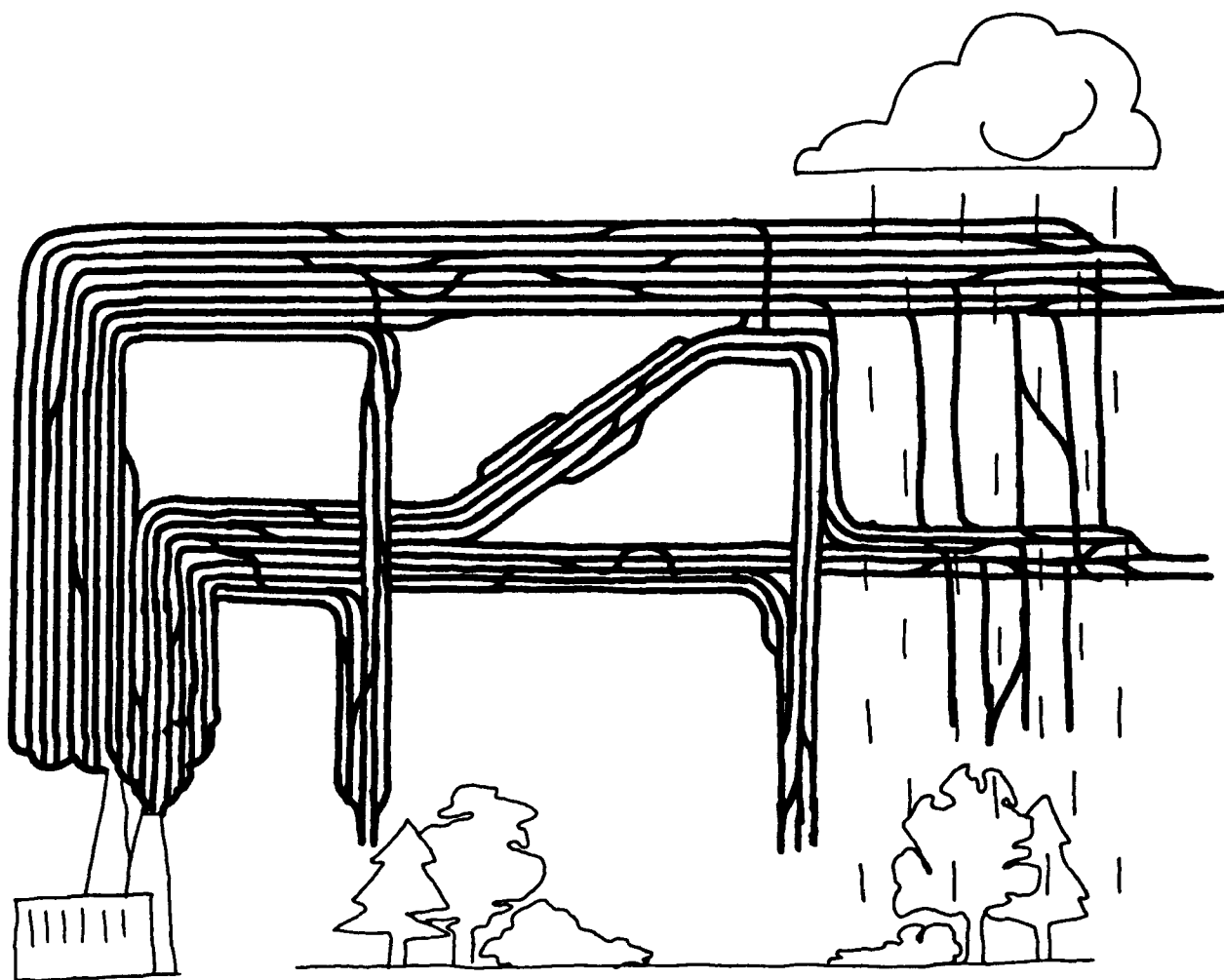


Figure III.3 Alternative pathways leading to acidic deposition. The multiplicity of branching and recombining lines represents the multiplicity of processes present in a detailed examination of acidic deposition.

Site selection. A site can fail to provide representative information because it is too close to particular sources, its local topography leads to unusual meteorological patterns (this problem can be acute in mountainous regions or near large bodies of water), or it provides contaminants (blown soil, bird droppings, etc.). Assuming that the sites are reasonably representative, the number of sites and their spatial distribution determine the spatial resolution.

Collection of samples. Three types of collection methods have been used: wet-only samples in which the bucket is exposed only while it is raining, wet/dry samples in which one bucket is exposed only during rain while a second bucket is exposed the remaining time, and bulk samples in which one bucket is continuously exposed. Wet-only or wet/dry sampling are definitely preferable. Information from bulk sampling cannot be compared reliably from one site to another. The samples may have an undetermined amount of evaporation; contamination is more likely and, as we shall see later (Section A.2.1.7), the amount of dry deposited material in the collector is an unknown component of the material available for dry deposition. While wet-only and wet/dry samples should provide reliable purely wet deposition samples, contamination (particularly from failure of seals in the automatic covering mechanism) can be a serious problem and probably limits the usefulness of much of the older network data.

The choice of sampling time is important in determining the temporal resolution of a network and in attempting to compare the measurements made at one site with those made at another. Choices that have been made include sampling by precipitation events and daily, weekly, or monthly samples. Reliable information on rainfall amounts is needed if shorter-term measurements are averaged for comparison with longer-term data. Researchers attempting to characterize what happens during a rainstorm have made a few very short duration measurements.

Sample handling. While field analysis of samples is possible and has been done, any large-scale network operating over a reasonable length of time will collect samples and deliver them to a central laboratory for analysis. Storage and handling can lead to chemical change due to biological activity, contamination, or ongoing chemical processes. Varying the techniques used to prevent such changes can make data from one set of samples not comparable with those from another. Biological activity in particular can affect the amount of organic acid present so that, except for pH lower than 5.0, pH measurements may indicate manmade acidification poorly. [CARP A-8.4.2]

Chemical analysis. Standard chemical techniques exist for measuring the most important ions that appear in rainwater: anions (sulfate, nitrate, chloride) and cations (calcium, magnesium, ammonium, sodium, potassium, and hydrogen). Another anion, bicarbonate, is not readily measured. Its concentration is usually calculated by assuming equilibrium with atmospheric carbon dioxide. Bicarbonate is unimportant for rainfall with a pH less than 5.0. Because the anion sum should equal the cation sum (in the absence of measurement errors), an analytic check is available: measured pH should agree with the pH calculated from the amounts of the other ions listed. Because the ion concentrations in most samples are quite low, great care must be taken in

measuring them; even direct pH measurement at typical rainwater concentrations is susceptible to instrument calibration failures.

Quality assurance. The preceding discussion makes clear that major efforts at quality control for each of the four steps are necessary for long-term network data to be reliable. Equally important is documentation of quality control efforts so information from different networks can be compared. One problem deserving special attention is rare extreme events. Statistical outliers may result from contamination or measurement error, but a small number of high concentration events may, in fact, provide a significant portion of the annual chemical wet deposition at a site. An important check on the comparability of procedures from one contemporary network to another involves co-located sites. At present, uncertainties about quality control have made all comparisons of historical data controversial and have meant that reliable information about deposition trends is difficult or perhaps impossible to extract.

#### A.2.1.2 WHAT IMPORTANT COLLECTIONS OF DATA HAVE BEEN MADE AND ARE ONGOING? [CARP A-8.2.4]

The wet deposition data bases available for North America have been summarized by many authors. Miller (1981) points out that the history of precipitation chemistry measurements in North America has been very erratic, with networks being established and disbanded without thought of long-term considerations. Miller suggests one possible time grouping of network data:

1. 1875-1955, the period when agricultural researchers measured nutrients in precipitation to determine the input to the soil system;
2. 1955-1975, the period when atmospheric chemists were measuring the major ions in precipitation to better understand chemical cycles in the atmosphere; and
3. 1975-present, the period when network measurements were often primarily to evaluate ecological effects.

Table III.1 by Miller summarizes the "agricultural data bases" taken from a review by Eriksson (1952).

Table III.2 summarizes some regional- and national-scale wet deposition networks in Canada and the United States that have begun operation since 1955. These networks were generally not established to monitor acidic precipitation. The first two are no longer operating. The PHS/NCAR and EML-DOE networks include sites influenced by large urban areas, thus are not as useful in addressing regional acidic precipitation issues. All the networks followed the pattern of the Junge network in measuring the major inorganic ions that account for most of sample conductance. Sulfate was measured in all the networks; pH was not measured in the Junge network.

In addition to regional- and national-scale wet deposition networks, local sites and networks have provided data that may be useful either in interpreting time trends of chemical concentrations in precipitation or in studying characteristics of urban or power plant plumes.

TABLE III.1. AGRICULTURAL DATA BASES (1875-1955)

Period	Number of studies	Locations of sites
1875 - 1895	3	Missouri, Kansas, Utah
1895 - 1915	7	Ottawa, Iowa, Tennessee, Wisconsin, Illinois, New York Kansas
1915 - 1935	8	Kentucky, Oklahoma, New York, Illinois, Texas, Virginia, Tennessee
1935 - 1955	6	Alabama, Georgia, Indiana, Minnesota, Mississippi, Tennessee, Massachusetts

TABLE III.2. SOME NORTH AMERICAN WET DEPOSITION DATA BASES (1955-PRESENT)

NETWORK	PERIOD	APPROXIMATE NUMBER OF SITES	SAMPLING MODE <sup>a</sup>	SAMPLING INTERVAL
<u>National</u>				
Junge	1955-1956	60	W-M	Daily (with monthly compositing)
PHS/NCAR <sup>b</sup>	1959-1966	35	W	Monthly
WMO/EPA/NOAA <sup>c</sup>	1972-Present	17	W	Monthly (weekly after joining NADP in 1980)
CANSAP <sup>d</sup>	1977-Present	54	W	Daily (with monthly compositing) (monthly before 1980)
NADP <sup>e</sup>	1978-Present	115	W-D	Weekly
<u>Regional</u>				
US Geological Survey Eastern (USGS)	1964-Present	18	B	Monthly
Canadian Centre for Inland Waters (CCIW)	1969-Present	15	W	Monthly
Tennessee Valley Authority (TVA)	1971-Present	9	W-D	Biweekly
MAP3S <sup>f</sup>	1976-Present	9	W	Daily

TABLE III.2 CONTINUED

NETWORK	PERIOD	NUMBER OF SITES	SAMPLING MODE <sup>a</sup>	SAMPLING INTERVAL
Canadian APN <sup>g</sup>	1978-Present	8	W	Daily
EML-DOE <sup>h</sup>	1977-Present	7	B, W-D	Monthly
EPRI-SURE <sup>i</sup>	1978-1981	9	W	Daily
UAPS <sup>j</sup>	1981-Present	20	W	Daily
U.S. EPA <sup>k</sup> Great Lakes	1977-Present	30	B, W	Monthly and Weekly

<sup>a</sup>B for bulk, W for wet-only with automatically opening device, W-M for wet-only via manual operation, W-D for wet-dry with automatic device.

<sup>b</sup>U.S. Public Health Service/National Center for Atmospheric Research.

<sup>c</sup>World Meteorological Organization/U.S. Environmental Protection Agency/National and Oceanic and Atmospheric Administration. These sites are now part of NADP.

<sup>d</sup>Canadian Network for Sampling Acid Precipitation.

<sup>e</sup>National Atmospheric Deposition Program. There were 115 operating sites on 1 July 1983 and the network was growing rapidly. In 1983, many of the NADP sites were also named as sites for inclusion in the National Trends Network (NTN).

<sup>f</sup>Multistate Atmospheric Power Production Pollution Study.

<sup>g</sup>Canadian Air and Precipitation Network.

<sup>i</sup>Electric Power Research Institute-Sulfate Regional Experiment.

<sup>h</sup>Environmental Measurements Laboratory of the U.S. Department of Energy.

<sup>j</sup>Utility Acid Precipitation Study. This was preceded at some of the same sites and with the same central laboratory by the 9 site, wet-only, daily sampling EPRI/SURE network.

<sup>k</sup>United States Environmental Protection Agency.



The largest U.S. network now in continuous operation is the National Atmospheric Deposition Program (NADP). Its 170 sites give it an average spatial resolution of about one site per 21,300 sq mi (54,400 sq km). The density of sites in the eastern United States is somewhat higher, one site per 10,000 sq mi (25,000 sq km).

#### A.2.1.3 WHAT ARE THE PATTERNS FOR WET DEPOSITION OF SULFATE, NITRATE AND HYDROGEN IONS? [CARP A-8.4.1]

One choice has to be made immediately in presenting data on wet deposition: that is, whether to present total amounts deposited per year per area or to present amounts deposited per amount of rainfall. Because amounts of rainfall differ in different locations, the patterns differ and either choice could be appropriate depending on the types of effects considered. Because the qualitative features of either pattern are similar and because we are primarily interested in presenting information about the total loadings of the important ions, we show in Figures III.4, III.5, and III.6, the total wet deposition in 1980 for sulfate, nitrate, and  $H^+$ , respectively, measured in the NADP, the CANSAP, and other networks. The patterns for all three ions are similar, with the highest deposition rates roughly centered on a line drawn from the upper Ohio Valley to northern New York, with high deposition areas extending northeast and southwest. For comparison, we show in Figure III.7 the 1980 average hydrogen ion concentration per amount of rainwater, measured as pH; it shows a similar spatial pattern. The amount of sulfate wet deposited ranges from 15 to 45 kg ha<sup>-1</sup> yr<sup>-1</sup> for most of North America east of the Mississippi River. [Note: 1 hectare (ha) equals about 2.5 acres.] In the West, amounts deposited range from 2 to 10 kg ha<sup>-1</sup> yr<sup>-1</sup>. The amount of nitrate wet deposited ranges from 10 to 30 kg ha<sup>-1</sup> yr<sup>-1</sup> in the East and 2 to 10 kg ha<sup>-1</sup> yr<sup>-1</sup> in the West. Hydrogen ion deposition ranges from 0.2 to 0.8 kg ha<sup>-1</sup> in the East and 0.0005 to 0.1 kg ha<sup>-1</sup> yr<sup>-1</sup> in the West. The pH of rainfall ranges from 4.0 to 4.8 in the East and from 5.0 to 6.0 in the West.

The reader should note the choice of unit for presenting these data: kg of sulfate, nitrate, or hydrogen. Other choices are possible and often appear in the literature, hence the potential for confusion. In particular, data on sulfate and nitrate deposition are often presented in terms of kg of sulfur or nitrogen (because they are the conserved species). Because sulfate has the chemical formula  $SO_4$ , while nitrate has the formula  $NO_3$ , the mass of sulfur deposited is about 1/3 that of sulfate, and that of nitrogen is about 2/9 that of nitrate. Thus, in the eastern United States, deposition rates of 15 to 45 kg ha<sup>-1</sup> of sulfate correspond to deposition rates of 5 to 15 kg S ha<sup>-1</sup>; deposition rates of 10 to 30 kg ha<sup>-1</sup> of nitrate correspond to deposition rates of 2 to 6 kg N ha<sup>-1</sup>.

#### A.2.1.4 WHAT IS THE SPATIAL AND TEMPORAL VARIABILITY OF THE WET DEPOSITION PATTERNS? [CARP A-8.4]

Spatial variation. A close look at Figures III.4 to III.7, along with other analyses of deposition patterns, yields two observations: 1) great spatial variability exists in the eastern data on a small spatial scale (neighboring network stations distant from major sources can differ in annual amounts wet

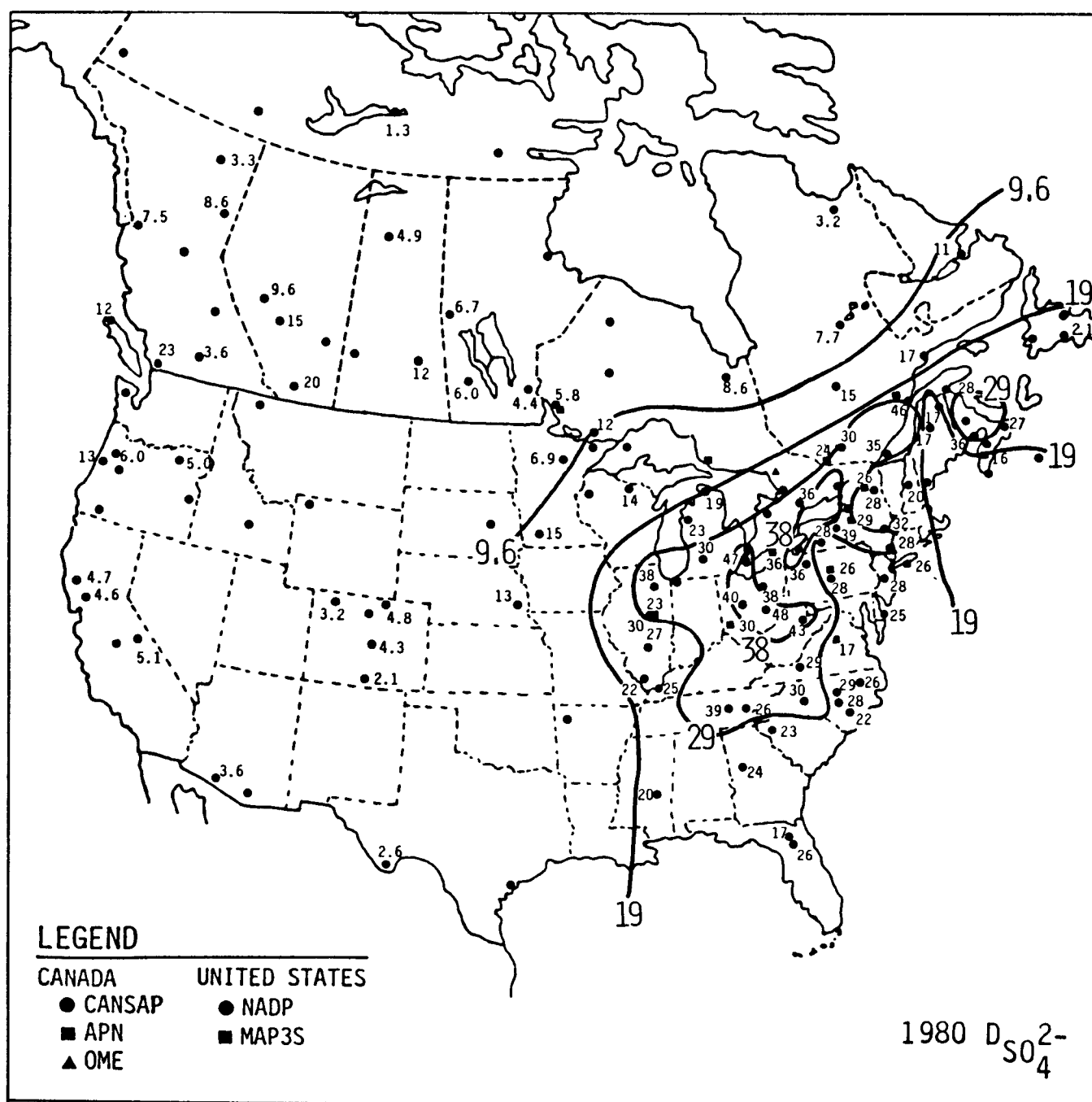


Figure III.4 Sulfate ion deposition for 1980 for wet deposition samples ( $\text{kg ha}^{-1}$ ). Adapted from Barrie et al. (1982).

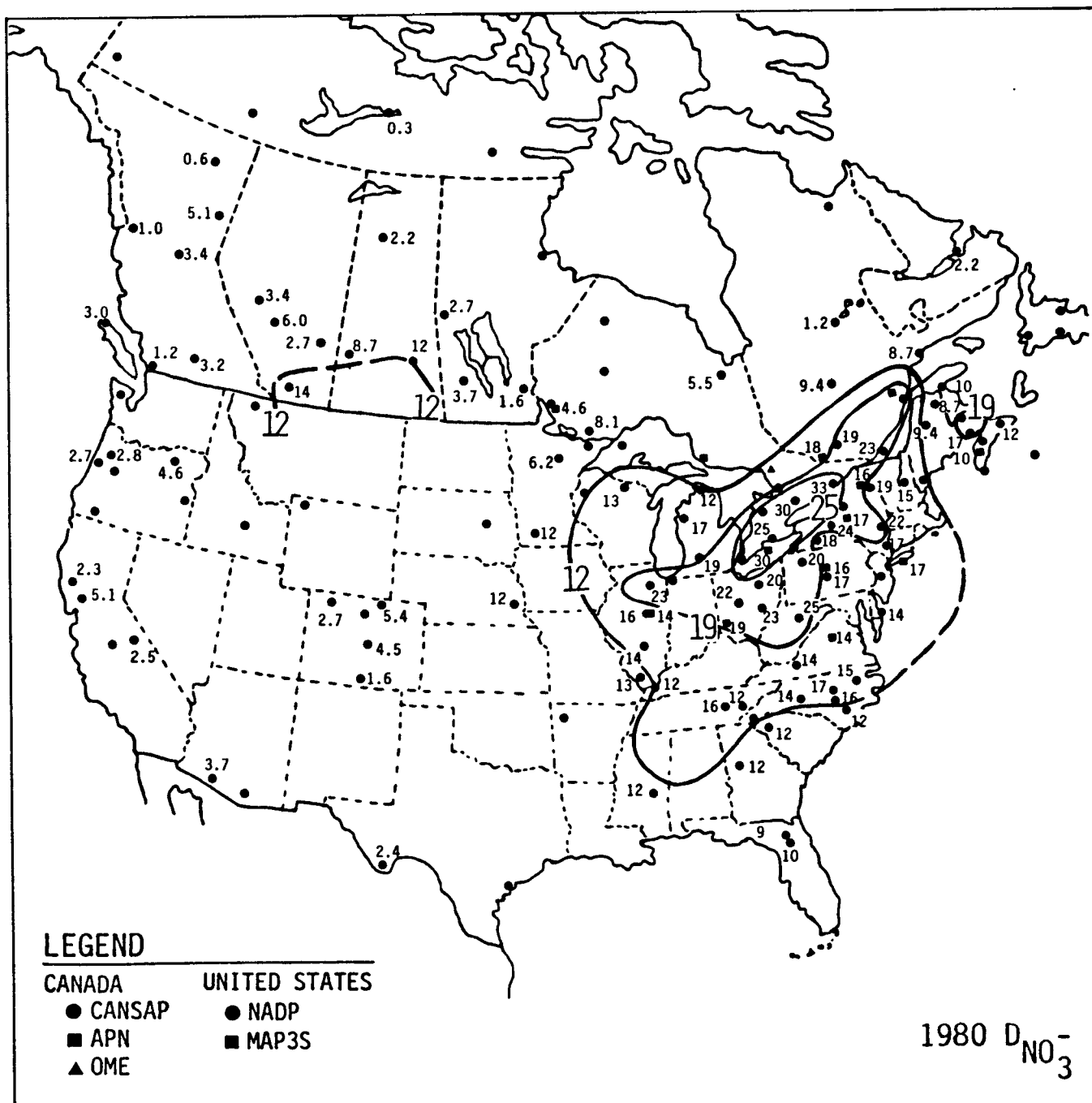


Figure III.5 Nitrate ion deposition for 1980 for wet deposition samples ( $\text{kg ha}^{-1}$ ). Adapted from Barrie et al. (1982).

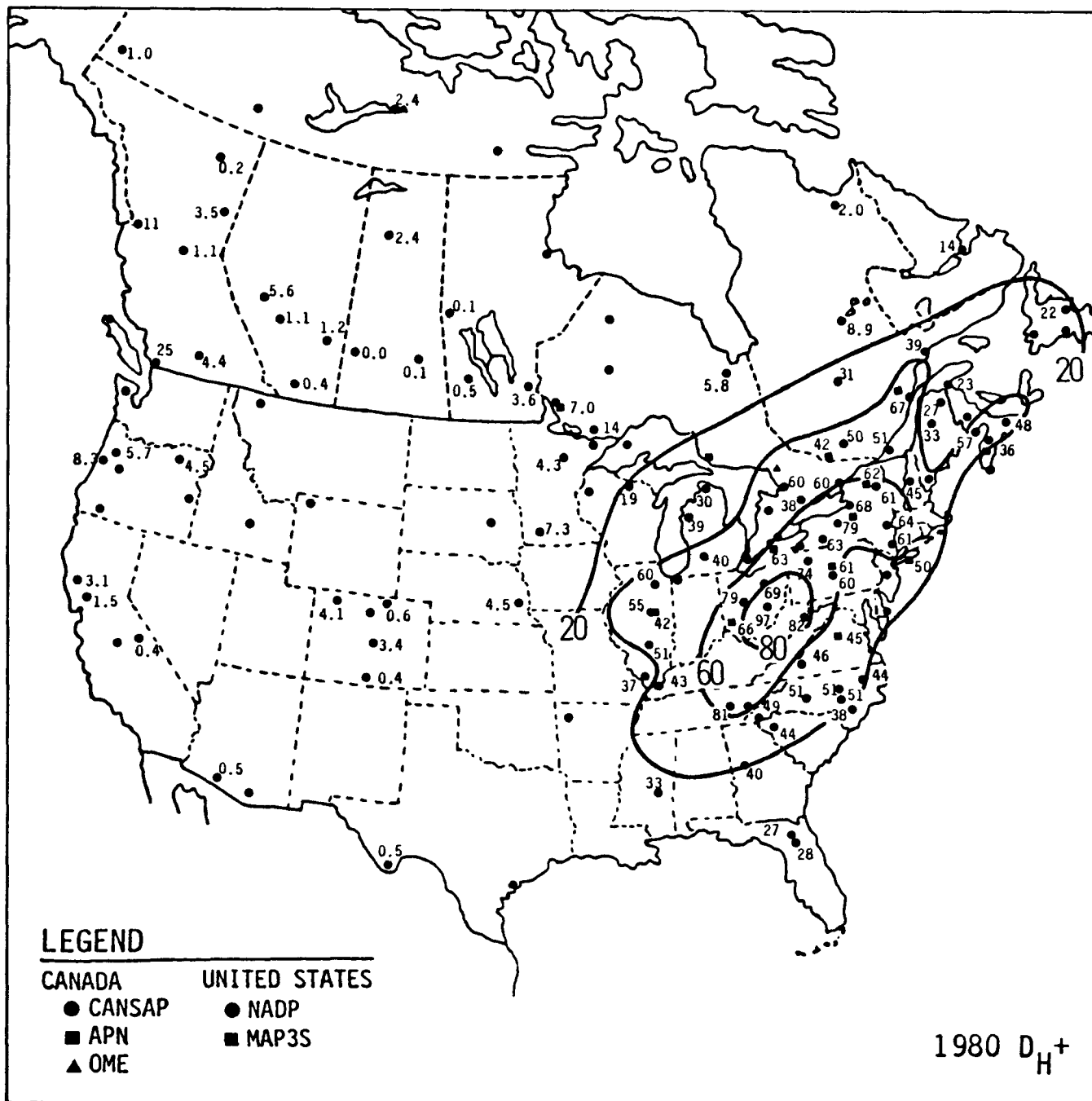


Figure III.6 Hydrogen ion deposition for 1980 for wet deposition samples ( $\text{meq m}^{-2}$ ). Adapted from Barrie et al. (1982).

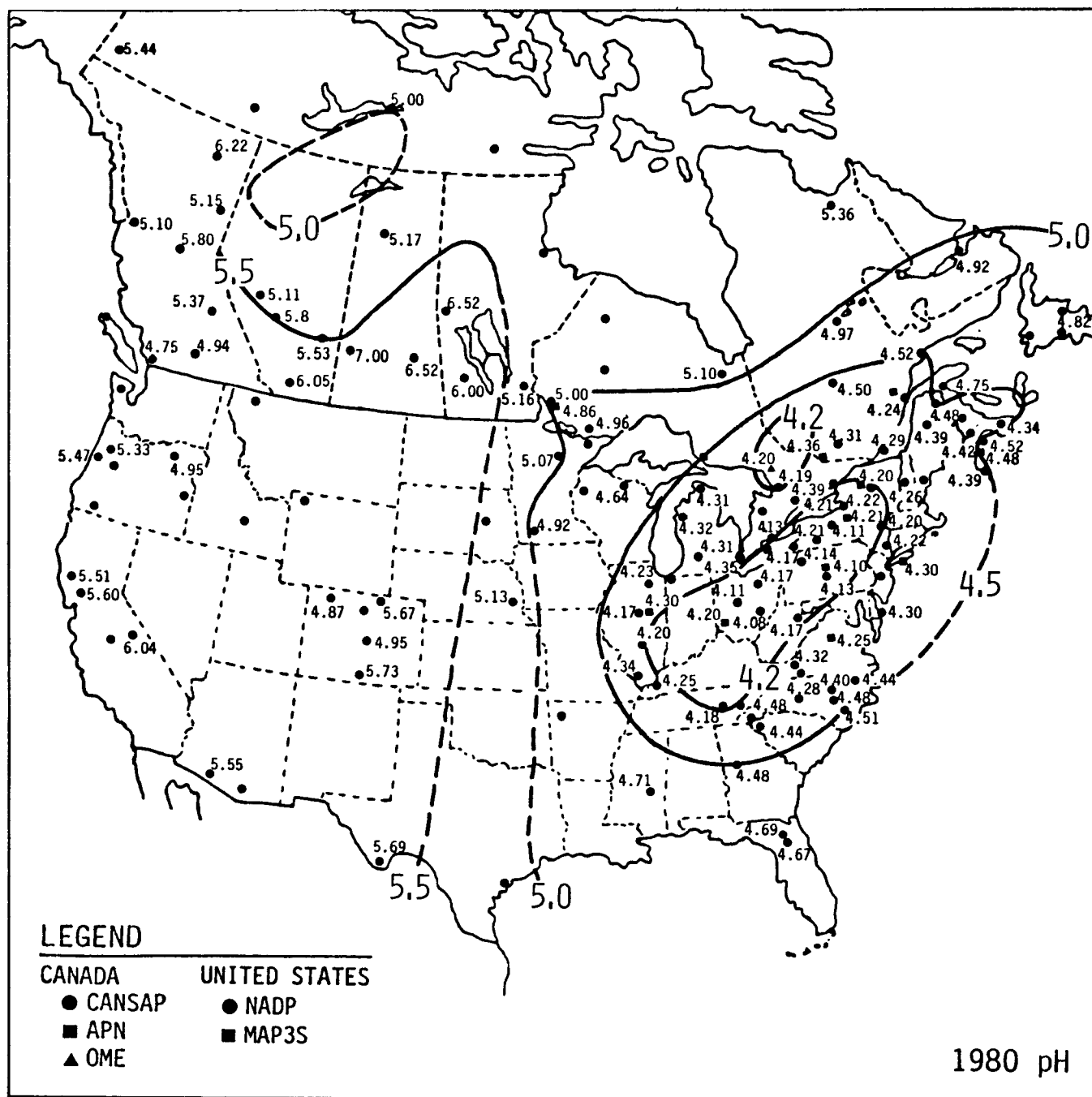


Figure III.7 pH from weighted-average-hydrogen ion concentration for 1980, for wet deposition samples. Adapted from Barrie et al. (1982).

deposited by as much as a factor of 2), so the observed patterns are only broad averages; and 2) the resolution of the network west of the Mississippi is so coarse that it does not suitably define any clear pattern of deposition, beyond the observation that total annual deposition of sulfate, nitrate, and hydrogen ion per unit area is generally smaller than in the East.

Although the patterns of sulfate, nitrate, and hydrogen ion deposition appear superficially similar, it is interesting to try to compare them more quantitatively. Figure III.8 shows the molar ratio of sulfate to nitrate ions [ $\#$  of sulfate ions/ $\#$  of nitrate ions or  $(62/96) \times$  mass of sulfate wet deposited/mass of nitrate wet deposited] (NAS 1983). If the patterns of sulfate and nitrate deposition were exactly the same, then the ratio would be approximately constant over the region studied; this is what is observed. The ratio tends to be slightly higher near the Ohio Valley and in the southern Appalachians and in remote parts of Maine and eastern Canada.

Temporal variation. The year to year variation in total wet deposition of sulfate, nitrate, or hydrogen ions as observed in 1978-80 for the NADP network is at least 30 percent. Individual sites show yearly variation of more than 50 percent. The variation is somewhat less for wet deposition concentrations; apparently variability in annual rainfall amounts contributes significantly to the variability in amounts wet deposited (NAS 1983). [CARP A-8.4.1]

Seasonal variation in sulfate wet deposition is substantial, and even more variability occurs in sulfate and nitrate deposited from one rainfall event to another, as can be seen from Figure III.9. Variation in ion concentrations during a single storm can be as high as 1000 percent.

The seasonal variation in sulfate wet deposition and the absence of seasonal variation in nitrate deposition, shown in Figure III.9 are characteristic of sites across most of the eastern United States (although some seasonal variations have been seen in the southeast; Bowersox and Stensland 1981). Thus a marked seasonal dependence of the molar ratio of sulfate wet deposited to nitrate wet deposited occurs. The ratio is roughly 0.7 in winter and 1.4 in summer (NAS 1983).

#### A.2.1.5 WHAT HISTORICAL TRENDS CAN BE SEEN IN WET DEPOSITION DATA? [CARP A-8.4.3]

Because no continuously operating wet deposition monitoring network existed over a substantial period of time in North America, all attempts to reconstruct historical trends in deposition have been controversial. What consensus exists may be summarized by the following conclusions quoted from Section A-8.6 of the CARP:

- a. "On the broad scale, nitrate in U.S. precipitation has likely increased since the 1950's, in conjunction with  $\text{NO}_x$  emissions increases."

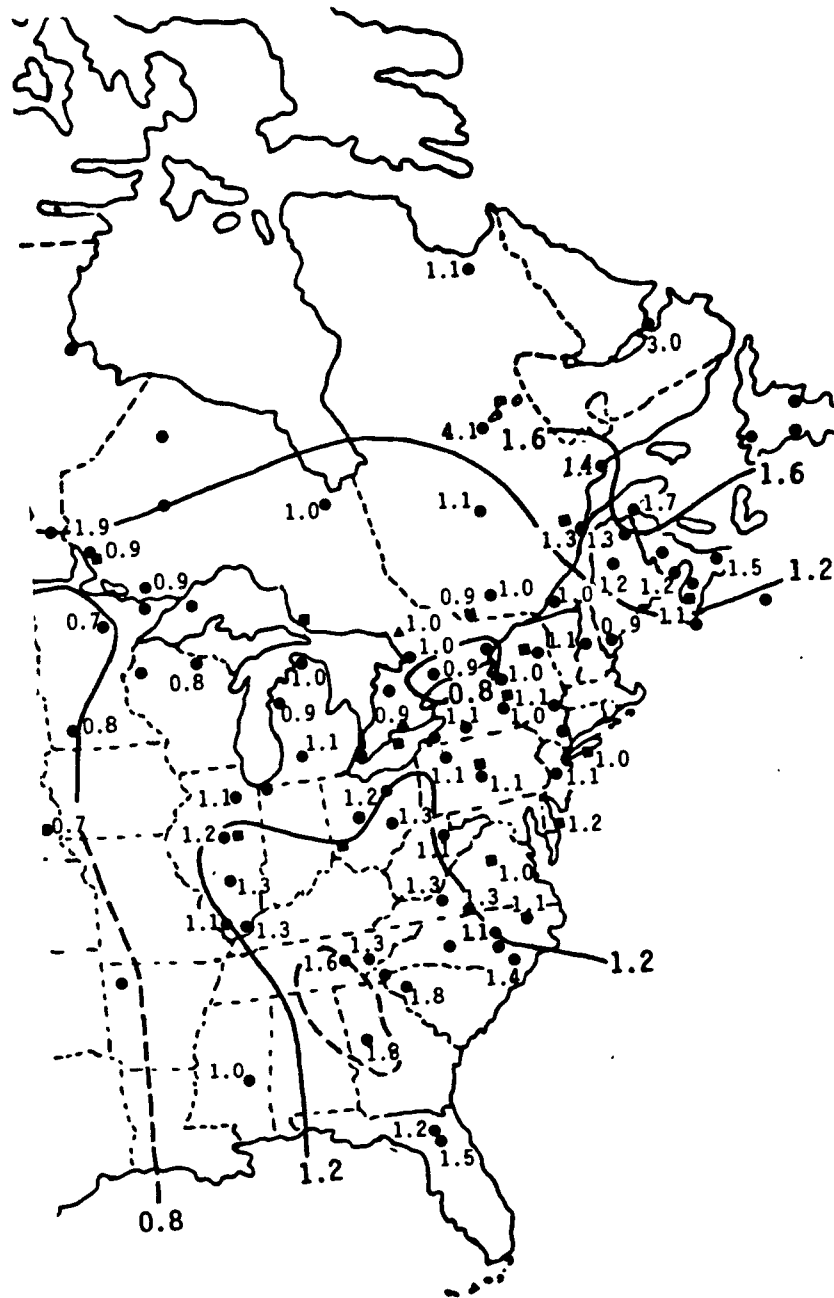


Figure III.8 Average molar ratio of sulfate to nitrate in precipitation in eastern North America in 1980. Adapted from NAS (1983).

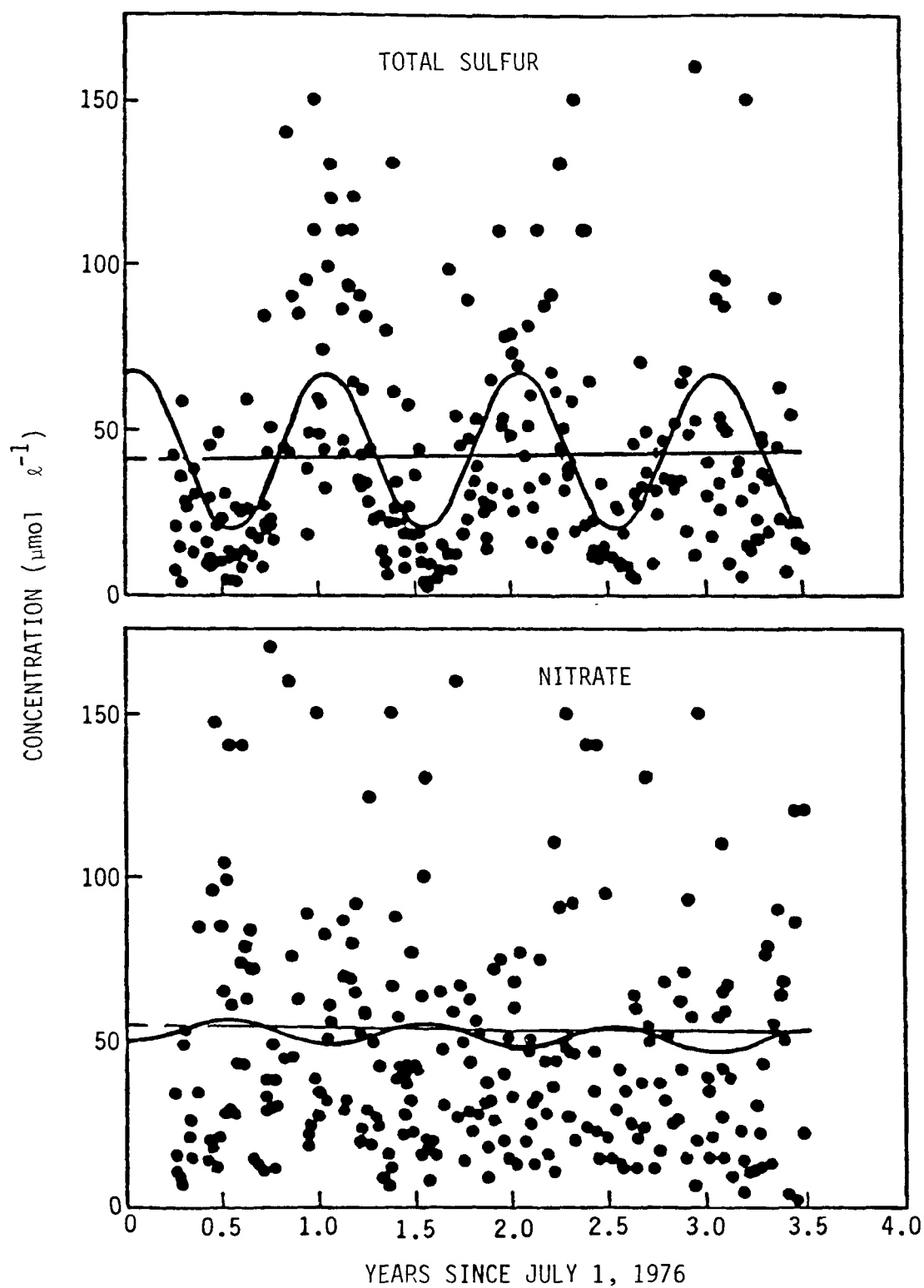


Figure III.9 Sulfate and nitrate concentration data for event precipitation samples collected at Penn State University, PA. Lines are least-squares of linear and periodic functions (MAP3S/RAINE 1982).



- b. "Calcium measured in U.S. precipitation has decreased, perhaps due to lack of extreme drought recently as compared to the 1950's, but more certainly due to improved sampling procedures." (Other possible contributing reasons are a decrease in unpaved roads and a decrease in particulate emissions, shown in Figure III.19.)
- c. "A combination of drought effects and the mixing of urban data with more regionally representative data, the mixing of bulk data and lower quality wet-only data with higher quality wet-only data, has led to statements concerning increasing acidity of precipitation which are difficult to support. In general, it appears difficult to use historical U.S. network data to discern the precipitation pH time trend as related to the acid precursor emissions."
- d. "The most reliable long-term trends for precipitation chemistry are available for the Hubbard Brook Forest site in New Hampshire (record continuous since 1964). The nitrate data record suggests an erratic trend of increasing nitrate from 1964 to about 1971, followed by a leveling off or slight decrease from 1971 to 1981. Wet sulfate at the site declined by about 33 percent from 1965-66 to 1979-80. Emissions of  $\text{NO}_x$  and  $\text{SO}_x$  are generally consistent with these observations for wet sulfate and nitrate.... From 1964-77 there was no statistically significant trend in precipitation pH at the Hubbard Brook site."

Broadly distributed data for estimating a trend in sulfate deposition are not presently available. The basic problem in estimating trends is that neither a single year (1956-6: the Junge network), nor a single site (Hubbard Brook), can be expected to provide representative data for a period of years or for a broad area. A closer look at other local data may provide some further information. Future trends, at least, should be measured by the National Trends Network (NTN) of the National Acid Precipitation Assessment Program (NAPAP) and NADP network.

Polar and glacial studies until now have provided some evidence for transport of anthropogenic emissions to remote northern regions and provide some historical evidence for the variability of natural background deposition in those remote areas, but they do not provide clear information about global trends. [CARP A-8.5]

#### A.2.1.6 HOW IS DRY DEPOSITION OF ACIDIFYING SUBSTANCES MEASURED? [CARP A-8.3.2]

The settling and dry deposition of large particles ( $20\text{ }\mu\text{m}$  in diameter or larger) depends principally on gravity. Their dry-deposition rates are quite well measured by sampling buckets or other sampling surfaces. However, deposition from small particles and gases, which pretty much move with the rest of the atmosphere, is very difficult to measure unambiguously. Unfortunately, most dry deposition of sulfate and nitrate comes from small particles and gases. Field measurements of dry deposition of small particles and gases have been made by various techniques, such as comparing concentrations of the pollutant in air during updrafts with concentrations during

downdrafts, or by careful measurements of vertical differences in concentration. These techniques are, as yet, not suitable for long-term network use. Current estimates of dry deposition are made in a two-step process: (1) concentrations of the pollutant in question are measured or estimated; (2) a deposition velocity that depends on that pollutant and the surrounding surface characteristics is estimated based on field studies. The deposition rate is then given by the product,

deposition rate = concentration x deposition velocity.

#### A.2.1.7 WHAT CAN BE CONCLUDED ABOUT DRY DEPOSITION RATES FROM THE DATA AVAILABLE? [CARP A-8.3]

The major conclusion is that with present data the amount of acidifying material dry-deposited over a region can be only roughly estimated. Uncertainties of a factor or two or three are to be expected and uncertainties of an order of magnitude are quite possible.

The most important limitations for calculation of dry deposition are the following [CARP A-8.3.3]:

- No monitoring program in the United States reports air concentration of pollutants in a manner such that dry-deposition fluxes of acidic and acidifying pollutants can be readily evaluated, although several networks offering suitable information have operated for limited periods. Such networks are operating in Scandinavia and in Canada.
- Deposition velocities vary by at least two orders of magnitude depending on surface characteristics and vegetation, time of day, season, and meteorological conditions; deposition velocities representative of a broad region can, with the present field data, be only approximate.
- Concentrations of the important pollutants  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2$ , and  $\text{NO}_3^-$  at a particular location also vary substantially (up to an order of magnitude) with time of day, season, and meteorology. It is not likely to be true that (average deposition rate) = (average concentration) x (average deposition velocity). Instead, correlations between concentration and deposition velocities must be taken into account.

In spite of all the uncertainties and limitations cited above, a few further conclusions, based on information on atmospheric concentrations to be developed in the following subsection, are pertinent.

- Sulfate concentrations in rural eastern North America are somewhat lower than  $\text{SO}_2$  concentrations (Section A.2.2).  $\text{SO}_2$  deposition velocities are typically 2 to 10 times greater than sulfate deposition velocities (Section A.2.3). Hence, the bulk of sulfur dry deposition comes from the gaseous  $\text{SO}_2$ .

- ° Concentrations of  $\text{NO}_2$  are typically five times those for  $\text{NO}_3$  (including nitric acid), and  $\text{HNO}_3$  deposition velocities, though rapid, are not likely to exceed those for  $\text{NO}_2$  by a compensatory amount. Consequently, the bulk of nitrate deposition probably comes from  $\text{NO}_2$ .
- ° Based on typical deposition velocities ( $0.3$  to  $0.7 \text{ cm s}^{-1}$ ) and typical rural concentrations of  $\text{SO}_2$  ( $10$  to  $40 \mu\text{g m}^{-3}$ ), dry deposition of sulfur compounds is  $5$  to  $40 \text{ kg ha}^{-1}$ , or close to the amount of sulfur wet deposited in eastern North America. (Note the units: deposition here is measured in kg of sulfur).
- ° Similarly, the amounts of dry-deposited nitrates are close to the amounts wet deposited. A concentration of  $10 \mu\text{g m}^{-3}$  of  $\text{NO}_2$  and a deposition velocity of  $0.5 \text{ cm s}^{-1}$  would lead to an annual deposition rate of  $5 \text{ kg N ha}^{-1}$ . This number should only be treated as an order of magnitude estimate, however.

#### A.2.1.8 WHAT IS THE QUALITY OF THE DATA FOR WET AND DRY DEPOSITION? [CARP A-8.3]

Estimates of current annual amounts of wet-deposited sulfate or nitrate over a broad region in the eastern United States may be correct to within  $\pm 30$  percent. Estimates of the amount expected to be wet deposited in the West or in a small area of the East or over a short time period will be substantially less certain. Estimates of current annual amounts of sulfate or nitrate dry deposited are uncertain by at least a factor of two or three.

What are the most important sources of uncertainty? The answer depends on whether wet or dry deposition is at issue.

For the case of wet deposition we have observed that numerous problems with sampling, sample handling, and analysis cause significant problems in problems in comparing measurements from one network with those from another. The best remedies for these problems are formal quality assurance programs for each network and the establishment of overlapping sites for different networks. We have also noted that data from bulk sampling are difficult to interpret.

A second class of problems in interpreting wet-deposition data comes from the intrinsic variability in the data. Substantial variation occurs in annual deposition both from one year to another, and from one location to another, i.e., adjacent network sites whose locations may be as near as one or two hundred miles. To determine the representativeness of yearly data and to identify trends, significantly longer records from particular networks will be needed. To obtain more detailed spatial patterns and to obtain an annual deposition budget with higher confidence, better spatial resolution (more sites) will be needed. These, rather than the limitation in measurement techniques, appear to be the most significant deficiencies in wet-deposition measurements.

In contrast, for the case of dry-deposition, the present limitation is primarily the lack of data. Routinely collected network information on rural concentrations of the important acidifying species is the most urgent need. In addition to such a network, more measurements giving deposition velocities for a broader range of surfaces and meteorological conditions would be very useful.

#### A.2.2 WHAT ARE THE AMBIENT CONCENTRATIONS OF SUBSTANCES IMPORTANT IN ACID DEPOSITION? [CARP A-5]

##### A.2.2.1 HOW ARE CONCENTRATIONS MEASURED?

SO<sub>2</sub> concentrations have been measured routinely through the use of chemically-impregnated filters; short-term measurement can be made using a wide range of techniques including ultraviolet absorption, flame photometry, and laser techniques. It is important to note that many of the network SO<sub>2</sub> measurements have been near the limit of detectability for the sampling equipment used. [CARP A-5.2.2]

Sulfate concentrations have been measured through collection on filters, with or without sorting by size. There is some debate over the losses from various sampling means, and added amounts of sulfate detected are also possible from the conversion of SO<sub>2</sub> to sulfate on the filter. In the eastern United States, a large fraction of light scattering is due to sulfate particles, so light scattering and visibility measurements are potentially useful as indirect means of measuring sulfate concentrations and trends. [CARP A-5.2.3]

Nitrogen oxides include nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>). Nitric oxide is the principal oxide of nitrogen produced in combustion (see Section 2.7); however, it is fairly rapidly oxidized to NO<sub>2</sub> so that in urban areas NO represents 30 to 50 percent of gaseous nitrogen oxides, while in rural areas NO is 10 to 30 percent of the oxides. Independent measurements of NO and NO<sub>2</sub> are not usually made. Rather, NO<sub>2</sub> is reduced to NO, and NO is detected by chemiluminescence. Problems, particularly in measurements at low concentration, have arisen because of uncertainties in the amount of NO<sub>2</sub> that is converted to NO, and because other nitrogen compounds may also be converted. [CARP A-5.3.2]

The important nitrates found in the atmosphere include nitric acid (HNO<sub>3</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), and peroxyacetyl nitrates (PAN). Nitric acid is usually measured by continuous coulometry or by infrared spectrometry; both techniques are suitable only for short time periods. PAN is identified by electron-capture gas chromatography, another short-time technique. Nitrate particles are collected on filters, but serious problems both with losses and additions have been identified, so most reported particulate nitrate measurements are questionable, and only recent measurements using diffusion-denuder tubes appear reliable. [CARP A-5.3.6, A-5.3.8]

Ammonia (NH<sub>3</sub>) is the gaseous precursor of the ammonium cation (NH<sub>4</sub><sup>+</sup>). It has been measured in the atmosphere by various techniques that are best suited for short time periods. [CARP A-5.3.5]

Several oxidants are important to the conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  (see Section 2.5). These include ozone ( $\text{O}_3$ ), which is an important air pollutant in its own right, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and the short-lived OH radical. Most ozone measurements since 1970 have used a chemiluminescent ozone analyzer, a technique considered quite reliable. Hydrogen peroxide measurements have been made both in air and in rainwater, using a variety of techniques. One technique using chemiluminescent oxidation of luminol is suitable for continuous monitoring. However, questions have been raised about the validity of measurements of  $\text{H}_2\text{O}_2$  in air because of generation of  $\text{H}_2\text{O}_2$  in aqueous solution. The high variability of measurements in rainwater raises questions about how representative these values are of conditions in clouds or at cloud level. [CARP A-5.4, A-5.5]

#### A.2.2.2 WHAT COLLECTIONS OF DATA HAVE BEEN MADE?

The National Air Sampling Network was established in the 1950's, but  $\text{SO}_2$  was measured only after the early 1960's. This network is concentrated almost entirely in urban areas and has only six rural sampling areas. The Electric Power Research Institute's (EPRI) Sulfate Regional Experiment (SURE) provides the only presently available network data on nonurban  $\text{SO}_2$  and sulfate concentration in the eastern United States. It operated for five months between August 1977 and October 1978 with 54 stations in the eastern United States and continued through 1979 with 9 stations. In addition, various measurements of concentrations of the different substances have been made at one or several sites for relatively short periods; these comprise the remaining field information on concentrations in the eastern United States. The Air and Precipitation Monitoring Network (APN) in Canada has six rural sites measuring  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  east of Manitoba.

#### A.2.2.3 WHAT CONCENTRATIONS OF IMPORTANT SUBSTANCES HAVE BEEN OBSERVED? [CARP A-5.9]

Table III.3 summarizes the ranges of concentrations observed in rural areas by the measurements described in Section 2.2.1. The table distinguishes between eastern and western U.S. measurements and gives annual averages in the case of  $\text{SO}_2$  and sulfate, for which substantial amounts of data exist.

For sulfate and  $\text{SO}_2$  the SURE network provided sufficient information to indicate spatial patterns of concentration. These patterns are shown in Figure III.10. The patterns are, generally speaking, consistent with the wet deposition pattern of Figure III.4, with the highest concentrations in an oval running southwest to northeast, centered on a line from the Ohio valley to northern New York. The fall off with distance from the highest concentrations is steeper for  $\text{SO}_2$  than for sulfate.

The six rural stations of the NASN network (ME, NH, MD, VA, NY, IN) are insufficient to provide information on spatial distribution, but some comparisons and observations on seasonal dependence and trends are noteworthy [CARP A-5.9]:

- Sulfur dioxide concentrations have been high in urban areas but have decreased from the 1960's through the 1970's.

TABLE III.3. CONCENTRATIONS OF SULFUR, NITROGEN, AND CHLORINE COMPOUNDS AT RURAL SITES IN THE UNITED STATES IN THE 1970's<sup>†</sup>

Compound	Range of Average concentrations, $\mu\text{g m}^{-3}$	
	East	West
Sulfur dioxide	10-40 <sup>a</sup>	NA
Sulfur aerosols (as sulfate)	5-15 <sup>a</sup>	1-3 <sup>a</sup>
Nitrogen dioxide	5-20 <sup>b</sup>	$\leq 2^c$
Nitrate aerosols	1 <sup>c</sup>	NA
Nitric acid	0.3-3 <sup>c</sup>	$\leq 1^c$
Peroxyacyl nitrates	0.5-3 <sup>c</sup>	0.1-1 <sup>c</sup>
Ammonia	0.5-2 <sup>c</sup>	0.5-2 <sup>c</sup>
Hydrogen chloride	NA	1-10 <sup>c</sup>
Chloride aerosols		
Maritime	1-10 <sup>c</sup>	1-10 <sup>c</sup>
Inland	$\leq 1^c$	$\leq 1^c$
Ozone	40-200	40-200

<sup>a</sup>Annual average.

<sup>b</sup>Summer months: August to December averages.

<sup>c</sup>Limited number of measurements.

NA=Not available.

<sup>†</sup>Modified from CARP A-5, Table 5-13. Information from Tables 5-1, 5-2, 5-4, 5-6, 5-9, 5-13 and Section 5.4.1.

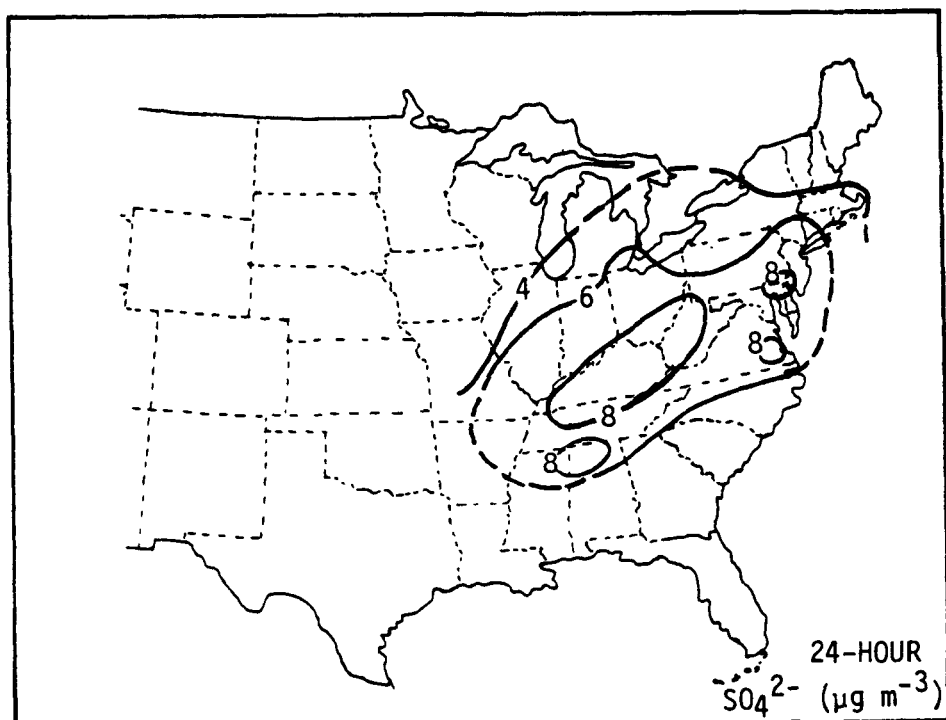
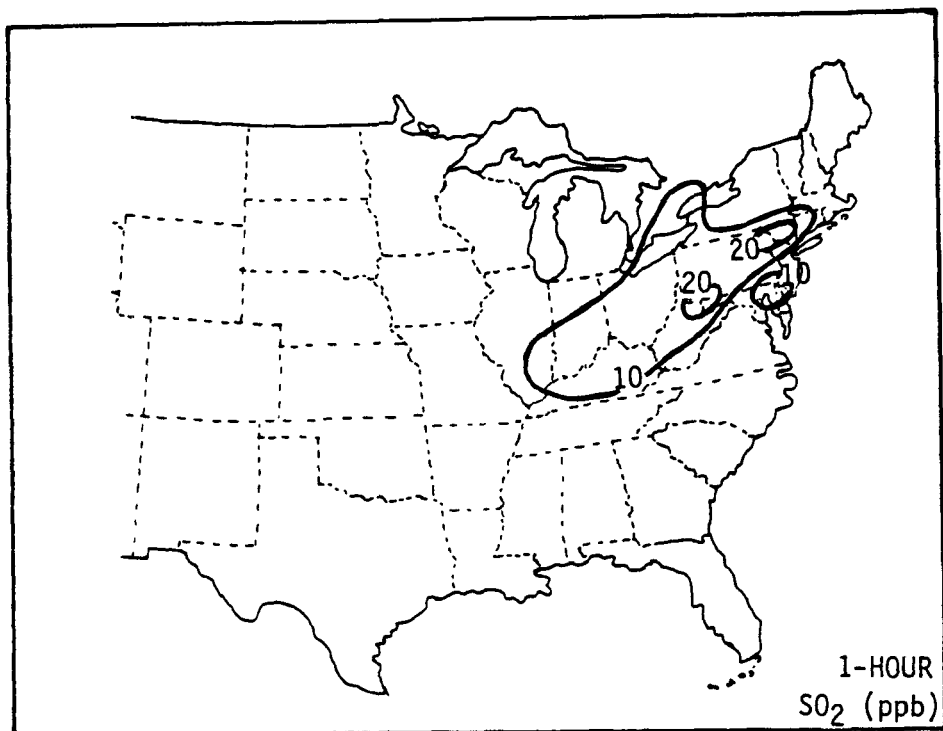


Figure III.10 Sulfur dioxide (arithmetic mean) and sulfate (geometric mean) concentrations. Data obtained during 5 months between August 1977 and July 1978. Adapted from Hilst et al. (1981). Note: 10 ppb SO<sub>2</sub> is approximately 28 µg m<sup>-3</sup> SO<sub>2</sub>. If this were all oxidized to SO<sub>4</sub><sup>2-</sup>, it would form approximately 37 µg m<sup>-3</sup> SO<sub>4</sub><sup>2-</sup>.

- Sulfur dioxide concentrations in rural areas have fallen very little since the 1960's. They are now approximately one-third the average urban levels.
- Sulfate concentrations in eastern urban areas have decreased except in the third quarter of the year.
- Sulfate concentrations as annual averages have not decreased in rural areas, and they have increased in summer months.
- Sulfate aerosols can contribute one-third to one-half the sulfur budget (sulfur dioxide plus sulfate) in rural areas in the summer, but a smaller portion in the winter.
- Sulfate aerosols occur predominantly in the small particle size range, with most of the mass concentrated in particles between 0.1 and 1  $\mu\text{m}$  in diameter.
- Sulfur dioxide and sulfate concentrations in eastern North American rural sites are a factor of 10 to 100 greater than concentrations measured in remote areas.

#### A.2.2.4 WHAT IS THE SPATIAL AND TEMPORAL VARIABILITY OF THE DATA? WHAT IS THE QUALITY OF THE DATA?

There is great variation over time in concentration measurements. Daily average values of  $\text{SO}_2$  and sulfate concentrations can vary over a factor of fifty (within the 5 to 95 percent frequency range) from one day to another [CARP A-5.2.3.3]. The variation from one year to another in yearly averages appears to be 30 to 60 percent from the NASN network. Much of this variation appears statistical; however, strong seasonal effects can be observed also. Rural sulfate concentrations appear greater in the summer than in the winter by up to a factor of 3 or 4 [CARP A-5.2.3.2], while  $\text{SO}_2$  concentrations are greater in the winter than in the summer by similar factors [CARP A-5.2.2.2]. There is limited evidence that winter rural concentrations of  $\text{NO}_2$  are greater than summer values [CARP A-5.3.2.4]. It is likely that substantial variation of average concentration occurs from one rural site to another over distances of a few hundred miles or less occurs. Even more than with wet deposition network data, the limitation on the use of existing concentration data for  $\text{SO}_2$ , sulfate,  $\text{NO}_2$ , and nitrate is the absence of any reasonably dense network operations over an extended time.

Certain concentration measurements have specific problems. Until recently, nitrate measurements have been questionable. Debate about the interpretation of hydrogen peroxide measurements continues.

#### A.2.3 WHAT IS KNOWN ABOUT DRY DEPOSITION PROCESSES? [CARP A-7]

##### A.2.3.1 WHAT ARE THE IMPORTANT MECHANISMS IN DRY DEPOSITION? [CARP A-7.2]

Large particles (of radius greater than 10  $\mu\text{m}$ ) settle out of the atmosphere. Typical settling velocities (which depend on the density and



shape of the particle) are  $1.0 \text{ cm s}^{-1}$  for a  $10 \text{ }\mu\text{m}$  spherical particle of density  $1 \text{ g cm}^{-3}$  and  $40 \text{ cm s}^{-1}$  for a  $50 \text{ }\mu\text{m}$  particle. Because these settling velocities are much smaller than the vertical velocities of turbulent wind fluctuations, the particles will follow a complex path; however, on the average the net flow out of the atmosphere will be given by the settling velocity, and the deposition rate will be given by

$$\text{deposition rate} = \text{concentration} \times \text{settling velocity}.$$

In the case of trace gases and small particles for which the settling velocity becomes very small ( $0.01 \text{ cm s}^{-1}$  for a  $1 \text{ }\mu\text{m}$  particle), two kinds of processes are important in dry deposition. One kind of processes involves the effectiveness of the surface together with the layer of air immediately adjacent to the surface in capturing the material. The second kind is the mixing of air that has been depleted of material (from its contact with the surface) with less depleted air farther up; this mixing replenishes the supply of material near the surface. In an analogy with the case of settling particles, we can still summarize these complicated processes by defining a deposition velocity such that

$$\text{deposition rate} = \text{deposition velocity} \times \text{concentration}.$$

One other dry-deposition process, deposition by fog and cloud nuclei, must be mentioned. This might be thought of as wet deposition because the processes, formation of water droplets, and reaction of acidifying materials are determined by water droplet properties similar to rain. However, the motion and capture of fine water droplets is analogous to dry deposition, and networks do not generally collect and measure such deposits. Such deposits occasionally contribute significantly to total deposition, especially in high-elevation forests.

#### A.2.3.2 HOW DO DRY DEPOSITION RATES DEPEND ON SUBSTANCE, AMBIENT CONCENTRATION, METEOROLOGICAL CONDITIONS, AND SURFACE CHARACTERISTICS? [CARP A-7.2]

There are two ways in which deposition rates depend on substance [CARP A-7.2]. One is the aerodynamic properties of the material; the second is its chemical and physical interaction with the surface. We have already noted that large particles fall faster than small ones or gases. We will discuss the substance/surface interaction when we discuss types of surfaces.

The dependence on concentration is generally linear. Deposition rates usually are proportional to the concentration of material in the air; that is the justification for defining a deposition velocity.

The dependence on meteorology is at least threefold. Atmospheric turbulence increases mixing and helps replenish material near the surface. This turbulence is greatest in sunny weather, thus making summer months and daytime of greater importance. Finally, the amount of water vapor can also strongly affect dry deposition rates. Moisture, such as from rain or dew, on surfaces may increase the deposition velocity, especially for  $\text{SO}_2$  which is highly soluble, and deposition by fog can be important in its own right.

Surface characteristics can affect adjacent air and also the likelihood of capture [CARP A-7.5]. In general, increased surface roughness increases deposition. For SO<sub>2</sub> gas, uptake by plants is largely by stomata during the daytime, with about 25 percent direct collection on leaf surfaces. At night, uptake through the stomata will decrease substantially (as the stomata close) while leaf surface deposition will be unaltered. The gas NO<sub>2</sub> is slightly less easily taken up by plants and is less soluble in water; however, nitric acid is very soluble and has a high affinity for moist surfaces. For most surfaces, HNO<sub>3</sub> has the highest deposition velocity; SO<sub>2</sub> has significantly lower deposition velocity; NO<sub>2</sub> appears to be similar<sup>2</sup> to SO<sub>2</sub> with a slightly smaller deposition velocity, the effective rate of deposition may be even smaller if some deposition occurs through oxidation of the surface and re-emission of NO. Small particles, sulfates, and nitrates other than HNO<sub>3</sub> are not as reactive as the gases and are taken up more slowly by vegetation.

#### A.2.3.3 WHAT ARE TYPICAL DEPOSITION VELOCITIES? [CARP A-7.4]

Deposition velocities from a large number of laboratory and field studies are summarized in Table III.4. The numbers in the table should be taken as representative only. Where ranges are given, they correspond to an unscientific selection of more than one measurement; equivalent uncertainties are to be expected even when no range is given. Noteworthy in Table III.4 are the following: SO<sub>2</sub> deposition tends to be more rapid than deposition of sulfate or nitrate particles; deposition velocities vary greatly from day to night, partly due to more rapid atmospheric mixing in daytime and, equally or more important, changes in foliage characteristics. For these reasons substantial seasonal variation in deposition velocities is likely, with winter deposition much slower on the average than summer. A great deal of variability occurs from surface to surface. A great deal of residual variability occurs, so deposition velocities for a particular type of surface are not well determined. Taken together, these uncertainties probably amount to well over a factor of two, so present day science only provides deposition velocities to within an order of magnitude.

#### A.2.4 WHAT IS KNOWN ABOUT WET DEPOSITION PROCESSES? [CARP A-6]

##### A.2.4.1 WHAT ARE THE IMPORTANT MECHANISMS IN WET DEPOSITION? [CARP A-6-2]

In a very general sense pollutant material may participate in four major events prior to its wet removal from the atmosphere. These events are shown in Figure III.11.

- 1-2 The pollutant and the condensed atmospheric water (cloud, rain, snow) must intermix.
- 2-3 The pollutant must attach to the condensed water elements.
- 3-4 The pollutant may react physically and/or chemically within the aqueous phase.

TABLE III.4. SUMMARY OF TYPICAL FIELD AND LABORATORY MEASUREMENTS OF  
DEPOSITION VELOCITIES (cm s<sup>-1</sup>)<sup>a</sup>

Substance	Surface	Deposition velocity (day)	Deposition velocity (night)	Deposition velocity (24-hr ave)
SO <sub>2</sub>	soil	0.5-1.0	0.3-0.5	
	grass	1.0-1.3	0.3-0.7	
	wheat			0.4-0.7
	soybean			1.3
	pinus			0.1-0.6
	snow	0.1-1.0		
NO <sub>2</sub>	soybean	0.6	0.06	
Small particles	soil			small
	grass	0.3-0.7		
	grain	0.4-0.8		0.2
	pinus			0.7
	deciduous forest (winter)			0
	snow			0.1-0.2

<sup>a</sup>From CARP A-7, Tables 7-5 and 7-6.

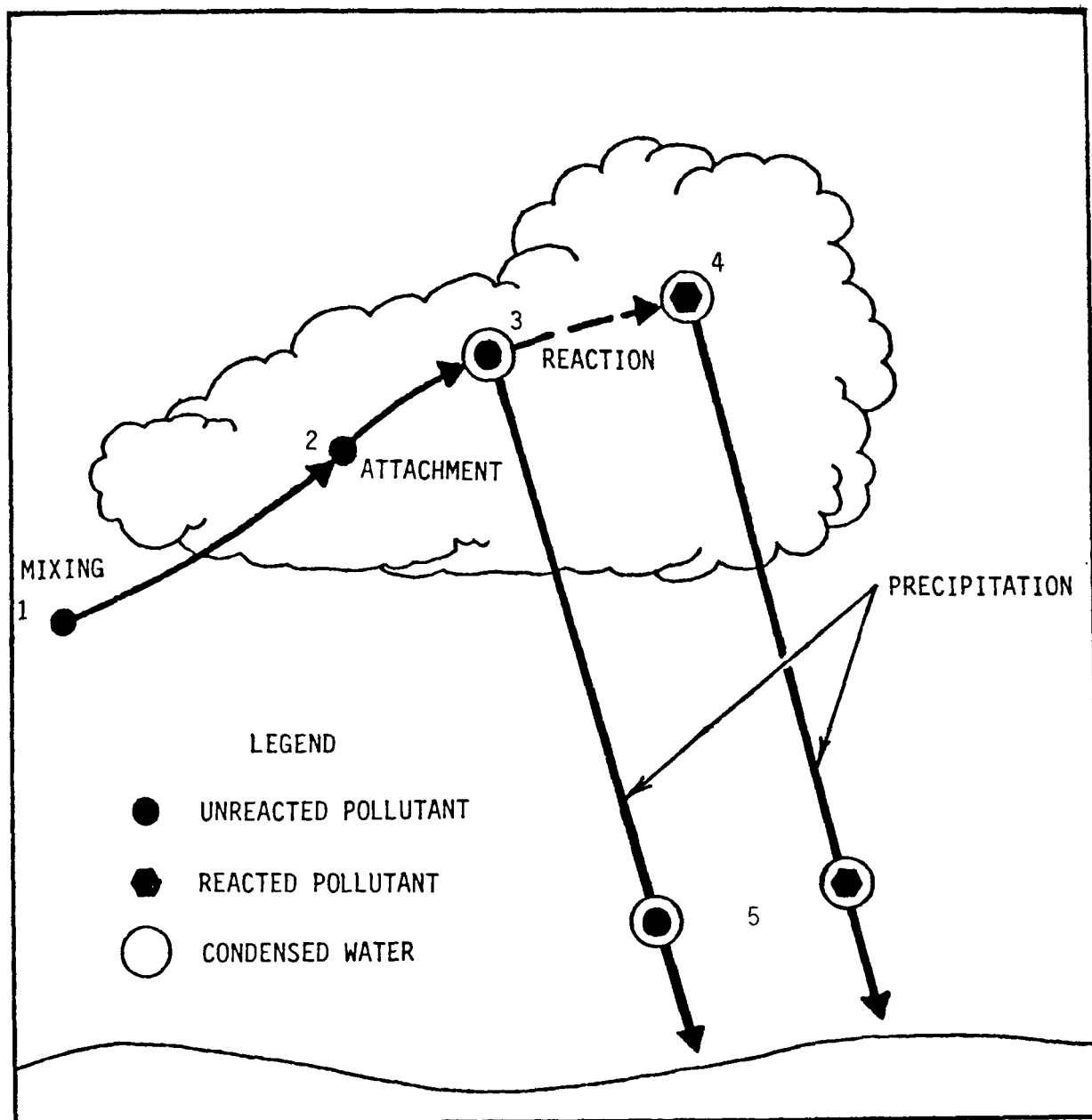


Figure III.11 Steps in the scavenging sequence: Pictorial representation.

3-5 or 4-5 The pollutant-laden water elements must be delivered to the Earth's surface as precipitation.

It is important to note that although Figure III.11 proceeds forward to deposition, with the exception of precipitation, the processes are reversible. The water droplet the pollutant has attached itself to may evaporate, for instance. So a particular pollutant molecule may experience numerous cycles before being deposited.

Another noteworthy feature is that precipitation scavenging of pollutant materials from the atmosphere is intimately linked with the precipitation scavenging of water. If we replace the word "pollutant" with "water vapor" all steps (except 3-4) provide a general description of the precipitation process. In view of this intimate relationship, it is not surprising that pollutant wet-removal behavior tends to mimic that of precipitation. Pollutant scavenging efficiencies of storms are often similar to water extraction efficiencies, a relationship useful in practically estimating scavenging rates.

#### A.2.4.2 HOW DOES WET DEPOSITION DEPEND ON SUBSTANCE, AMBIENT CONCENTRATION, AMOUNT OF RAINFALL, AND STORM TYPE? [CARP A-6.5]

It is convenient to characterize wet deposition by a few key parameters. Figure III.12 provides assistance in doing this by illustrating the material balances for water and pollutant entering and leaving a storm. We can define certain efficiencies of scavenging:

Efficiency for water removal  $\epsilon_p = W/W_{in} = \text{precipitation out/water vapor in}$

Efficiency for pollutant removal  $\epsilon = F/F_{in} = \text{scavenged pollutant/pollutant in}$ . We can further define a scavenging ratio

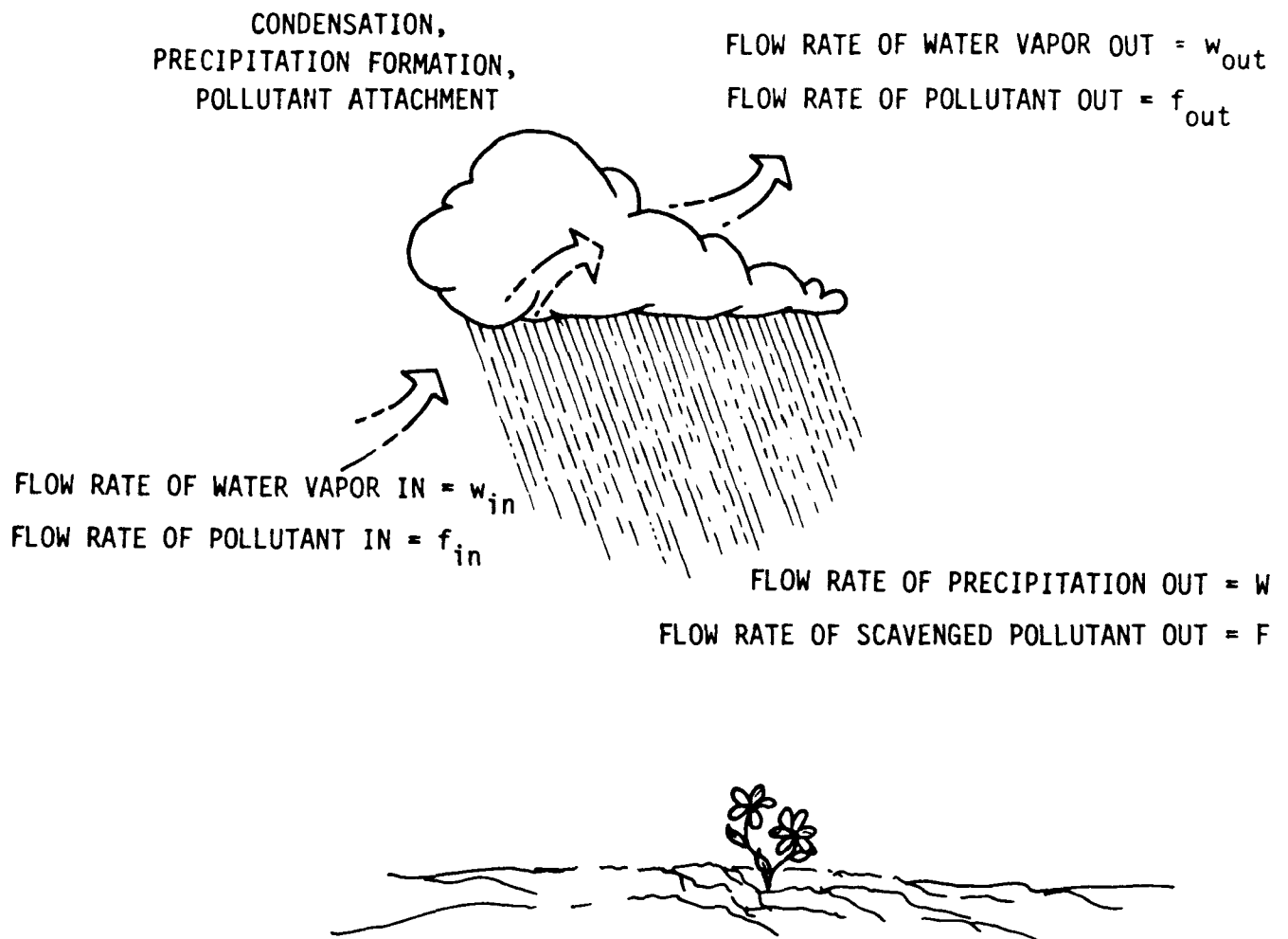
$$\xi = \frac{\text{concentration of scavenged pollutant in rainwater}}{\text{concentration of pollutant in air}}$$

If water extraction and pollutant scavenging occurred with equal efficiency then the scavenging ratio,  $\xi$ , would be

$$\xi = \frac{\text{density of water}}{\text{concentration of water vapor in air}} \approx 10^5\text{--}10^6.$$

Experimental measurements often give scavenging ratios in this range, though wide variation is found. Scavenging appears to be more effective within the cloud than below it.

What accounts for the variability? The substance scavenged is important.  $\text{SO}_2$  and  $\text{NO}_2$  are apparently less efficiently scavenged than sulfate and nitrate. The concentration of  $\text{SO}_2$  affects the scavenging efficiency; lower concentration favors scavenging, since aqueous phase reactions are important in preventing loss of  $\text{SO}_2$  from droplets, and the amount of  $\text{SO}_2$  that reacts is limited by the availability of oxidant.



#### DEFINITIONS OF EFFICIENCIES:

WATER REMOVAL

$$\epsilon_p = W/w_{in}$$

POLLUTANT REMOVAL

$$\epsilon = F/f_{in}$$

Figure III.12 Schematic of a typical macroscopic material balance.

The nature of the storm affects the scavenging efficiency considerably. A decrease in the rate of precipitation over an order of magnitude increases the scavenging ratio an order of magnitude or less depending on storm type. This suggests that often a storm may extract almost all of the accompanying pollutant. Convective storms tend to be efficient scavengers; they also inject some material into the free troposphere, where it loses contact with normal deposition mechanisms. Warm front storms can be expected to be effective scavengers of pollution originating from within the warm air mass. Scavenging of pollutants from the underlying cold air mass will take place below cloud level where scavenging is usually less effective.

#### A.2.4.3 WHAT FRACTION OF THE AMBIENT POLLUTION IS WET DEPOSITED? [CARP A-6.3]

One other parameter characterizes precipitation scavenging--the scavenging coefficient which tells how rapidly the pollutant is depleted. A scavenging coefficient of ( $1 \text{ hr}^{-1}$ ) means that in an hour the concentration will have fallen to  $1/e$  or roughly 37 percent of its initial value. Scavenging coefficients typically range between ( $1 \text{ hr}^{-1}$ ) and ( $0.1 \text{ hr}^{-1}$ ). Hence, a storm of long duration can remove most of the pollution within it.

The other important determinant of whether a pollutant will be wet deposited is how likely it is to encounter a storm system. In the Northeast for instance, precipitation is occurring roughly 10 percent of the time both in winter and in summer, but the characteristics of the storms are very different. In winter, fewer storms occur but they are of significantly longer duration. Hence, the pollutant is more likely to spend several days without encountering precipitation in winter than in summer.

#### A.2.4.4 WHAT IS THE SPATIAL AND TEMPORAL VARIABILITY OF WET DEPOSITION RATES? [CARP A-6.3]

Unlike dry deposition which, at a single location, is a continuous process, most of the material wet deposited is deposited in comparatively few events. Statistically this means that fluctuations are likely to be significant compared to average amounts. This is particularly true because of the dynamics of storm systems. Within an individual storm in the amount of material scavenged and deposited varies enormously, so places a short distance apart can experience large differences in the amount deposited; it should be noted that the characteristic spatial scale over which this variability exists is much smaller than the separation of wet deposition network stations.

Patterns of storm systems introduce their own spatial and temporal variability [CARP A-6.3.5]. Figure III.13 shows average storm tracks for low pressure (cyclonic) centers across the United States. These are long-term composite averages: there is marked seasonal variability; the pattern from one year to another may be substantially different; there is good evidence that long-term trends shift these patterns; finally, the flow processes within a storm mean that the paths feeding pollutants into the storm are not the same as the trajectory of the cyclonic center. Despite these complexities, from Figure III.13 we can conclude that important precipitation

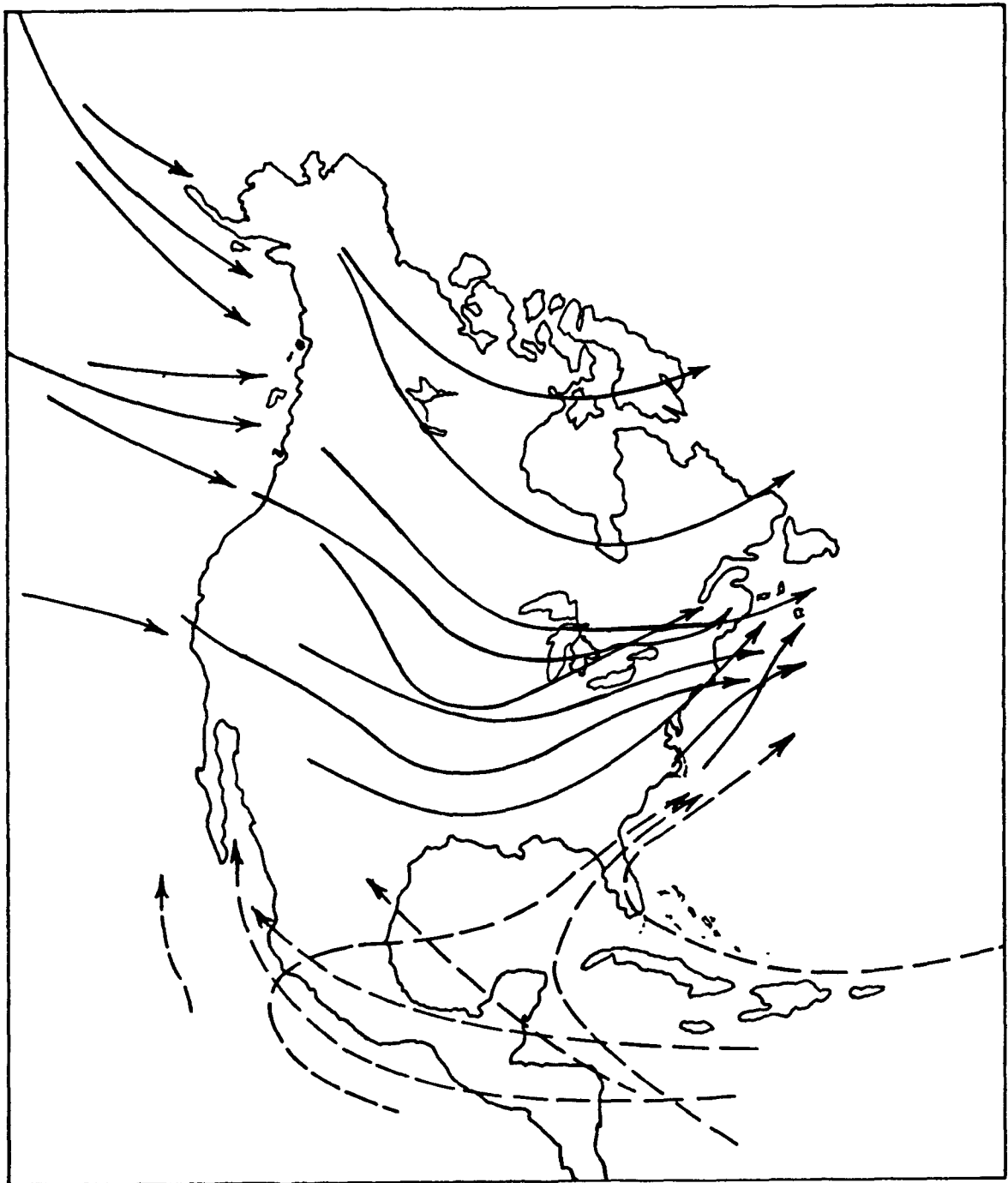


Figure III.13 Major climatological storm tracks for the North American continent. Adapted from Haurwitz and Austin (1944). Dashed lines denote tropical cyclone centers, and solid lines denote those of extratropical cyclones.



events have spatial structure and flow patterns that will not be properly accounted for if only average wind flow patterns without regard to precipitation are used in modeling or other data interpretation. The fluctuations also imply that data over substantial periods (years) are needed to discover representative wet deposition loadings.

#### A.2.4.5 WHAT GENERALIZATIONS ARE POSSIBLE FOR AMOUNTS WET DEPOSITED BY SEASON OR REGION? [CARP A-6.2, A-6.3]

The close connection of the precipitation scavenging of pollutant with the precipitation scavenging of water means that, as a very rough approximation, amounts wet deposited in a region will be proportional to average rainfall and to the average concentration of pollutant present. This rule of thumb is consistent with the wet-deposition network results and the very limited data on concentrations. Thus, the eastern United States, with both high concentration and high rainfall, receives much more acidifying material than the western United States. Figure III.14, long-term monthly average rainfall statistics by weather station, shows the substantial variation of rainfall by season and region.

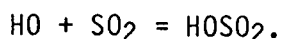
#### A.2.5 WHAT IS KNOWN ABOUT CHEMICAL CHANGES OF ACIDIFYING SUBSTANCES IN THE ATMOSPHERE? [CARP A-4]

The chemical changes of concern are (1) those in which  $\text{SO}_2$  is oxidized to sulfate, including sulfuric acid: we have already observed that the chemical/physical form of  $\text{SO}_2$  gas compared with  $\text{SO}_4$  aerosol strongly affects both wet and dry deposition rates; (2) those in which  $\text{NO}$  is oxidized to  $\text{NO}_2$  and  $\text{NO}_2$  is oxidized to nitrate, especially nitric acid, and (3) those in which sulfuric acid or nitric acid is made into a neutral salt. The first two of these chemical changes can take place either while the  $\text{SO}_2$  or  $\text{NO}_2$  is a gas (gas-phase reaction) or after scavenging into water droplets (aqueous reaction). The third takes place only in water. These possibilities and the important reacting substances are illustrated in Figure III.15.

##### A.2.5.1 WHAT ARE THE IMPORTANT PROCESSES LEADING TO $\text{SO}_2$ OXIDATION? [CARP A-4.2, 4.3.5]

Both gas-phase and aqueous-phase reactions are important to the production of sulfate. In addition reactions on the surfaces of airborne particulates may contribute significantly in special circumstances. In much of the West where water droplets are less frequent, it is likely that gas-phase transformations are most important; in much of the East it is likely that aqueous-phase reactions dominate, though gas-phase transformations may be as important or more important in the summer.

The most important initiating reaction for gas-phase  $\text{SO}_2$  oxidation is with the  $\text{HO}$  radical:



The  $\text{HOSO}_2$  then is converted to sulfuric acid,  $\text{H}_2\text{SO}_4$ , via an as yet uncertain chain of reactions. An important characteristic of the  $\text{HO}$  radical

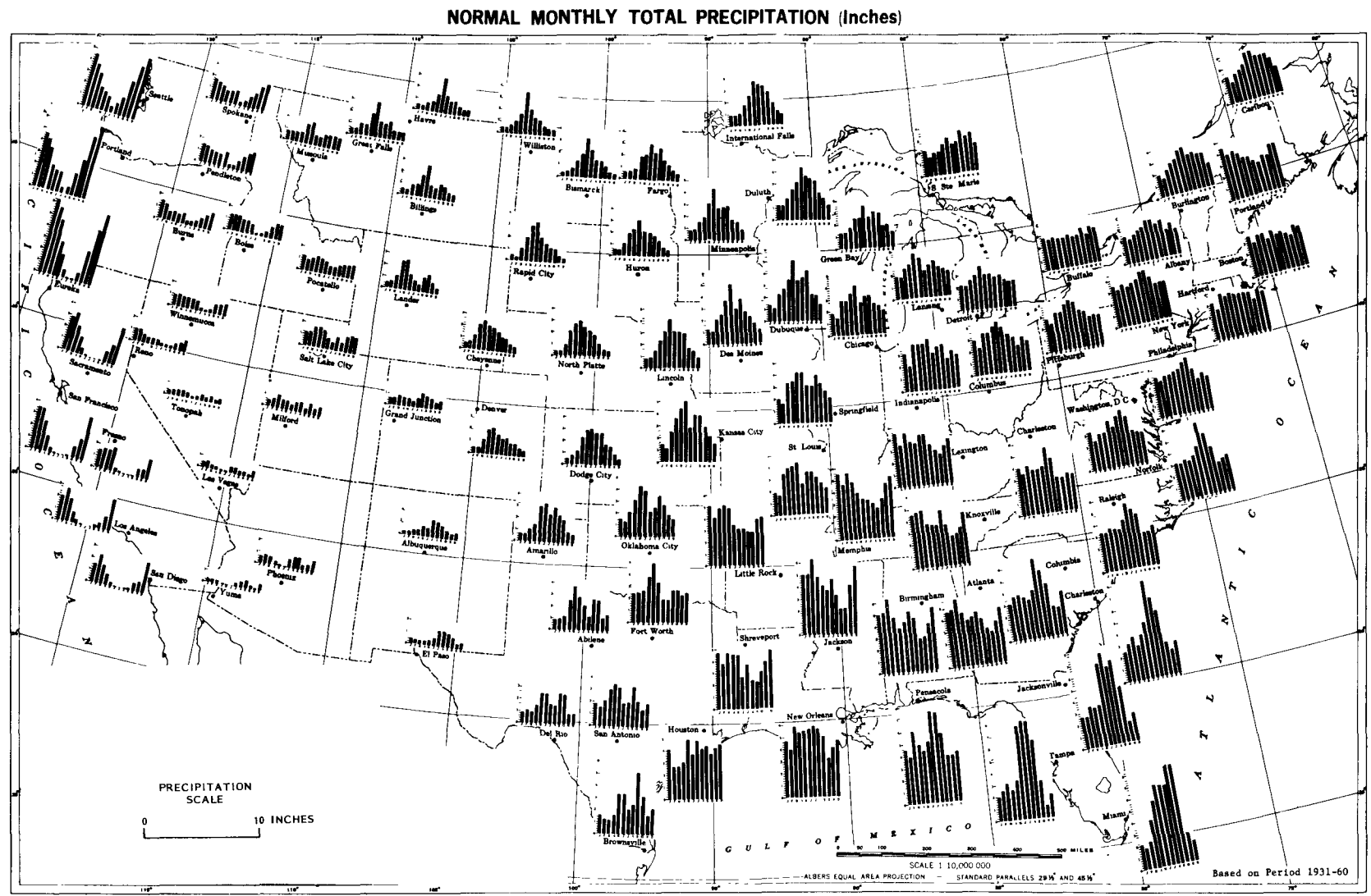


Figure III.14 Climatological Summary of U.S. Precipitation. From U.S. Climatological Atlas (1968).

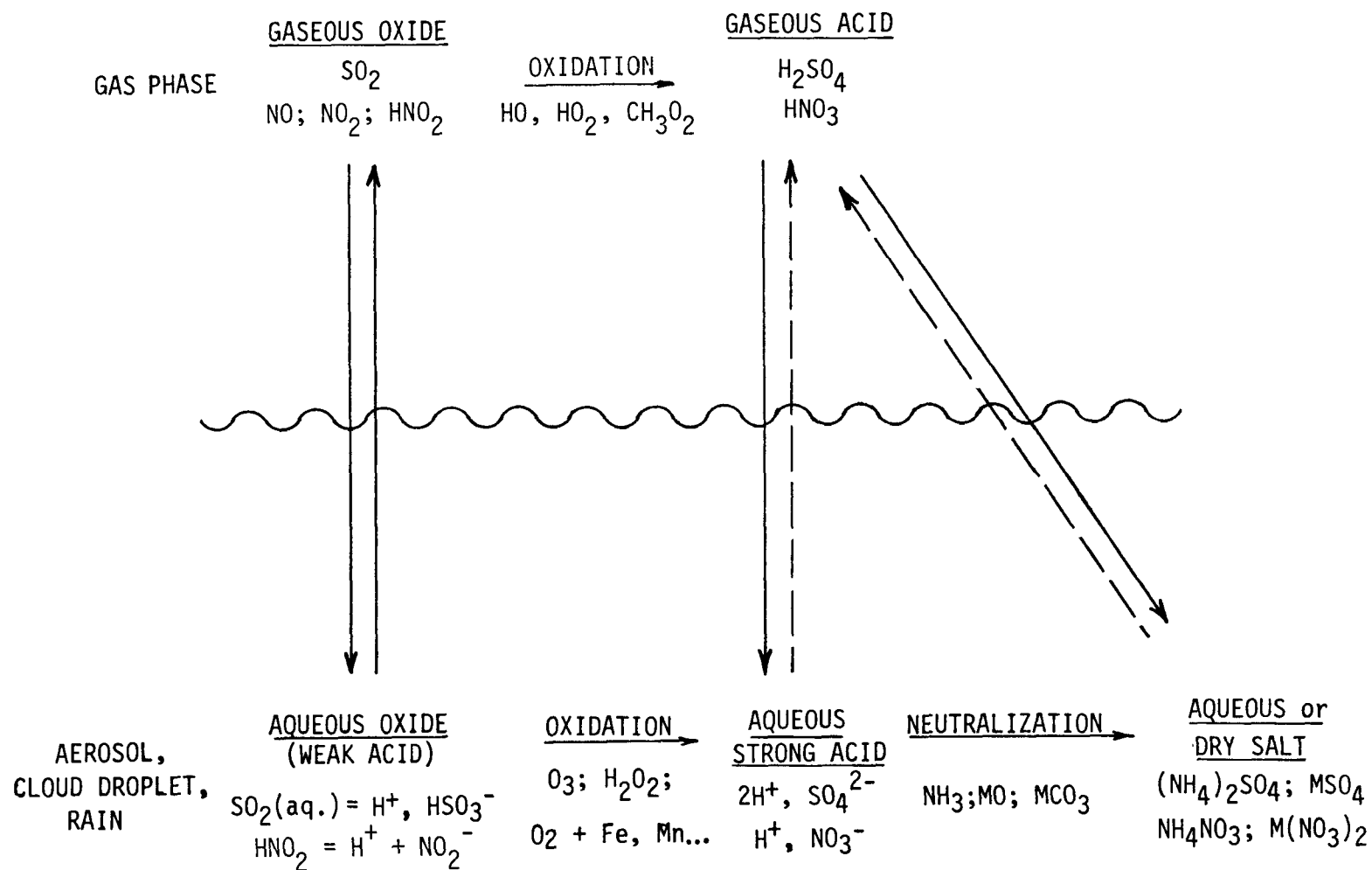


Figure III.15 Schematic representation of pathways for atmospheric formation of sulfate and nitrate. Adapted from Schwartz (1982).

is that its concentration appears to be principally determined by other photochemical reactions, including those involving nitrogen oxides. Its concentrations do not appear sensitive to pollutant, and reactions with  $\text{SO}_2$  at normal atmospheric concentrations are not likely to deplete the  $\text{HO}$ .

The initiating reactions for  $\text{SO}_2$  oxidation in water depend on the concentrations of the substances present. Most important in the more polluted air of the eastern United States is reaction with hydrogen peroxide,  $\text{H}_2\text{O}_2$ . The conversion rate, determined by both hydrogen ion and gas solubility, is independent of pH, unlike reactions with dissolved ozone ( $\text{O}_3$ ) or dissolved oxygen ( $\text{O}_2$ ) in the presence of metallic catalysts. For "polluted" clouds with low pH,  $\text{H}_2\text{O}_2$  reactions will dominate. However, at higher pHs, reaction with ozone or catalyzed reaction with oxygen can be more important. The relative importance of the various reactions depends on the concentration of  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  or metals as well as pH; as we noted in Section A.2.2, little is known about  $\text{H}_2\text{O}_2$  concentration in clouds. At plausibly estimated concentrations for urban polluted air, the  $\text{H}_2\text{O}_2$  reaction will produce acid quite quickly, and since the reactions are not pH limited (above pH 1.8), only acid neutralization prevents pHs from dropping to values lower than are typically seen.

A.2.5.2 WHAT ARE TYPICAL RATES OF OXIDATION: HOW DO THEY DEPEND ON TIME OF DAY, SEASONS,  $\text{SO}_2$  CONCENTRATION, CONCENTRATION OF OXIDANTS, METEOROLOGICAL CONDITIONS? [CARP A-4.4.4, 4.4.5]

$\text{SO}_2$  oxidation rates measured in urban and power plant plumes range from 0 to 30 percent  $\text{hr}^{-1}$ . Average daytime conversion rates seem to lie between 3 to 5 percent  $\text{hr}^{-1}$ , while there is evidence suggesting that winter and nighttime conversion rates are less than 1 percent  $\text{hr}^{-1}$ . Most of these studies, particularly the power plant plume studies, are probably weighted toward gas-phase oxidation. Observed liquid-phase oxidation rates range from 0 to 100 percent per hour and depend on the extent of pollutant contact with water vapor as well as on chemical reaction rates. The somewhat high oxidation rates observed in urban plumes suggest that, as expected, higher concentrations of oxidants or possibly catalysts in the urban polluted air produce increased oxidation rates. The wide scatter in the data, however, with the limited measurements of oxidant, has not given clear results. Atmospheric mixing rates and the amounts of water vapor are certainly important as well, but we lack quantitative verification of their role.

A.2.5.3 WHAT IS KNOWN ABOUT OXIDATION OF NITROGEN COMPOUNDS? [CARP A-4.2, 4.3.4]

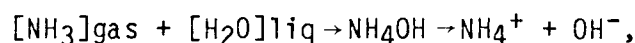
The atmospheric chemical cycles for nitrogen oxides, which involve more species, are both more complicated and less well studied than those for sulfur oxides. Probably the reaction of  $\text{NO}_2$  with the hydroxyl radical,  $\text{HO}$ , is most important, and, in contrast with  $\text{SO}_2$ , aqueous-phase reactions are essentially unimportant.  $\text{NO}_2$  to nitrate conversion rates are 3 to 10 times the rates for gas-phase  $\text{SO}_2$  oxidation; they also peak at midday and in the summer. A significant fraction of  $\text{NO}_2$  is converted to  $\text{N}_2\text{O}_5$  and to peroxyacetyl nitrate (PAN). Little is known about the ultimate fate of these compounds.

#### A.2.5.4 WHAT IS KNOWN ABOUT NEUTRALIZATION OF ACIDIFYING MATERIALS? [CARP A-4.3.6]

Neutralization can take place before or after deposition. Furthermore, neutralization need not be permanent. For instance, as discussed in Section II.A.2.1.3, the biological oxidation of ammonium ions generates acidity, so deposition of neutral salts such as ammonium sulfate and ammonium nitrate may lead to acidification in ecosystems.

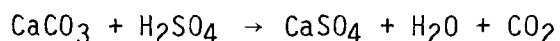
Probably the most important neutralization process in the atmosphere is the absorption (or hydration) of ammonia ( $\text{NH}_3$ ) by acid aerosols and hydrometeors (cloud drops and rain). The preeminence of this process is because  $\text{NH}_3$  is the only basic gas of wide-spread common occurrence in the atmosphere.

The hydration and dissociation of  $\text{NH}_3$ ,



occurs very rapidly, much more rapidly than any of the oxidizing reactions. For that reason it is possible to calculate the neutralizing capability of ammonia as a simple function of its concentration.

The widespread occurrence of calcium cations in water has led to suggestions that calcium carbonate and dolomite from soils and perhaps even calcium oxide from fly ash play a role in neutralizing sulfuric acid. The prototypic reaction is



and since hydrogen ion is lost from the system, the substitution is neutralizing. The interesting point about these minerals is that they have low solubility in neutral water, while the solubility increases with acidity. Thus, as they dissolve they act as buffers. The amount of material available for such buffering is highly variable.

#### A.2.6 WHAT IS KNOWN ABOUT ATMOSPHERIC TRANSPORT? [CARP A-3]

##### A.2.6.1 WHAT ARE THE IMPORTANT MECHANISMS IN TRANSPORT? [CARP A-3.2, A-3.3]

Four meteorological variables are particularly significant in the transport and dispersion of air pollution: the mixing height below which air and pollutants mix freely, and the wind, temperature, and moisture within this layer. The Earth's atmosphere is about 100 km deep. Most anthropogenic pollutants are confined and transported within the daily maximum mixing height of the atmosphere, typically 2 km in summer and somewhat lower in winter. The layer below the mixing height is called the planetary boundary layer. The wind within this layer is driven by the flow of air above it combined with the influence of the surface below. The result is complex patterns of flow which depend on time, on location, and on the height above the surface. The dispersion of pollutants results from the spatial and temporal inhomogeneities of the winds. The dispersive capacity is strongly

influenced by temperature distribution, particularly the variation of air temperature with height, which in turn depends on the amount of solar radiation and the nature of ground surface. Upward vertical motions in the planetary boundary layer enable moisture, transported from upwind as well as local evaporation of surface water, to condense to form clouds and precipitation.

Meteorological behavior has different characteristics depending on the spatial scale over which it is evaluated. Typically the scales are classified as micro, meso, synoptic, and global. The meteorological microscale is set by a typical maximum mixing height. This distance is 1 to 2 km; a typical time associated with such distances is 10 minutes (the approximate time it takes for a plume to spread over that vertical distance). The important microscale phenomena include convection--vertical air motion driven by differences in temperature and, linked to convection, turbulence--random fluctuations of the wind speed and direction. These are responsible for mixing.

The meteorological mesoscale extends out to about 500 km, and the associated time is about a day, the approximate time needed for mean transport over that distance. Mesoscale transport is affected by the daily variation in mixing height and by the vertical variation of the wind below it. It is also strongly influenced by surface terrain, by heat, and by moisture fluxes. Within the range of the mesoscale a plume from a power plant or an urban area will lose its identity by mixing with other plumes and by diluting into the background. Transport over microscale and mesoscale distances is commonly referred to as short and intermediate range transport, respectively.

Beyond the mesoscale is the synoptic scale, the scale of weather maps, characterized by horizontal dimensions of 1000 to 2000 km; the associated transport times are 1 to 5 days. Characteristic of the synoptic scale are major weather patterns. Beyond the synoptic scale is the global scale (or better, hemispheric scale) that includes trans-hemispheric as well as inter-continental transport.

The height of the mixing layer changes continuously; it grows during the daytime, typically to heights of 1 to 2 km, due to thermal convection, and subsides at night to heights ranging from zero to a few hundred meters. When the mixing height subsides at night, the pollutant that was mixed through the daytime mixing layer does not subside with it; it is transported by a wind field that has lost contact with the ground and is characterized by much less turbulent mixing. We can thus define a transport layer for any day as the layer between the surface and the peak mixing height of that day. When the mixing height is low, emissions from tall stacks will produce a plume in the transport layer above the mixing height (the effective height of release of a power plant plume is significantly above the top of the stack because of the buoyancy of the plume). The plume can then spend a substantial fraction of a day decoupled from the ground. This situation is illustrated in Figure III.16 [CARP A-3.4]. On this occasion there was considerable cloud formation (and presumably aqueous-phase chemical reactions). Note at the far right of this figure the subsiding of the mixing layer, with SO<sub>2</sub> distributed more or less uniformly through the transport layer.

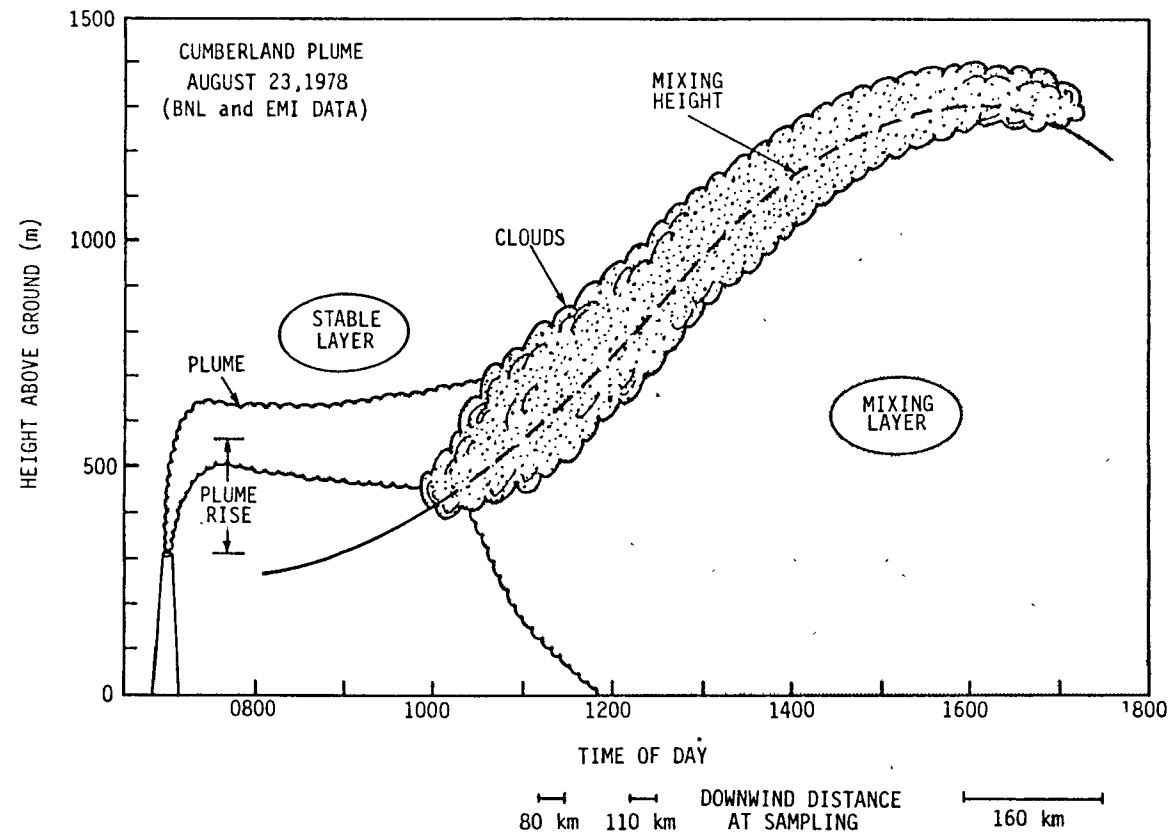


Figure III.16 The physical behavior of a tall-stack plume on a rather typical summer day. The plume shown is the reconstruction of the Lagrangian transport of the 0700 release on 23 August 1978 from the 305 m tall stacks of the 2600 MWe Cumberland Stream Plant in northwestern Tennessee. The reconstruction is based on aircraft sampling, ground-based lidar returns, and tetron transport data (Gillani and Wilson 1983).

Much of the complexity of atmospheric transport arises because the wind speed and direction vary with height through the transport layer; the variation depends on mixing height, since the air that is above the mixing height is no longer subject to the same frictional drag caused by the surface. An illustration of this, Figure III.17, shows the average variation of wind direction with height for day and night and winter and summer at a single location. Wind speeds also show a comparable variation in magnitude. In the summer situation, after the sharp shear of wind direction in the first 50 m, which affects only a small fraction of the pollutant transported, the daytime wind direction is relatively constant. Nighttime winds, however, continue to vary in direction with height; this means that material at different heights can be widely separated after a night's transport. This separation, with the mixing that takes place during the next day, accounts for most of the dispersal of pollutants for mesoscale and farther distances.

Other meteorological complexities can also be important in transport. Two examples follow:

Special types of weather patterns. Certain weather conditions are especially important to deposition patterns. We noted in Section A.2.4 that storm systems have characteristic wind patterns (see Figure III.13). It is probably appropriate to separate wind field data for precipitating and non-precipitating conditions, because the use of average wind data based mostly on non-precipitating conditions could give an unrealistic picture of transport leading to wet deposition. Another special set of conditions is stagnation in which high concentrations of acidifying substances can build up over a broad region. Figure III.18 shows the distribution of frequency of such conditions. They too might merit special treatment. A third example is highly convective air motion, as takes place in thunderstorms. Such motion may vent significant amounts of acidifying substances above the planetary boundary layer, where they can spend a long time decoupled from the ground.

Shorelines and complex terrains. The special temperature and moisture patterns produced at a shoreline can strongly affect wind motion and precipitation patterns, both on a local scale and for large-scale weather systems.

Urban areas can provide local elevation of the mixing height at night as a result of the heat island effect. Hills and mountains can also alter local and mesoscale flow.

#### A.2.6.2 WHAT METEOROLOGICAL INFORMATION IS NEEDED TO CHARACTERIZE TRANSPORT OVER VARIOUS SPATIAL/TEMPORAL SCALES? [CARP A-3.2, A-3.3]

Three items of meteorological information are crucial to transport calculations. One is the height of the mixing layer and its variation over time. The second is wind velocities as a function of height up to the top of the transport layer (2 km). The third is the synoptically derived weather conditions--precipitation and cloud formation.



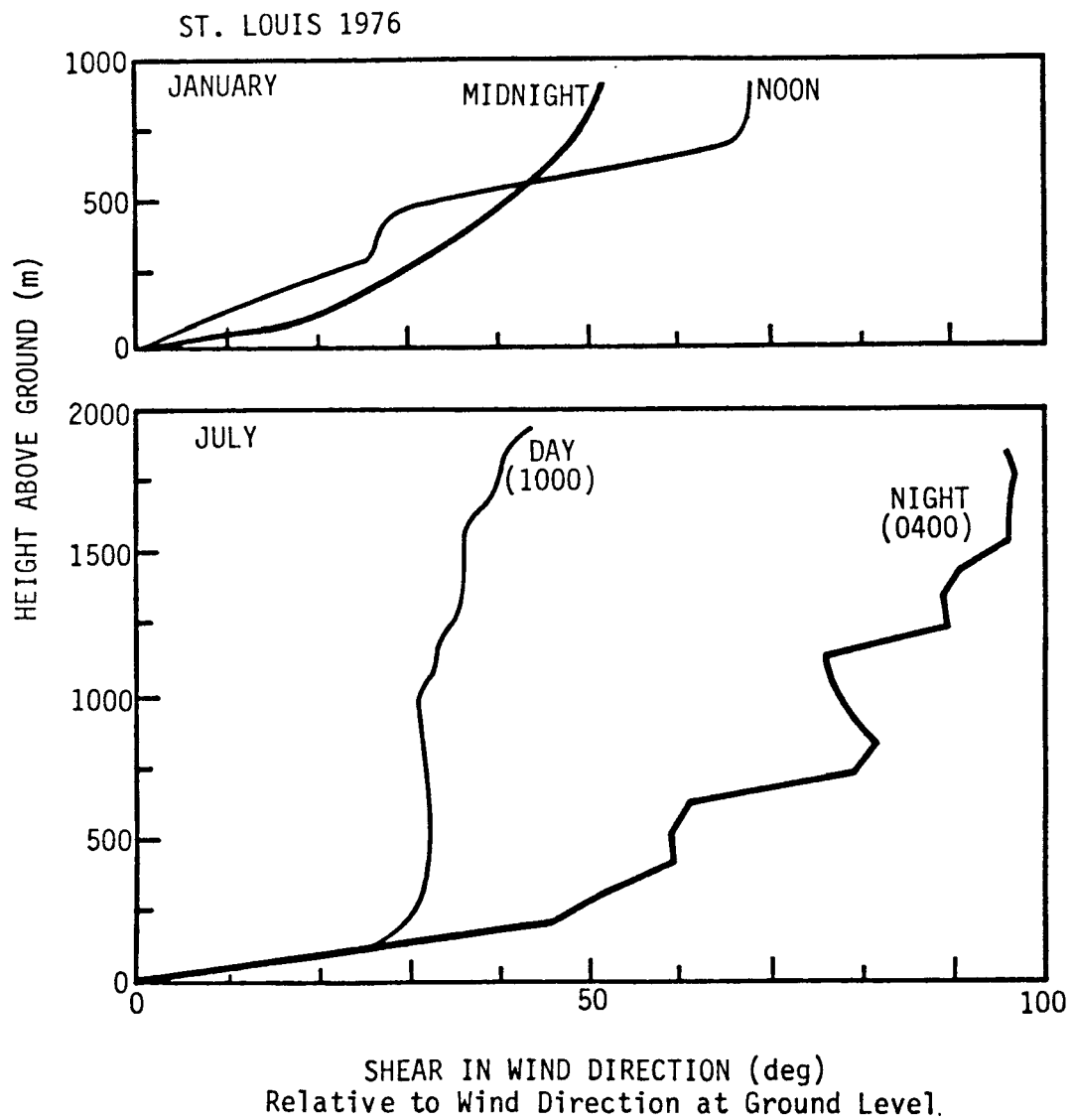


Figure III.17 Monthly-average absolute change in wind direction with height relative to wind direction at ground level. Data are for July 1976 near St. Louis, MO.

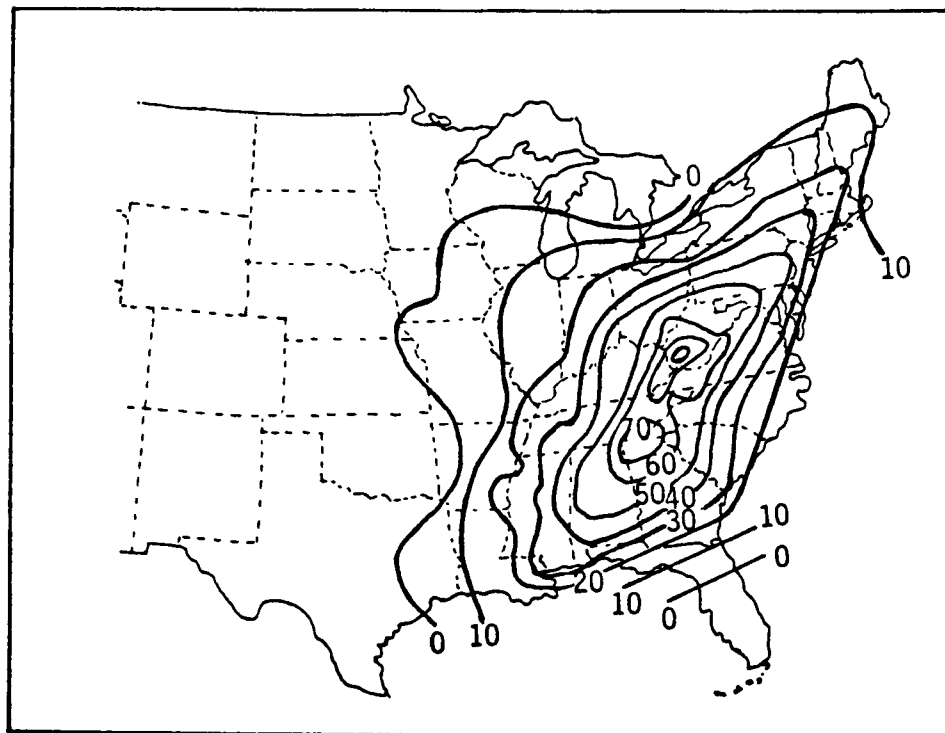


Figure III.18 Climatology of air stagnation advisories issued over a ten-year period. Adapted from Lyons (1975).

A.2.6.3 TO WHAT EXTENT IS THE NEEDED METEOROLOGICAL INFORMATION ROUTINELY COLLECTED? WHAT DOES IT SHOW? [CARP A-3.5]

Weather conditions, such as precipitation, cloud cover, surface winds, are measured at more than two hundred stations. Although this does not provide resolution the size of many smaller storm systems, the density is greater than that for any of the acid deposition networks. Mixing height is routinely inferred at only a small number of stations. Fortunately the heights appear to be relatively uniform over broad regions. Upper air wind velocity measurements are also only made at about 50 locations over the United States, giving a spatial resolution of about 100,000 km<sup>2</sup>. The measurements are made only twice a day, noon and midnight EST.

The first conclusion to be drawn from the limited amount of upper air data is that neither the spatial nor temporal resolution of the upper air measurements is good enough to support calculations of actual (as opposed to "representative") patterns of flow. However, some further conclusions can be drawn from upper air measurements. The seasonal flow tends to be from west to east, with also a significant flow north from the Gulf of Mexico to the Great Lakes. Wind speeds in summer are lower than in winter. In particular, the Southeast has quite low mean velocities in summer; this means that average transport velocities will be lower in the summer, and the Southeast is particularly susceptible to stagnation episodes. The Midwest has strong nighttime wind shears, which are likely to lead to enhanced dispersion.

A.2.7 WHAT ARE THE SOURCES OF SUBSTANCES IMPORTANT TO ACIDIC DEPOSITION? [CARP A-2]

A.2.7.1 WHAT ARE THE NATURAL SOURCES OF THESE SUBSTANCES? [CARP A-2.2]

Sulfur compounds. Sulfur is a common trace element in soil and water, and, as we have seen, is found in the atmosphere even in remote areas. The natural sources of sulfur compounds emitted include both biological activity and the geophysical processes of volcanism and sea spray. For land areas probably the most important natural source is biological activity in soils. The emission rate from soil sources increases with ambient temperature and is highest for coastal wetlands. The most common sulfur compounds produced are hydrogen sulfide (H<sub>2</sub>S), carbonyl sulfide, (COS), and carbon disulfide (CS<sub>2</sub>). These compounds are converted in the atmosphere to SO<sub>2</sub> and/or sulfate. Volcanic activity produces both SO<sub>2</sub> and H<sub>2</sub>S and emits a more or less continuous component, with occasional major releases during eruptions. Sea spray produces mostly neutral sulfate aerosols. [CARP A-2.2.1]

Nitrogen Oxides. Most natural nitrogen oxide production occurs in the terrestrial biosphere; however, lightning and oceans are also significant sources. Biological production comes mainly from soils and appears to decrease with decreasing ambient temperature. [CARP A-2.2.2]

Ammonia. The identification of a biogenic source for ammonia and ammonium compounds exclusive of agricultural activities is more or less circumstantial. Dawson (1977) summarizes the evidence from which biogenic land

emission of ammonia can be inferred. First, ammonia is found in relatively high concentration in rainwater and, since there are no apparent atmospheric sources, a surface source must be inferred. Second, concentrations of  $\text{NH}_3$  in the air are directly related to pH of the underlying soil; they increase with soil temperature and are higher over land than over water. Furthermore the concentrations decrease with altitude, and during an inversion a build up of concentration can be observed. [CARP A-2.2.2.7]

Calcium and Magnesium Compounds. The principal natural source for these substances is dust from soils. [CARP A-2.2.4]

Oxidants. Most oxidant production--ozone, hydrogen peroxide, the HO radical, and others--occurs as the result of complicated chains of photochemical reactions in the atmosphere. The rates of production may be strongly influenced by sunlight and natural and anthropogenic emissions of nitrogen oxides and volatile organic hydrocarbons, though, as noted earlier, HO concentrations appear largely independent of pollutant concentration.

#### A.2.7.2 WHAT AMOUNTS ARE EMITTED BY NATURAL SOURCES? HOW ARE THEY DISTRIBUTED OVER SPACE AND TIME? [CARP A-2.2]

An attempt to measure the average biogenic emission of sulfur in the eastern United States was part of the EPRI-SURE experiment. The results, based on soil type are summarized in Table III.5 (Adams et al. 1981). The annual average, weighted by land area, is about  $0.03 \text{ g S m}^{-2}$ . Multiplied by the land area east of the Mississippi,  $2.2 \times 10^{12} \text{ m}^2$ , this yields an annual emission rate for the eastern United States of  $0.07 \times 10^{12} \text{ g S yr}^{-1}$  or 0.07 Tg. ( $10^{12} \text{ g}$  equals one teragram, abbreviated Tg, or one million metric tons. 0.07 Tg is approximately the annual sulfur emission of one large coal-fired power plant.) The same emission rate for the 48 contiguous states yields a total emission rate of  $0.23 \text{ Tg yr}^{-1}$ . This is probably an overestimate since arid lands are likely to have lower emission rates and since there is a lower percentage of coastal wetland area.

Volcanic emissions are not considered large for the United States except for an occasional major eruption. The estimated sulfur emissions from Mt. St. Helens from March 1980 to March 1981, which included the two major eruptions in May and June, were about 0.17 Tg S, about twice the annual emission of a major coal-fired power plant. The Pacific Ocean and Gulf of Mexico may be significant sources. Crude estimates give  $0.36 \text{ Tg yr}^{-1}$  and  $0.24 \text{ Tg yr}^{-1}$  of sulfur respectively for these two sources. The Atlantic Ocean is expected to contribute much less since the prevailing winds are offshore.

No comparable set of field measurements of biogenic nitrogen oxide emission has been developed, so the estimates have been based on material balances, either globally or locally, using the gradient of concentration. These methods are quite uncertain; aside from the statistical problem that they depend on taking differences of large quantities, they are also sensitive to the remote background concentration of  $\text{NO}_2$ , which is not well determined. The estimates range from 0.04 to  $1.5 \text{ Tg N yr}^{-1}$  for the eastern United States and from 0.15 to  $5.3 \text{ Tg N yr}^{-1}$  for the contiguous 48 states [CARP

TABLE III.5. SUMMARY OF ANNUAL SULFUR FLUX BY SOIL GROUPINGS  
WITHIN THE STUDY AREA (ADAPTED FROM ADAMS ET AL. 1981)<sup>a</sup>

Soil grouping	Sulfur flux <sup>b</sup> Tg S yr <sup>-1</sup>	Land area m <sup>2</sup>	Emission density g S m <sup>-2</sup> yr <sup>-1</sup>
Coastal wetlands	0.05	2.56 x 10 <sup>11</sup>	0.2
Inland high organic	0.01	6.85 x 10 <sup>11</sup>	0.02
Inland mineral	0.06	27.26 x 10 <sup>11</sup>	0.02
Total	0.1	36.7 x 10 <sup>11</sup>	0.03

<sup>a</sup>Adapted with rounding.

<sup>b</sup>Equals 10<sup>12</sup> g S yr<sup>-1</sup>.

A-2, Table 2.3]. Values toward the lower end of the range are based on more recent measurements of NO<sub>2</sub> levels and are preferred.

Natural biogenic emissions of ammonia are similarly uncertain; the estimates give ranges of 0.3 to 1.2 Tg N yr<sup>-1</sup> for the eastern United States and 1.1 to 4.3 Tg N yr<sup>-1</sup> for the 48 contiguous states.

The estimated calcium and magnesium emission rates are 3 Tg yr<sup>-1</sup> and 0.5 Tg yr<sup>-1</sup>, respectively, for the eastern United States. Estimates were made by assuming that calcium and magnesium appear in about the same proportion that they do in the Earth's crust (3.6 percent and 2.1 percent respectively). Dust emissions are estimated from the concentrations of "coarse particles" (2 to 10 μm in diameter). Clearly there is considerable uncertainty in these estimates, the more so because the dust concentration measurements are based on only 12 stations. No representative data on dust emission for the western United States are available.

All estimates of natural material emissions are too crude to permit much estimation of temporal variation; biogenic emissions will be strongly weighted toward the summer.

#### A.2.7.3 WHAT ARE THE ANTHROPOGENIC SOURCES? [CARP A-2.3]

Sulfur Compounds. Emission of sulfur compounds by man-made sources comes largely from burning fossil fuels to produce heat for industrial processes or for space heating or to generate electricity. In addition the smelting of sulfur-containing ores produces significant additional sulfur emissions. Most emissions are in the form of SO<sub>2</sub>, though some primary emission of sulfate occurs. Table III.6 lists estimated percentages that primary sulfate emissions are of total sulfur emissions for various categories of sources.

Nitrogen Oxides. Unlike sulfur oxides, which are produced from the burning of sulfur in fuel, nitrogen oxides are produced from the combination of the nitrogen and oxygen in the air at the high temperatures during combustion. The type of fuel being burned does not matter, but the nature of the combustion process as it affects temperatures matters considerably to the rate of nitrogen oxide formation. In particular, internal combustion engines, because of high temperatures associated with the explosion in the engine cylinder, are high emitters of nitrogen oxides when compared to an industrial boiler on a per amount of fuel burned basis. Most nitrogen oxide emissions are in the form of NO, which, as previously noted, is rapidly oxidized in the atmosphere to NO<sub>2</sub>.

Ammonia. Anthropogenic sources of ammonia are principally livestock wastes, fossil fuel combustion, and agricultural fertilizer use.

Calcium and Magnesium Compounds. The principal anthropogenic sources of calcium and magnesium compounds in the air are fly ash from coal burning and dust from dirt roads.

TABLE III.6. SULFATE EMISSIONS FACTORS FOR SOURCE CATEGORIES  
AND FUELS (after SHANNON ET AL. 1980)<sup>a</sup>

Source category	Sulfate emissions factor (%)
Coal point sources	1.5
Residual oil--utility and industrial	7.0
Residual oil--commercial and residential	13.4
Distillate oil	3.0
Mobile sources	3.0
Smelters	1-2
Miscellaneous	5.0

<sup>a</sup>Sulfate emissions factor is the percentage of total sulfur emissions released directly as sulfur in SO<sub>4</sub>.

<sup>b</sup>Estimated similar to coal point sources.

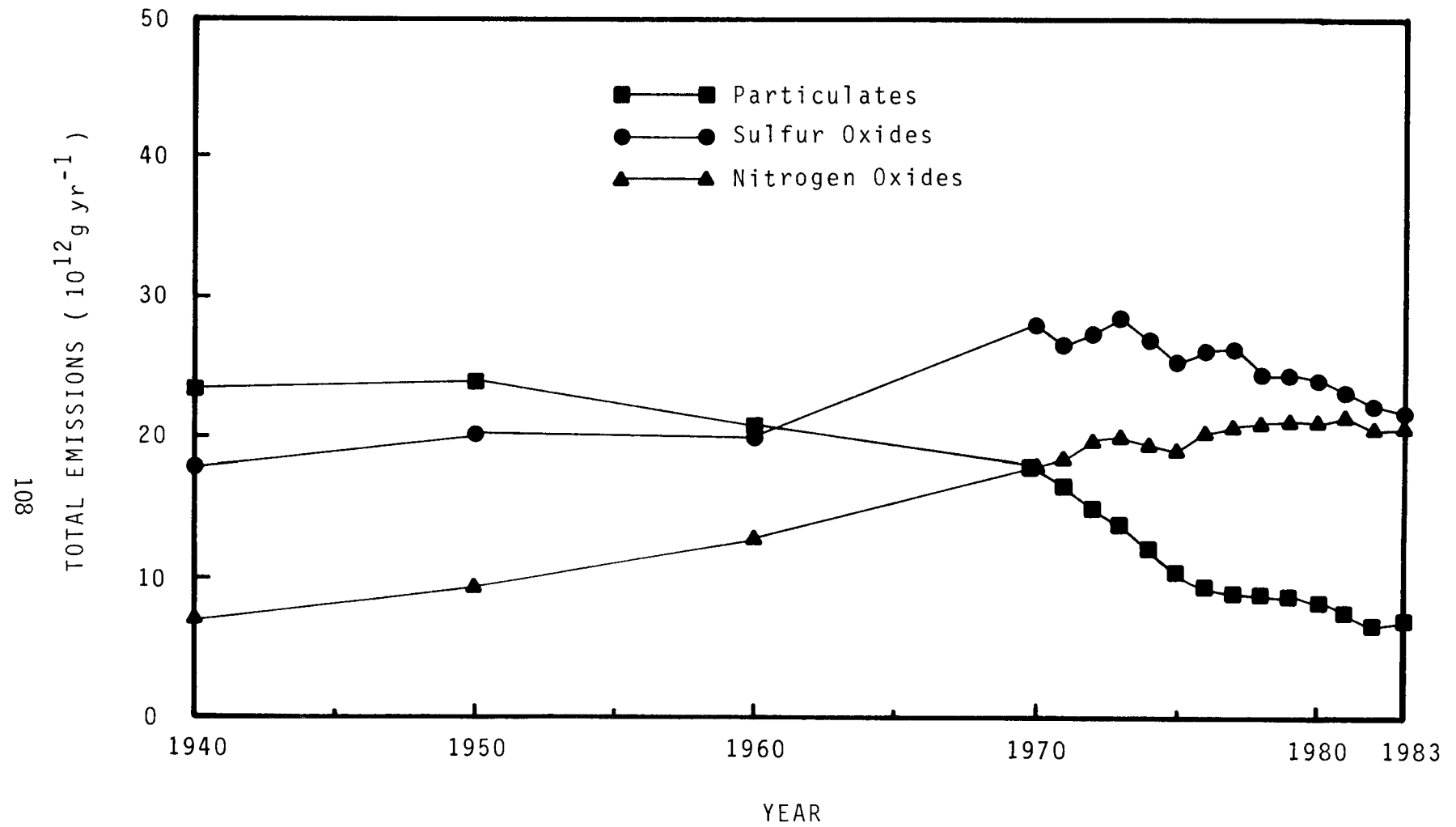


Figure III.19 Total emissions of particulate matter,  $\text{SO}_2$ , and  $\text{NO}_x$  for the United States from 1940 through 1983. Adapted from U.S. EPA (1984).



#### A.2.7.4 WHAT ARE THE ANTHROPOGENIC EMISSION RATES? HOW ARE THEY DISTRIBUTED IN SPACE AND TIME? [CARP A-2.3, UPDATED]

Annual emissions for the United States from 1940 through 1983 for SO<sub>2</sub>, nitrogen oxides, and total suspended particulates (TSP) are shown in Figure III.19. The trends are interesting: TSP remained relatively constant until the seventies and then declined as a result of emission controls. Sulfur dioxide emission increased about 50 percent from 1940 until the early seventies but has declined about 25 percent since then. Nitrogen oxide emission has increased nearly a factor of three as a result of major increases in motor vehicle use, as well as increased electricity generation and other combustion uses as the economy has expanded.

We now look, using another source with greater detail but lacking TSP, at the types of sources and their spatial distributions for this period (Gschwandtner et al. 1985). The study area considered is that considered in the CAD, based on Gschwandtner et al. 1981, but the improved emissions data of Gschwandtner et al. 1985 are used here to respond to peer reviewers' suggestions. Analyses of the 48 contiguous states based on this reference will be made in the 1985 Assessment. The area covered is the eastern half of the United States from Minnesota eastward, plus Texas, as shown in Figure III.20.

Sulfur Dioxide. Historical emissions of SO<sub>2</sub> for the study region by type of source are shown in Figure III.21. It is noteworthy that by 1980, about 2/3 of SO<sub>2</sub> emissions came from the generation of electricity, and the growth of SO<sub>2</sub> emissions from 1950 to 1980 can almost entirely be attributed to electric utility growth. The spatial patterns of SO<sub>2</sub> emission are also interesting; Figure III.22 shows emission rates by state. Highest emissions stretch along on an east-west band centered on the Ohio Valley.

Two changes in SO<sub>2</sub> emission patterns in recent years deserve attention. One change is the spatial distribution of emissions. In Figure III.23 we show changes in SO<sub>2</sub> emissions from 1970 to 1980 by state. Recently, increases in SO<sub>2</sub> emissions have been almost entirely in the South. Northeastern SO<sub>2</sub> emissions have generally declined.

A second change is the height of smokestacks. As noted in Section 2.6, the height at which SO<sub>2</sub> is released can affect significantly its subsequent fate. The increase in SO<sub>2</sub> emissions from electricity generation has included a substantial shift to tall stack emission. This shift is most pronounced in the highest density SO<sub>2</sub> emission region, the Ohio Valley area, and is illustrated in Figure III.24. The figure shows trends in total SO<sub>2</sub> emissions for three heights of emission, for all the power plants of capacity greater than 50 MW, located in a two-county row on either bank of the Ohio River in Illinois, Indiana, Ohio, Kentucky, West Virginia and Pennsylvania. These plants account for about 15 percent of the total annual U.S. emission of SO<sub>2</sub>.

Sulfate. That primary sulfate emission is a comparatively small fraction of the total emission of sulfur compounds is illustrated in Table III.6. The historical pattern is shown in Figure III.25. The sharp rise in primary sulfate emissions to 1970 results from fuel switching to residual oil; the

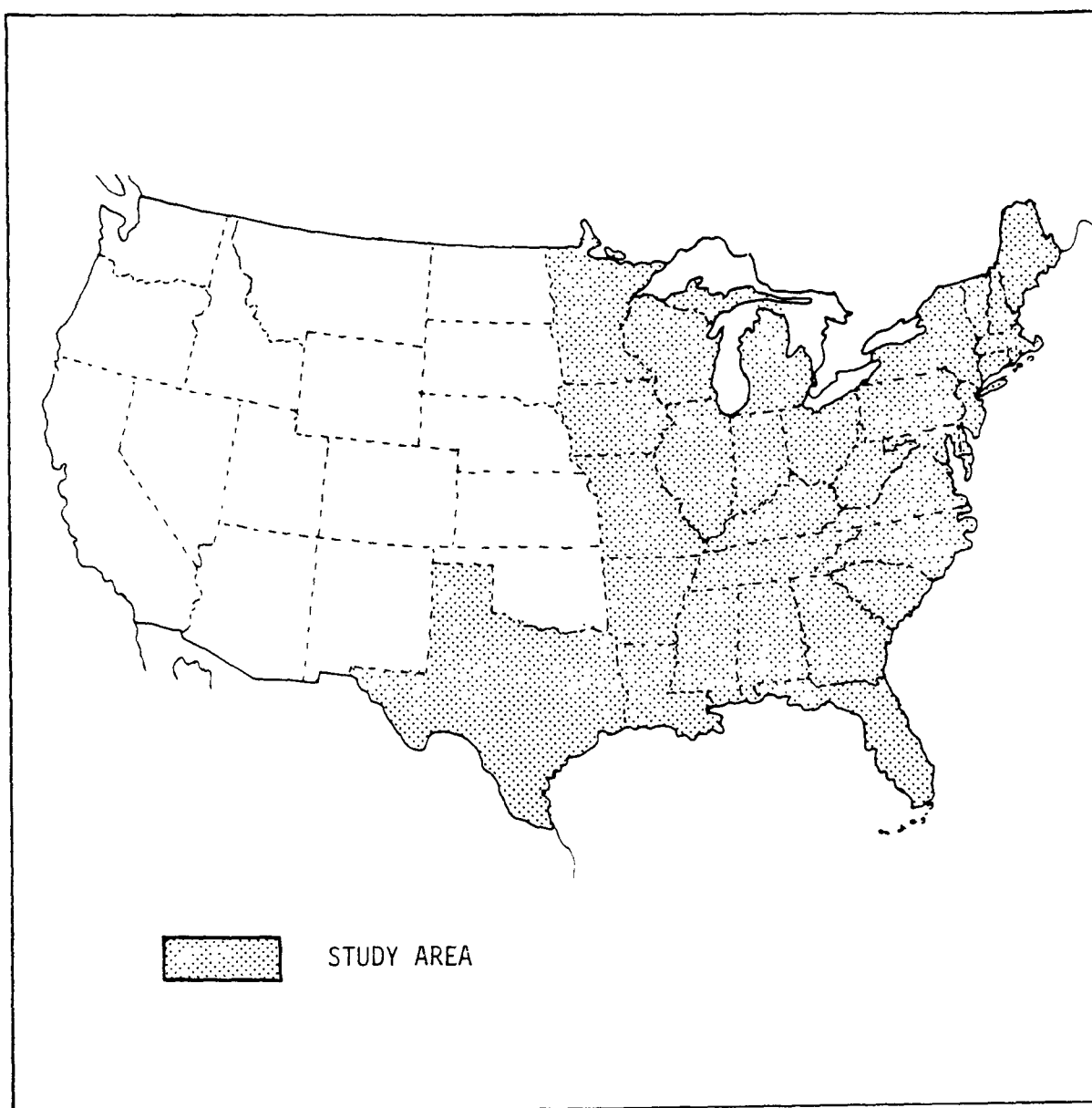


Figure III.20 Map showing the study area included for emissions density calculations. Adapted from Gschwandtner et al. (1981).

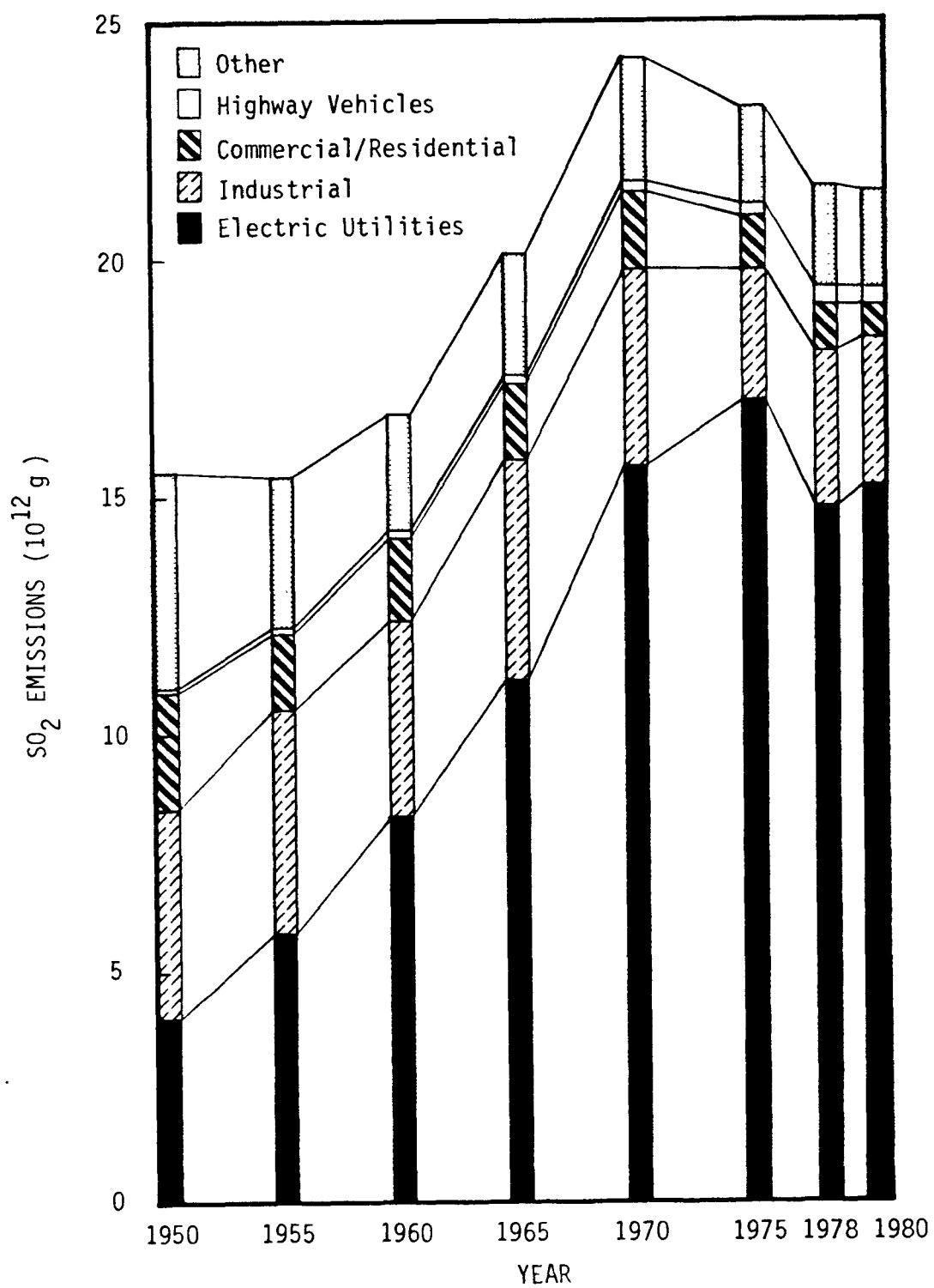


Figure III.21 Historical trends of sulfur oxide emissions by source category for the study area. Data are from Gschwandtner et al. (1985).

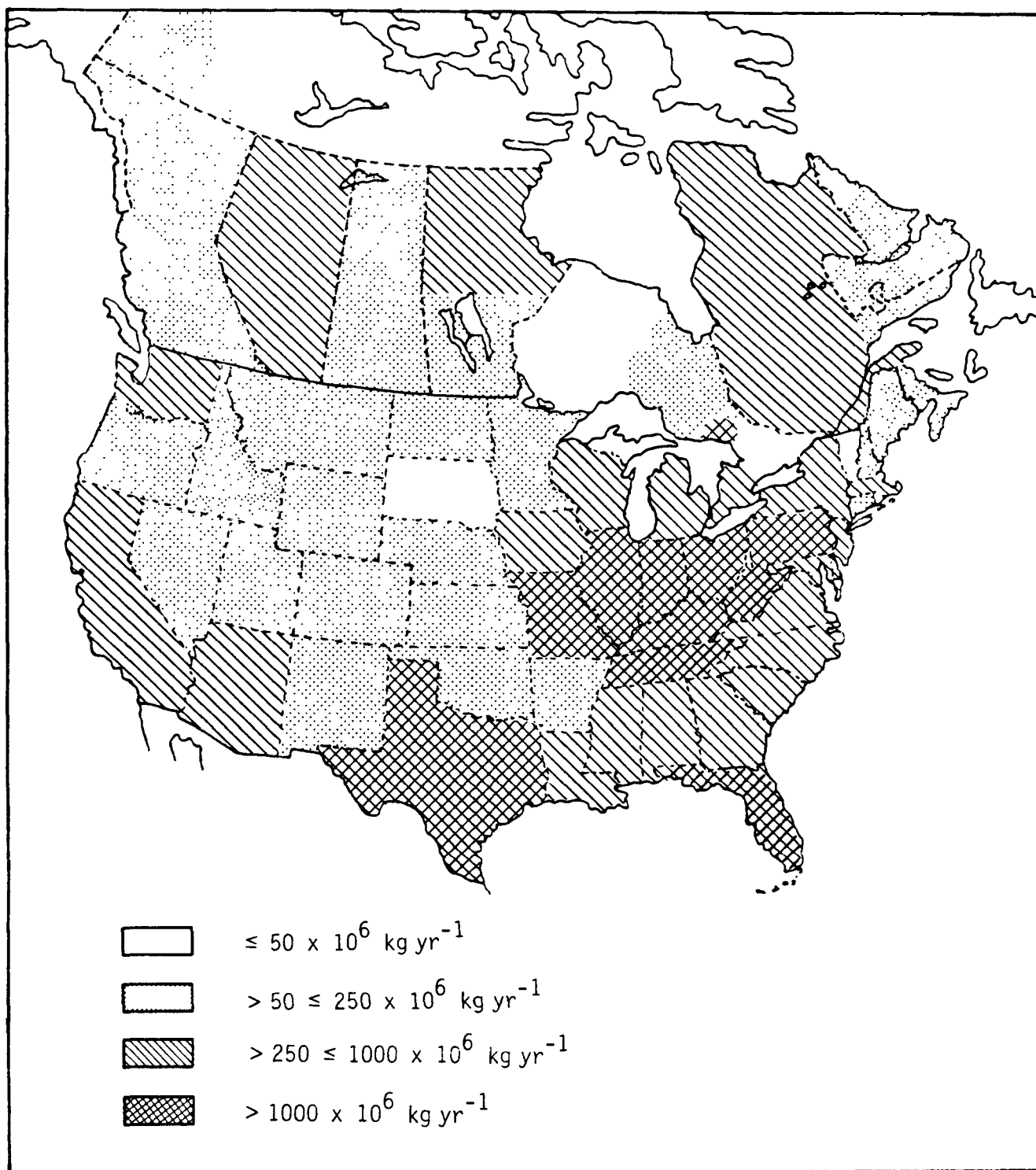


Figure III.22 Annual 1980 emissions of SO<sub>2</sub> by state. Data are from Toothman et al. (1984).

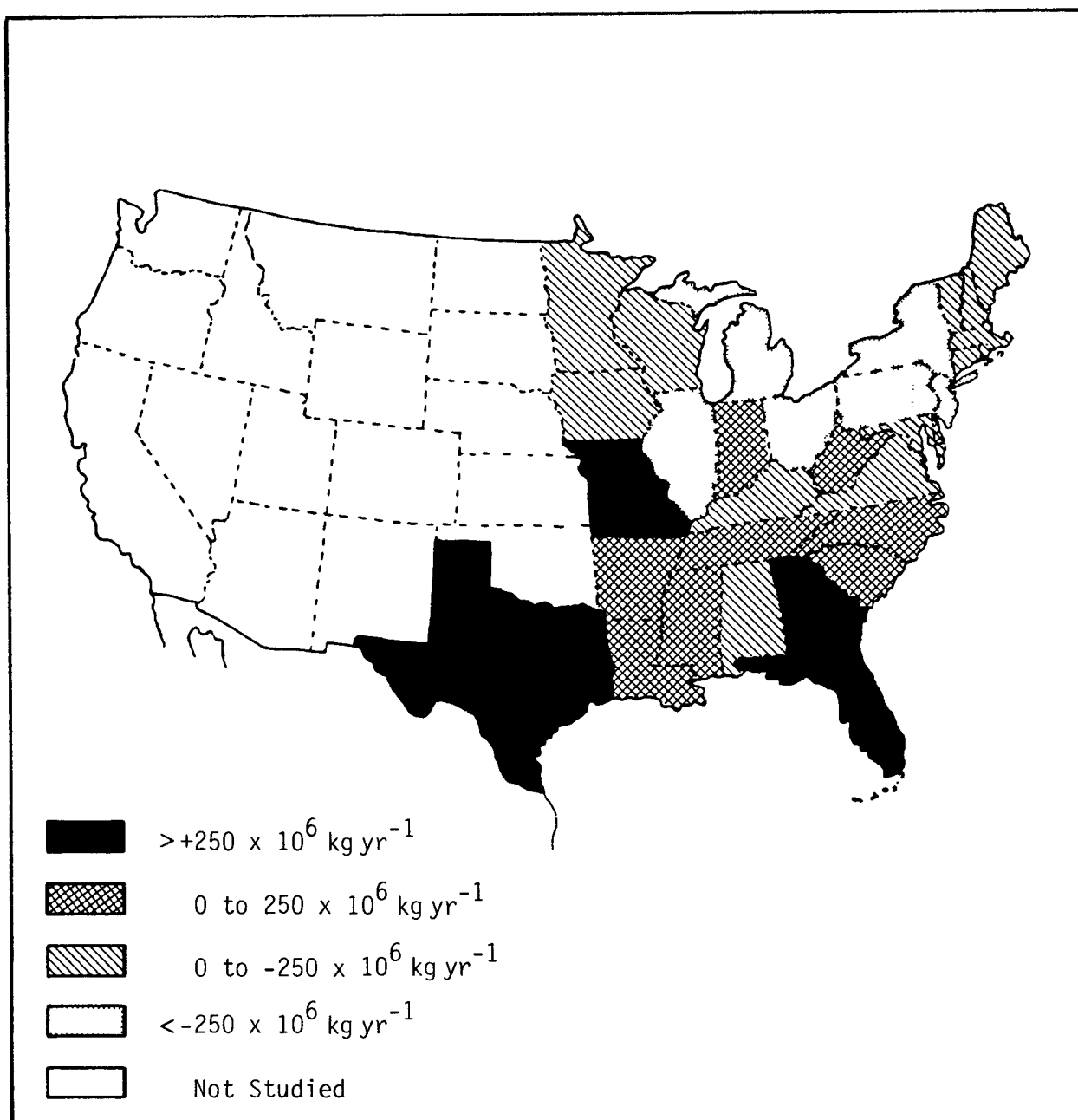


Figure III.23 Map showing changes in SO<sub>2</sub> emissions from 1970 to 1980 for each state in the study area. Data are from Gschwandtner et al. (1985).

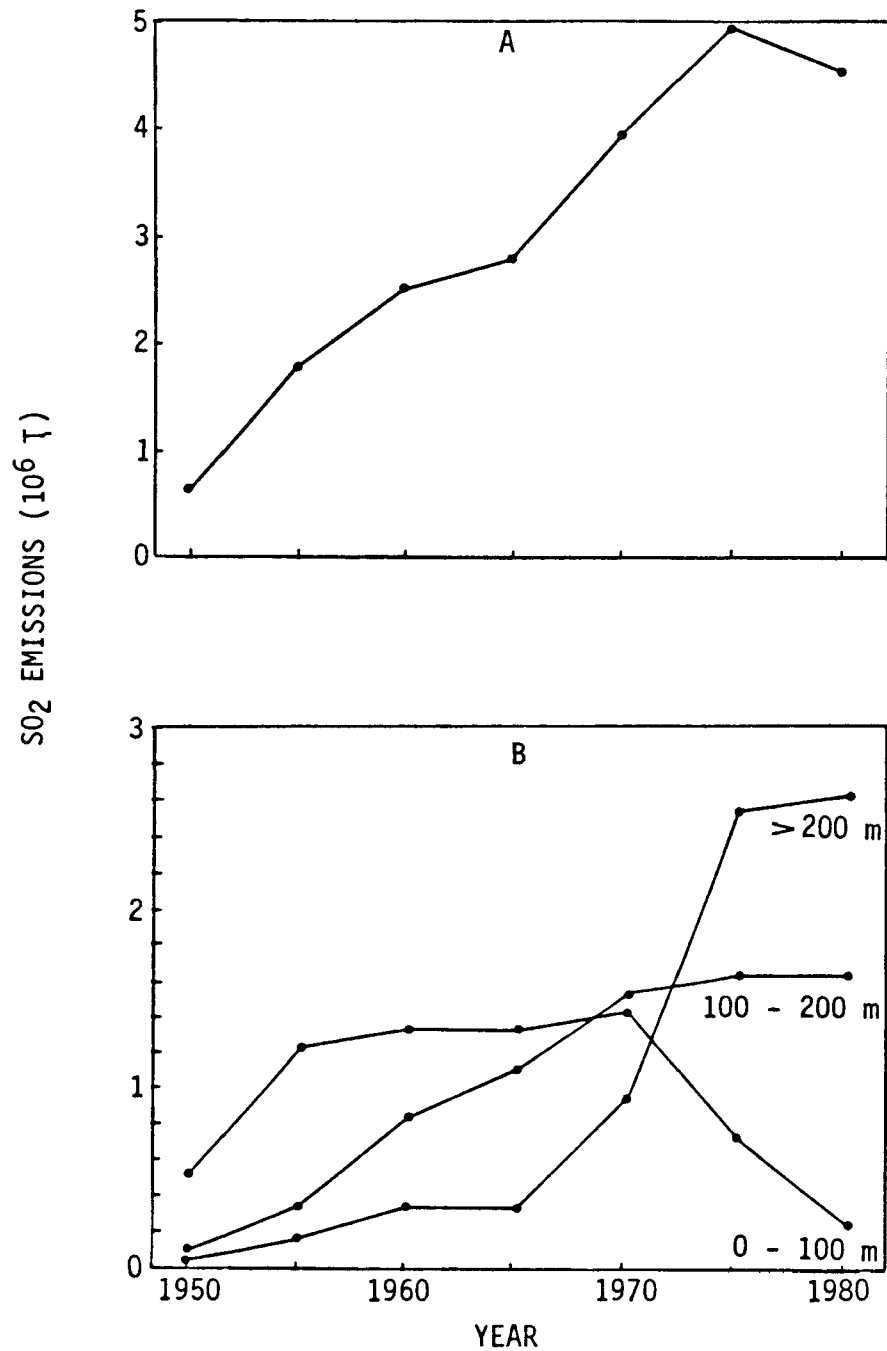


Figure III.24 Trend in emissions of SO<sub>2</sub> from 62 study power plants in the Ohio River Valley:  
 (A) Total tonnage;  
 (B) Tonnage breakdown according to specified physical stack height intervals.  
 Adapted from Koerber (1982).

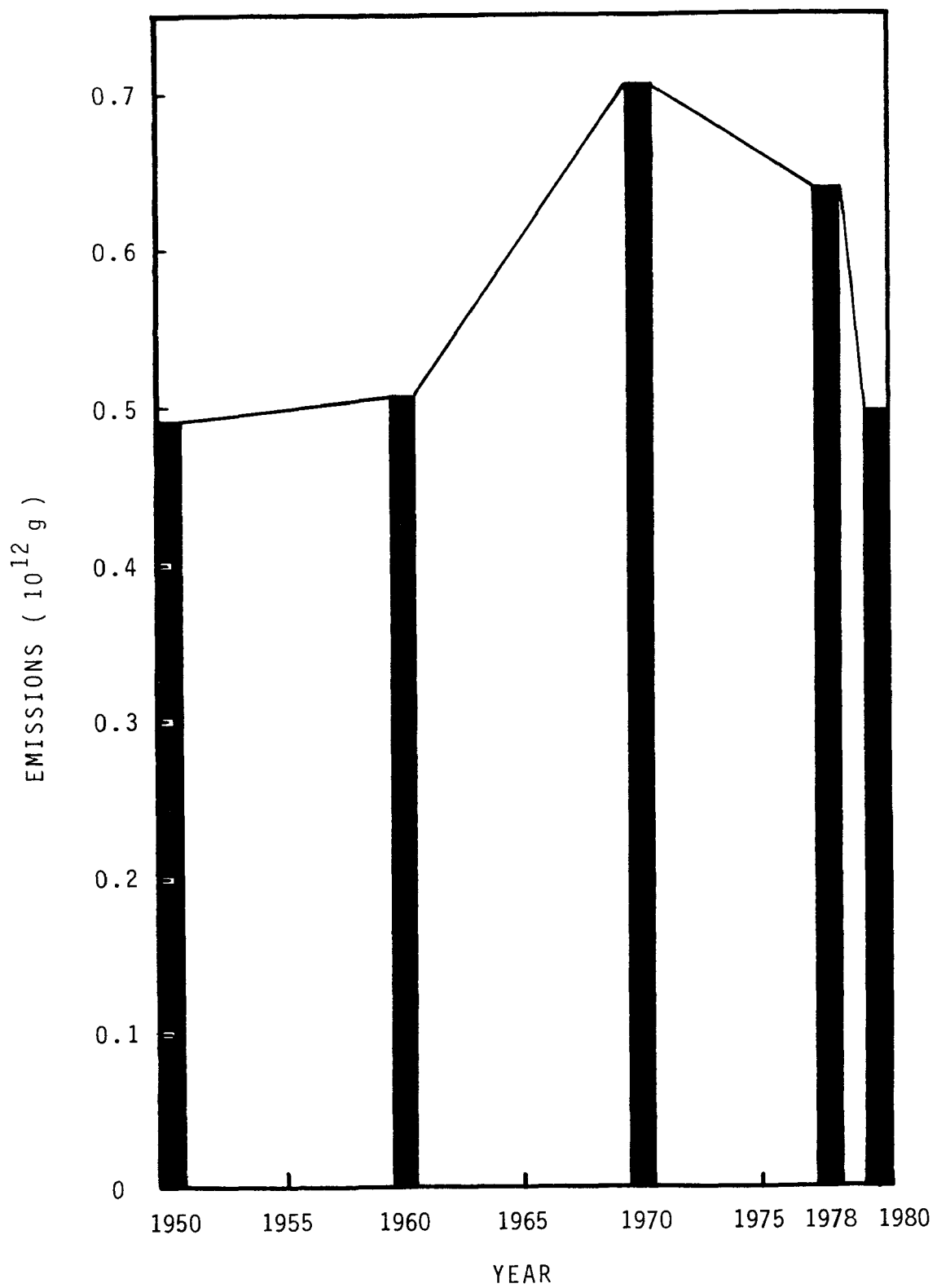


Figure III.25 Annual emissions of primary sulfate. Data are from CARP A-2.3, Table 2-17.

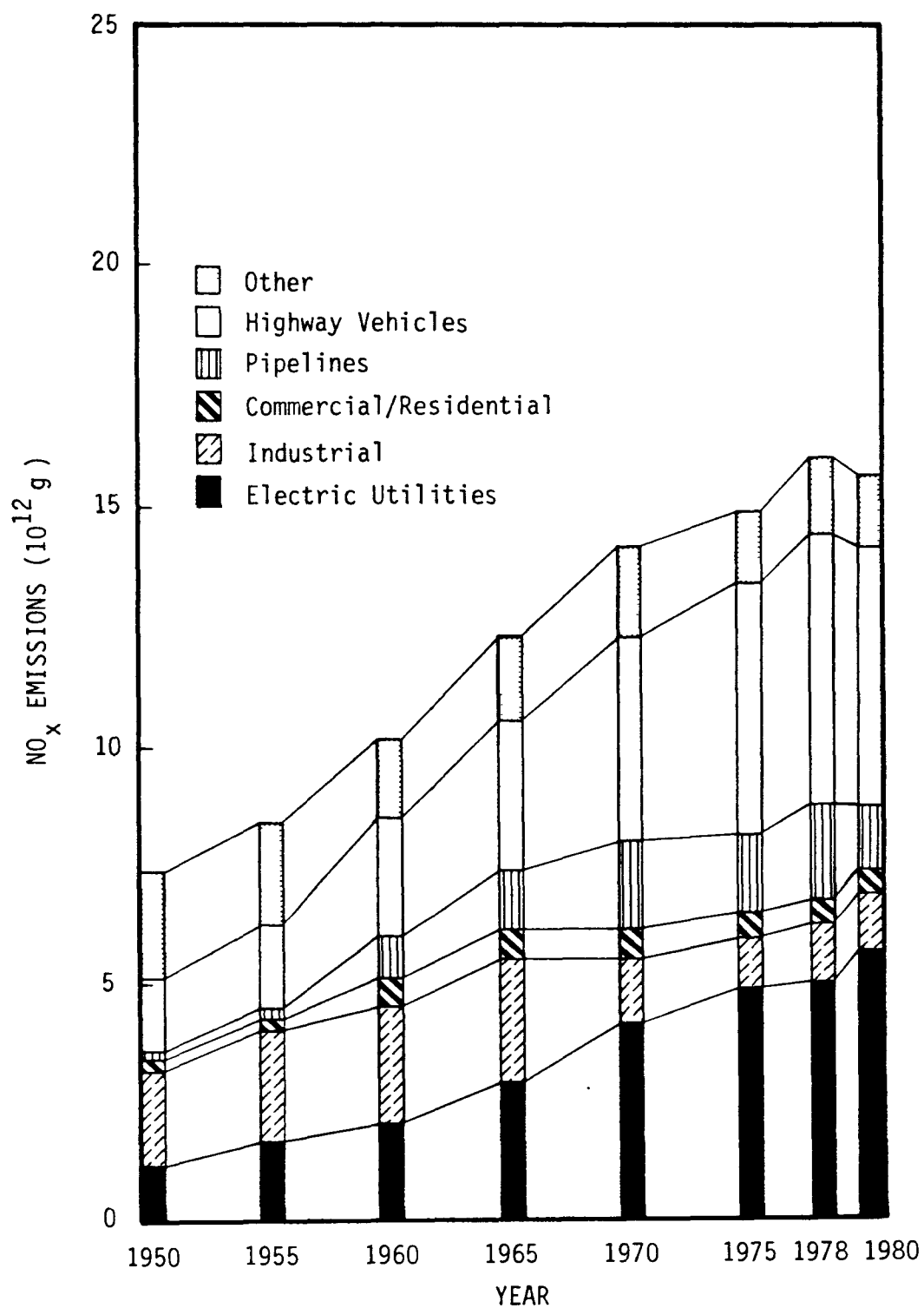


Figure III.26 Historical trends of nitrogen oxide emissions by source category for the study area. Data are from Gschwandtner et al. (1985).



sharp drop to 1980, from the subsequent shift away from residual oil in reaction to the oil embargo and OPEC price rises. Comparison of the spatial distribution of sulfate emissions to that for  $\text{SO}_2$  (Figure III.22) would show that the high density regions are shifted north and east, where residual oil use is most extensive.

Nitrogen Oxides. Historical trends for nitrogen oxide emission, by type of source, are shown in Figure III.26. The largest increases from 1950 to 1980 were in motor vehicle emission and in electricity generation. Unlike the case of  $\text{SO}_2$  emission,  $\text{NO}_x$  emission continued to rise through the 1970's. The spatial distribution of  $\text{NO}_x$  emission reflects the importance of electricity generation and motor vehicles. Figure III.27 shows that high emission areas are more broadly spread over the eastern United States, including both the Ohio Valley area and the population centers of the East.

Canadian Emission of  $\text{SO}_2$  and  $\text{NO}_x$ . Historical emissions of  $\text{SO}_2$  and  $\text{NO}_x$  by source category are shown in Table III.7. Several observations from this table are pertinent. One is the high emission of  $\text{SO}_2$  from copper and nickel smelting; these sources account for about half of Canada's  $\text{SO}_2$  emissions; they are mostly located in eastern Canada, especially Ontario. This is the most striking instance of a more general observation, that the mix of important sources for  $\text{SO}_2$  is quite different for Canada compared to the United States. Canadian  $\text{SO}_2$  emissions are a little less than 20 percent of U.S. emissions. Canadian emissions from electricity generators, however, are about 4 percent of U.S. utility emissions while Canadian emissions from non-ferrous smelting are more than half again as large as the U.S. emissions from this source category. Canadian emissions of nitrogen oxides are less than 10 percent those of the United States, a significantly smaller fraction than  $\text{SO}_2$  emissions. The distribution of  $\text{NO}_x$  emissions by source category is closer to the U.S. distribution, though electricity generation gives a significantly smaller fraction of the total. Most emissions occur within 200 miles (300 km) of the U.S. border; the highest emission rates occur in southeastern Ontario and southern Quebec. The nickel smelter in Sudbury, Ontario, is the largest single source of  $\text{SO}_2$  in North America.

Ammonia. Anthropogenically-derived emissions of ammonia are estimated to be about  $3 \text{ Tg yr}^{-1}$ . The major source is domestic animal wastes. There is considerable uncertainty in this estimate and little information on historical trends or spatial distribution of emissions.

#### A.2.7.5 HOW DO NATURAL AND ANTHROPOGENIC EMISSIONS OF ACIDIFYING SUBSTANCES COMPARE? [CARP A-2.2, A-2.3]

Sulfur Oxides. Natural emissions of sulfur compounds are estimated to be about  $0.3 \text{ Tg yr}^{-1}$  of sulfur for the eastern United States (including organic sources) and less than  $0.9 \text{ Tg yr}^{-1}$  of sulfur for the 48 contiguous states (Section A.2.7.2). Anthropogenic emissions are about  $11 \text{ Tg yr}^{-1}$  of sulfur in the eastern United States (note that emissions expressed as sulfur are  $1/2$  those expressed as of  $\text{SO}_2$  and  $1/3$  those as  $\text{SO}_4^{2-}$ ) and about  $13 \text{ Tg yr}^{-1}$  for the 48 states. Thus, in the East natural emissions are roughly 3 percent of anthropogenic emissions, while in the West natural emissions may

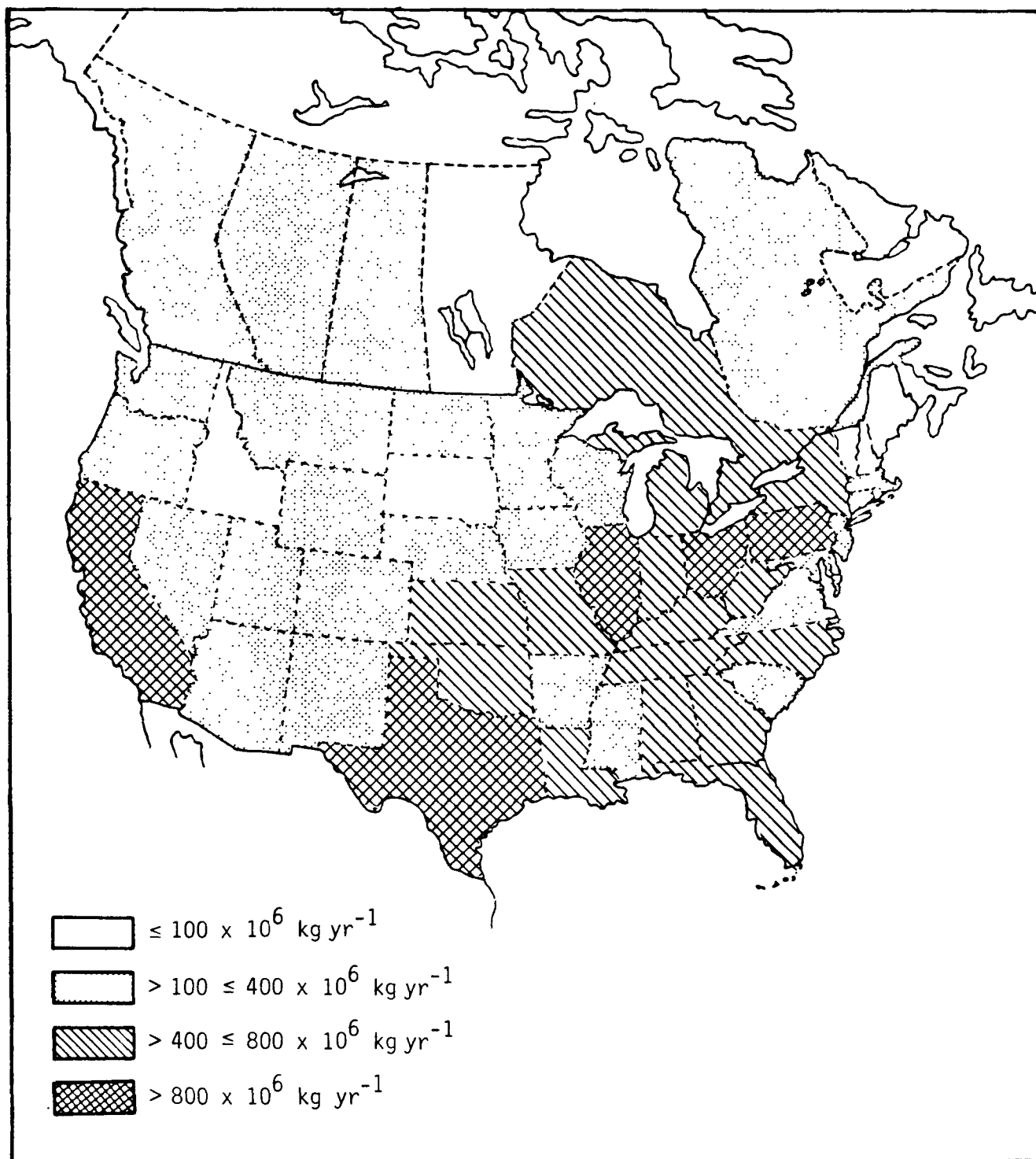


Figure III.27 Annual 1980 emissions of NO<sub>x</sub> by state. Data are from Toothman et al. (1984).

TABLE III.7. HISTORICAL EMISSIONS OF SO<sub>2</sub> AND NO<sub>x</sub> - CANADA  
(U.S./CANADA WORK GROUP 3B DRAFT REPORT 1982)  
(10<sup>3</sup> kg yr<sup>-1</sup>)

Sector	1955		1965		1976	
	SO <sub>2</sub>	NO <sub>x</sub> <sup>a</sup>	SO <sub>2</sub>	NO <sub>x</sub> <sup>a</sup>	SO <sub>2</sub>	NO <sub>x</sub> <sup>a</sup>
Cu-Ni smelters <sup>b</sup>	2,887,420	-	3,901,950	-	2,604,637	-
Power plants	56,246	10,335	261,837	57,402	614,323	206,454
Other combustion <sup>c</sup>	1,210,108	227,837	1,129,548	247,323	884,867	445,315
Transportation	83,474	323,785	48,669	511,868	77,793	1,017,936
Iron ore processing	109,732	-	155,832	-	175,829	-
Others	<u>189,876</u>	<u>68,065</u>	<u>1,095,341</u>	<u>33,778</u>	<u>954,215</u>	<u>190,327</u>
TOTAL	4,536,856	630,022	6,593,177	850,371	5,311,664	1,860,032

<sup>a</sup>NO<sub>x</sub> expressed as NO<sub>2</sub>.

<sup>b</sup>Includes emissions from pyrrhotite roasting operations.

<sup>c</sup>Includes residential, commercial, industrial, and fuelwood combustion. Industrial fuel combustion also includes fuel combustion emissions from petroleum refining and natural gas processing.

be as much 25 percent of anthropogenic, but probably are significantly less. On a continental or global scale, estimations of the natural biogenic emissions from all land areas range over more than an order of magnitude but appear comparable to the global anthropogenic emission of about 60 Tg S yr<sup>-1</sup>. Oceanic emissions are also of that order of magnitude, (Eriksson estimated 44 Tg S yr<sup>-1</sup>) but do not make a large contribution to the terrestrial sulfur cycle. [CARP A-2.2.1.6]

Nitrogen oxides. Natural emissions of nitrogen have been variously estimated at 0.04 to 1.5 Tg N yr<sup>-1</sup> for the eastern United States and 0.15 to 5 Tg N yr<sup>-1</sup> for the 48 contiguous states; the lower estimates are to be preferred. Current anthropogenic emissions are estimated to be about 3.5 Tg N yr<sup>-1</sup> in the eastern United States and 6 Tg N yr<sup>-1</sup> in the 48 states. It is likely that natural sources contribute less than 10 percent of the NO<sub>x</sub> emissions in eastern North America. In the West the amounts may be more nearly comparable (10 to 50 percent). On a global scale, natural and anthropogenic emissions of nitrogen oxides appear roughly comparable, with, however, great uncertainties in the estimate of natural emissions. [CARP A-2.2.2.2]

Ammonia. For the United States, anthropogenic emissions of ammonia (principally from domestic animal wastes) appear to be roughly three times natural emissions, but uncertainties of a factor of three or so exist in the estimates. [CARP A-2.2.2.9]

#### A.2.7.6 HOW WELL KNOWN ARE EMISSION RATES? [CARP A-2.2, A-2.3]

We have already observed that there are very large uncertainties, up to an order of magnitude, in the estimates of natural emission rates. The uncertainties in the estimates of anthropogenic emission rates are smaller, but still significant, if the estimates are to be used in calculating quantitative materials budgets. The principal sources of uncertainty are different for different sources.

Sulfur emissions. Sulfur emissions result from the burning of sulfur in fuel (and ore). Estimates of sulfur emissions are made by obtaining records of fuel consumption (and ore processed) and source of fuel, and estimates of the sulfur content of the fuel, and multiplying the two quantities together. For the case of major sources that have installed SO<sub>2</sub> scrubbers, an estimate of the effect of the scrubber must also be included. The greatest limitation in this procedure is the estimate of average sulfur content by fuel source; it contributes an uncertainty of 20 percent at least.

Nitrogen Oxide Emissions. Because most of the nitrogen emitted as nitrogen oxides comes from the air rather than fuel, estimates of nitrogen oxides must be based on records of fuel consumption for various categories of combustion, and estimates based on measurements of average emission factors telling the amount of NO<sub>x</sub> emitted per amount of fuel consumed for various categories of sources. Because a major emission source is motor vehicles and because NO<sub>x</sub> emissions vary enormously from one car to another, or for even the same car depending on how well tuned it is, substantial uncertainty in the emission estimates, probably 30 percent or more is likely.

TABLE III.8. NATIONAL U.S. CURRENT AND PROJECTED SO<sub>2</sub> AND NO<sub>x</sub> EMISSIONS (Tg yr<sup>-1</sup>)<sup>a</sup>

Source category	Current 1980		Projected 1990		Projected 2000	
	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	NO <sub>x</sub>
1. Electric utilities	15.0	5.6	15.9	7.2	16.2	8.7
2. Industrial boilers and process heaters	2.4	3.5	3.4	3.0	6.5	4.0
3. Nonferrous smelters	1.4		0.5		0.5	
4. Residential/commercial	0.8	0.7	1.0	0.7	0.9	0.6
5. Other industrial processes	2.9	0.7	1.2	0.8	1.5	1.1
6. Transportation	<u>0.8</u>	<u>8.5</u>	<u>0.8</u>	<u>7.8</u>	<u>1.0</u>	<u>9.7</u>
TOTALS	24.1	19.0	22.8	19.5	26.6	24.1

<sup>a</sup>Summarized from U.S./Canada Work Group 3B Draft Report (1982).

#### A.2.7.7 WHAT ARE PROJECTED FUTURE EMISSIONS OF ACIDIFYING SUBSTANCES?

The uncertainties in estimating current emission levels will also appear in predictions of future levels. Such predictions may be valid as relative predictions, however, and even if they turn out to be wrong they may be useful as pointing to trends in the current development of technology and regulation processes. In Table III.8 we show one set of predictions for U.S. emissions of  $\text{SO}_2$  and  $\text{NO}_x$  in 1980, 1990 and 2000. The projections are about a 10 percent increase in  $\text{SO}_2$  emissions and about a 25 percent growth of  $\text{NO}_x$  emission by the year 2000. More interesting are the predictions for 1990, which are for essentially constant emissions.

## SECTION B. RELATIONSHIPS BETWEEN THE EMISSION AND DEPOSITION OF ACIDIFYING SUBSTANCES

The processes of atmospheric transport, transformation, and wet and dry deposition, which we have treated separately up to now, are closely linked. The amount of sulfur transported over some distance, for instance, depends on the amount of  $\text{SO}_2$  and sulfate emitted, the rate at which  $\text{SO}_2$  is transformed into sulfate, the rates of dry deposition for  $\text{SO}_2$  and sulfate, and the likelihood of encountering a rainstorm or snowstorm, and the efficiency of scavenging. The direction of transport of material, even, depends on deposition and transformation rates: the vertical distribution of material depends on deposition rates, which in turn depend on the chemical form of the substance; and the frequent pronounced shear in wind direction, particularly at night, means that material at different heights can travel to different regions.

In this part, the linkages between the different atmospheric processes are examined as we attempt to answer questions of two sorts: Do certain characteristics distinguish one kind of source from another? What is known about the relationship between emission and deposition?

As we have learned from the effects section, we are concerned with the answers to these questions for sulfur compounds, for nitrogen compounds and for the production of acidity. The linkages are better understood for sulfur compounds at present; so, our approach will be to present information first for sulfur, then to compare nitrogen with sulfur, and finally to attempt to draw conclusions about acidity.

### B.1 ARE SOME SOURCES MORE IMPORTANT THAN OTHERS?

"Important" has to be defined, of course. For the purposes of this section, we mean, can we distinguish one kind of source from another in the fractional amount of acidifying material likely to be wet or dry deposited in previously specified sensitive areas? We shall return to this question, and the problem of defining "sensitive" in the concluding sections of this document. In the next three subsections, we discuss the general characteristics of source/receptor relationships and how they may be simulated with computer models or inferred from data analysis. In the remaining subsections we compare the deposition patterns predicted for various classes of sources.

#### B.1.1 WHAT SOURCE/RECEPTOR RELATIONSHIPS ARE OF INTEREST?

There is a surprising amount of confusion about how deposition (either wet or dry) at a receptor site may be related to emission from a source. Some of the confusion reflects the complexity of the processes, but some results from a failure to specify exactly what relationships between sources and receptors are at issue. The following need to be specified if the relationship is to be unambiguous:

- The emitted substance of concern and the amounts of relevant co-emitted species, (i.e. species which might participate in the production or depletion of oxidants).
- The background levels of the emitted substance and other relevant species (oxidants).
- The meteorological conditions affecting transport and deposition.
- The nature of the deposition of concern, wet, dry, or total.

In very general terms, for typical sources and receptors in the eastern United States, the dependence on background levels and on meteorology may be summarized by a simple classification of source/receptor relationships into four types based on whether one or many sources are considered and whether one or many receptor sites (localized within about 10 to 30 km) are considered.

Type I. One Source/One Receptor: Except for relatively short distances (usually less than 50 km even for short periods of time), the contribution of a particular emission source, even a large power plant, to background (ambient) levels is small. Consequently, in a type I source/receptor relationship it is appropriate to specify background levels independently from specifying characteristics of the source. The actual contribution of the source to deposition at the chosen receptor site will be very sensitive to the detailed specification of meteorological conditions. This is particularly true for wet deposition, where the variation in contribution from one year to another may be an order of magnitude or more. The variability results from two effects: most of the deposition will occur during only a few rain storms, and they are likely to have considerable local variation in duration and intensity; the actual path taken by the pollutants on a particular occasion will be sensitive to small variations in wind direction.

Type II. One Source/Many Receptors: Again, because there is only one source, the background in a type II source/receptor relationship can be specified independently from the source specification. In this case, however, it can be hoped that much of the dependence on meteorological variability will be averaged away when considering the average contribution over a substantial region. The averaging should smooth out the fluctuation in the path the pollutants follow and the local variability of rainstorms. Only broad-scale variation in annual rainfall or annual storm paths should remain.

Type III. Many Sources/One Receptor: Once we are considering many sources, the contribution of the sources to background cannot be neglected even at large distances. In fact, for a large enough group of sources, the sources may be responsible for almost all of the "background". Consequently, any dependence of oxidation rates, etc., on the levels of emitted substances and relevant co-emitted species must be included in the source/receptor relationship. Local variability in meteorology at the receptor site may still be important, particularly variation in rainfall intensity, duration, and season of occurrence.



Type IV. Many Sources/Many Receptors: For evaluation of acid deposition policies in the eastern United States, these relationships are probably most important. As with type III relationships, background cannot be specified independent of the source specification. As with type II relationships, some but not all meteorological variation will be averaged away on a year-to-year basis.

Only for the case of type III and type IV relationships are empirical data presently available. Since deposition measurements combine the contributions from all sources, single sources contribute too little to average deposition at a receptor site to provide an unambiguous signal. Unfortunately, as we have noted in Section A.2.1, there are not enough long term data to detect with confidence the effects of even changes in emissions. Nor are emissions well enough specified (see Section A.2.7.6) for the current data to be adequate to provide more than qualitative estimates of mass for wet deposition, while amounts dry deposited are still largely unmeasured.

#### B.1.2 ARE SOURCE/RECEPTOR RELATIONSHIPS EXPECTED TO BE LINEAR? [CARP A-4.4.3]

As is described below, some non-linearity is to be expected in relationships between deposition at a receptor site and emission from a source. However, for most type IV source/receptor relationships over periods of years, the authors believe the non-linearities are likely to be small, i.e., smaller than other uncertainties. In practical terms, a source/receptor relationship is useful if it can be used to predict a change in the deposition at the receptor site resulting from a change in the emission at the source site. Until very recently most modeling of acid emissions and deposition and most policy analyses have explicitly or implicitly assumed that the connection between emissions and deposition, however it depends on location and time, is linear: that is a change of X percent in the emission of sulfur from a source site or sites will result in a change of X percent in the deposition of sulfur attributable to the source(s) at a receptor site or sites. This assumption has generated a considerable amount of controversy often, as we shall see, based on disagreements over what are the appropriate source/receptor relations and what is assumed to be held constant when a change of X percent in emissions is proposed.

After all, any sulfur that is emitted will be deposited some place and the deposition processes appear to be largely linear. However, there are two species of sulfur compounds,  $\text{SO}_2$  and  $\text{SO}_4$ , that can be deposited at different rates; if the transformation of  $\text{SO}_2$  to sulfate is not proportional to the amount of  $\text{SO}_2$  present, then the spatial pattern of deposition and the relative amounts of sulfur wet and dry deposited may be altered. In particular, if a reduction in  $\text{SO}_2$  emissions leads to a smaller than proportionate reduction in sulfate production (as seems likely) the result will be a greater than proportionate reduction in dry deposition of sulfur (this will be more noticeable nearer the source) and a smaller than proportionate reduction in wet deposition of sulfur and the amount of sulfur carried across boundaries.

How significant could such non-linearity be to deposition patterns. Three considerations are important: how far from linear is the transformation

from  $\text{SO}_2$  to  $\text{SO}_4$ ; what is assumed to be held fixed in the source/receptor relationship under consideration; and, what is the relative importance of  $\text{SO}_2$  to  $\text{SO}_4$  in deposition at the sites.

The three most important processes for oxidation of  $\text{SO}_2$  (see CARP A-4, and CAD, Section III.A.2.5; the discussion here is based on Durham and Demerjian 1984) are gas-phase reaction with the OH radical, aqueous-phase reactions at low pH with  $\text{H}_2\text{O}_2$ , and aqueous-phase reaction at high pH with  $\text{O}_3$  and other oxidants. Each of these processes has a different dependence on the amount of  $\text{SO}_2$  present. Concentrations of the OH radical in the atmosphere appear to be quite insensitive to concentrations of the other pollutants present. Hence gas-phase oxidation of  $\text{SO}_2$  will be essentially proportional to the amount of  $\text{SO}_2$  present and thus linear, independent even of the amount of co-emitted species or background pollutants. It will, however, exhibit a marked dependence on time of day, season, latitude, and meteorological conditions.

Aqueous-phase reactions with  $\text{H}_2\text{O}_2$  proceed rapidly, independent of the pH, until either the  $\text{SO}_2$  or  $\text{H}_2\text{O}_2$  oxidant present is substantially consumed. If there is enough  $\text{H}_2\text{O}_2$  present for the reaction to consume  $\text{SO}_2$ , then the amount of  $\text{SO}_2$  oxidized by this mechanism is determined by the proportion of the  $\text{SO}_2$  that contacts with the aqueous solution, and the reaction is again linear. If, however, insufficient  $\text{H}_2\text{O}_2$  is present to oxidize all of the dissolved  $\text{SO}_2$ , the relative amount of  $\text{SO}_2$  oxidized can depend on the amount of  $\text{H}_2\text{O}_2$  present. This possibility, called oxidant limitation, is illustrated in Figure III.28. The figure shows a hypothetical case 1, the "present situation" in which the amount of sulfate is determined by the amount of oxidant ( $\text{H}_2\text{O}_2$ ) initially present and the available oxidant is substantially consumed by the transformation process. In the hypothetical case 2, the initial amount of  $\text{SO}_2$  is decreased but the initial amount of oxidant is the same. By assumption the initial amount of oxidant determines the amount of sulfate produced, so this will be the same for case 1 and case 2, and the reduction in the initial amount of  $\text{SO}_2$  translates only into a reduction in the final amount of  $\text{SO}_2$ .

Because the rates for aqueous-phase reactions involving  $\text{O}_3$  and other oxidants depend on pH, they too can exhibit non-linearity. As the dissolved  $\text{SO}_2$  is oxidized to sulfuric acid, the pH will decline, and the reaction will proceed more slowly.

It is likely that aqueous-phase reactions with  $\text{H}_2\text{O}_2$  are most important for oxidation in the eastern United States, with gas phase reactions producing a significant fraction of the sulfate also. Enormous variability occurs in the amounts of  $\text{H}_2\text{O}_2$  measured and in the aqueous phase reaction rates. It is likely, therefore, that oxidant limitation is sometimes significant and sometimes not, but there is little quantitative information available, at present, to specify for what fraction of the time, and for what regions.

When considering many sources, Type III or Type IV source/receptor relations, there may sometimes be changes in the emission of nitrogen oxides and hydrocarbons which can affect the background level of oxidants ( $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , not OH). Hence, to estimate the amount of  $\text{SO}_2$  converted to  $\text{SO}_4$

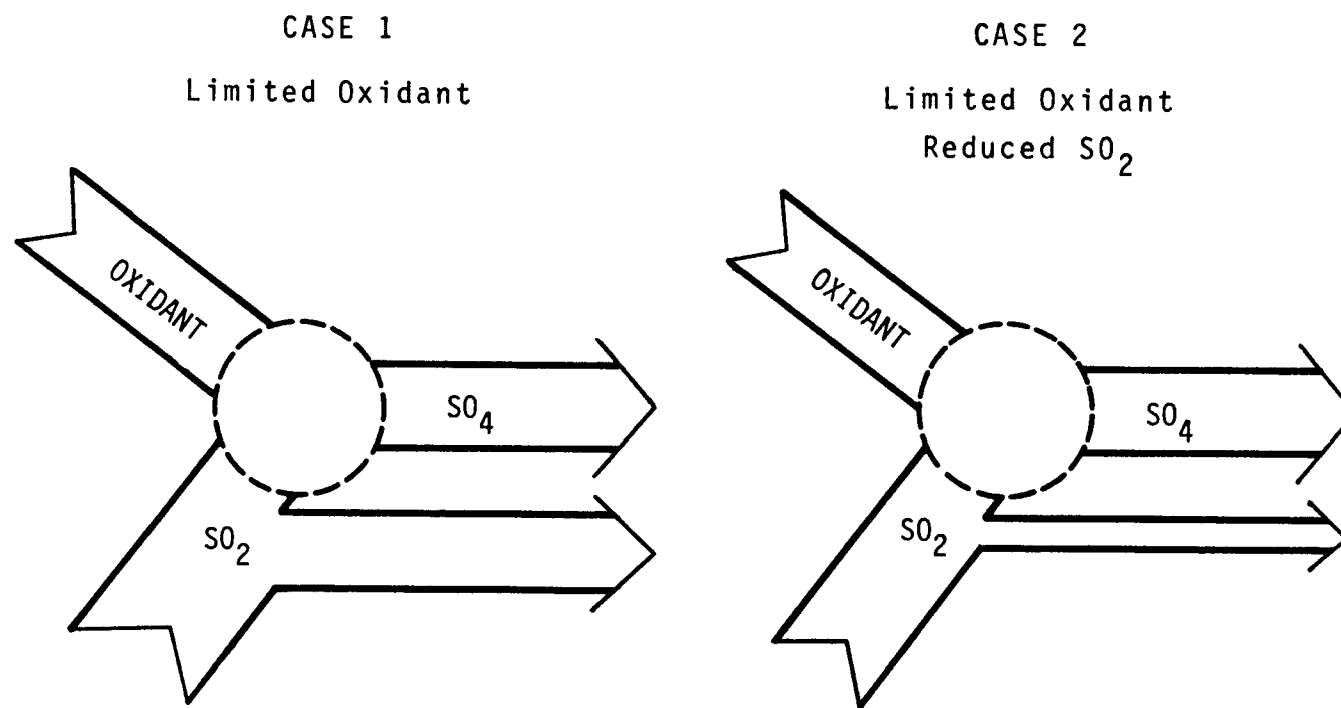


Figure III.28 Illustration of the possibility that a reduction in  $\text{SO}_2$  may not proportionately reduce  $\text{SO}_4$ .

after a substantial reduction in  $\text{SO}_2$  emissions, one must also specify whether the reduction affected other species.

Finally, we turn to the question, what is the effect of non-linearities in oxidation on deposition. Over most of the eastern United States, the mass of sulfur in the form of  $\text{SO}_2$  is greater than the mass of sulfur in sulfate.  $\text{SO}_2$  is significantly more efficiently dry deposited than sulfate; sulfate appears to be more efficiently wet deposited than  $\text{SO}_2$ , but the relative efficiencies are not well known. Because oxidant limitation appears significant at some times and at some locations, the effect of a reduction of X percent in  $\text{SO}_2$  emissions will be  $\text{SO}_2$  concentrations in the air that are reduced somewhat more than X percent and sulfate concentrations that are reduced somewhat less than X percent. The result will be a greater than X percent reduction of dry deposition (for most sites) and a reduction in wet deposition that might be somewhat more or somewhat less than X percent depending on the relative concentrations of  $\text{SO}_2$  and  $\text{SO}_4$  above the site and on the relative scavenging efficiencies. For most sites the change in total deposition resulting from a broad scale change in emissions is likely to be close to proportional.

The case of nitrogen compounds is somewhat different. Here the oxidized form  $\text{HNO}_3$  is dry deposited more readily. The basic oxidizing reaction appears to be in the gas phase with the OH radical, so one might expect linearity in  $\text{HNO}_3$  production; however, the existence of numerous nitrogen oxides and the reversibility of many of the production reactions makes this assumption dubious. There is no particular reason to expect strong non-linearities in deposition, however.

#### B.1.3 HOW ARE MODELS FOR LONG-RANGE TRANSPORT AND DEPOSITION USEFUL? [CARP A-9]

A constant theme of this section has been that the processes of transport, transformation, and deposition are complicated and inextricably linked in acid deposition. The complexity and linkages have spurred the development of many numerical models using computers which simulate the processes from emission to deposition. Such models provide an explicit framework to account for the complexities in the processes and the links between the various stages.

Models are very useful in learning how significant one aspect of the acid deposition problem is to another aspect. Models can provide answers to such questions as, how does the location of a source affect the amount of material deposited at a receptor site? What difference exists between the deposition pattern produced by tall stack and short stack emissions? What is the seasonal variation to be expected in deposition? How large are the uncertainties introduced by inadequate data on dry deposition rates, oxidation rates, concentrations, or amounts dry deposited?

How well can present day models answer such questions? They can do pretty well, in that they provide useful information otherwise difficult to obtain or information corroborating other answers that also have serious

uncertainties. It is important, however, not to have unreasonable expectations of model calculations.

It is unreasonable to expect any of the currently used models to serve as a master model that can numerically simulate all aspects of acid deposition; such a model would be very complex, and we are only gradually learning through the current research and model development process the most important intermediate processes and how to characterize them. As yet, no adequate database exists either to verify model conclusions or to provide the necessary internal parameters. Hence, a large number of models, each with different assumptions and different approaches to calculations are now available. Each model has been designed to be appropriate for answering certain sorts of questions, and, as a consequence, each is inappropriate for other questions.

It is unreasonable to expect different models to give exactly the same answers to questions; in particular, it is unreasonable to expect a model for which the question is inappropriate to agree with one for which it is appropriate.

It is unreasonable to expect quantitative answers to questions to be accurate to more than one significant figure; indeed, for many questions answers to within a factor of two or four are all that should be expected even from appropriate models. No amount of clever numerical simulation can make up for the lack of empirical data on key processes, the lack of data for testing model conclusions, or the lack of relevant input conditions on emissions and meteorology. An interesting example of what models can do in answering hard questions has been described by Husar (1983), based on the Memorandum of Intent comparison of models. The questions are 1) what is the relative importance of four broad source regions to total sulfur deposition in the Adirondacks? and, 2) what are the amounts dry and wet deposited? The answers come from three models, (AES, the Atmospheric Environment Service Long-Range Transport Model, Olson et al. 1979; ASTRAP, Advanced Statistical Trajectory Regional Air Pollution Model, Shannon 1981; and CAPITA, Center for Air Pollution Impact and Trends Analysis, Monte Carlo Model, Patterson et al. 1981). The answers provided by the three models to question 1 are shown in Figure III.29; agreement among the models on the percentages for the separate regions is within a factor of two. The answers to question 2 are shown in Table III.9. Agreement among the models is better than within a factor of two. According to Husar (one of the developers of the CAPITA Model) the models reproduce the sulfate aerosol concentration in the Adirondacks to about a factor of two; he judges the relative contributions of the four source regions to be correctly specified to a factor of two to four. Because these models, and others, have their parameters chosen to reproduce current emission and wet deposition data, their quantitative predictions using hypothetical emissions may be even less correctly specified.

How can models be tested and improved? What are the prospects for improvement? Obviously a great need exists for a much larger database on concentrations of pollutants, on dry deposition, and on the processes described in Part III.A of this review. Very important also is continued elaboration of models and the testing of one against another to determine the

# Dry+Wet Deposition Estimates by Three MOI Models

% contribution of each source region to Adirondacks

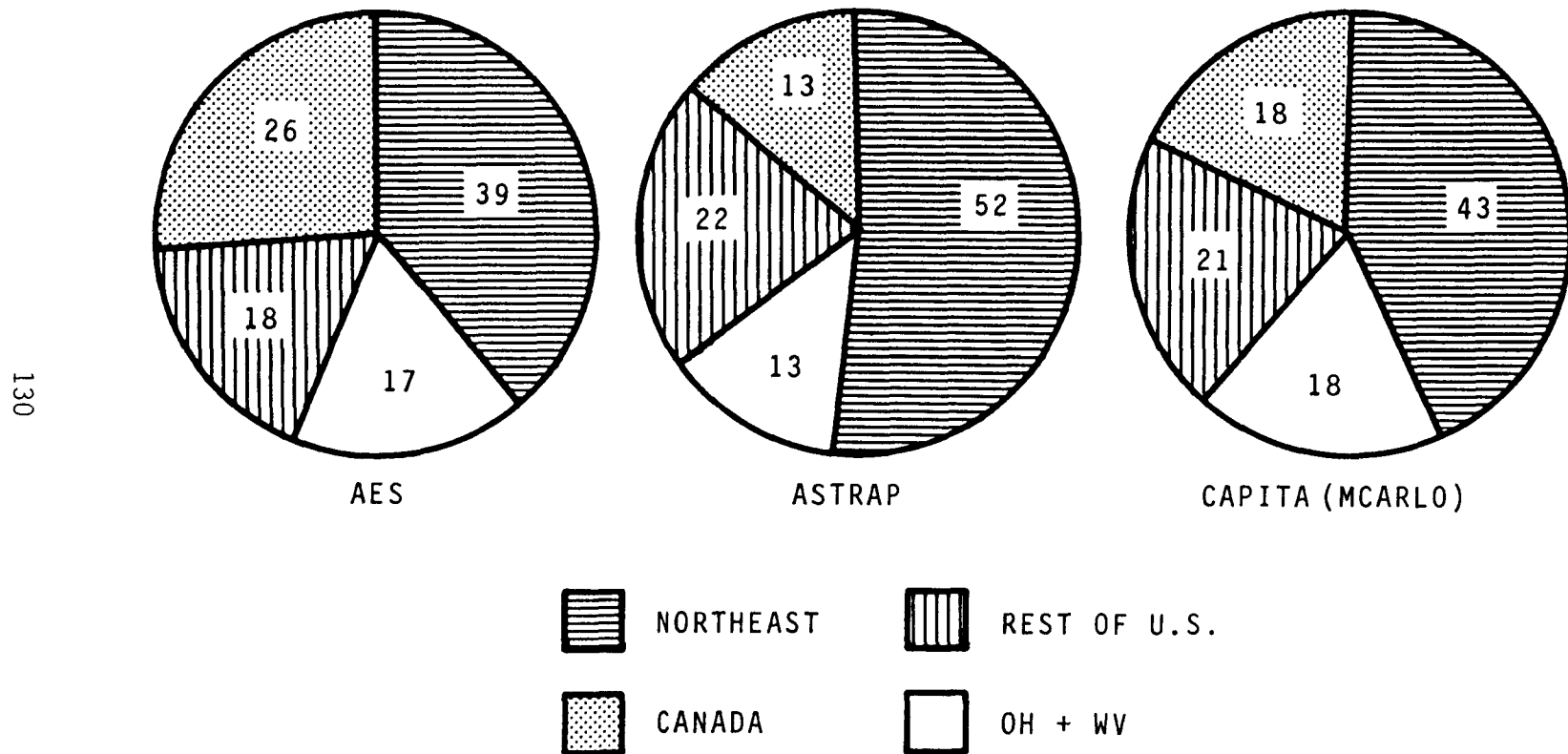


Figure III.29 Source attribution of dry plus wet deposition in the Adirondacks by three MOI models.

TABLE III.9 DRY AND WET DEPOSITION ESTIMATES  
AT THE ADIRONDACKS BY THREE MOI MODELS

Model	Dry Deposition	Wet Deposition	Total Deposition
AES	1.39 g m <sup>-2</sup> yr <sup>-1</sup> 51%	1.44 g m <sup>-2</sup> yr <sup>-1</sup> 49%	2.83 g m <sup>-2</sup> yr <sup>-1</sup> 100%
ASTRAP	1.72 g m <sup>-2</sup> yr <sup>-1</sup> 44%	1.35 g m <sup>-2</sup> yr <sup>-1</sup> 56%	3.07 g m <sup>-2</sup> yr <sup>-1</sup> 100%
MCARLO	2.42 g m <sup>-2</sup> yr <sup>-1</sup> 69%	1.08 g m <sup>-2</sup> yr <sup>-1</sup> 31%	3.5 g m <sup>-2</sup> yr <sup>-1</sup> 100%

sensitivity of results to the choice of parameters, assumptions, and calculational methods. Thus, deposition pattern and amounts deposited may be quite sensitive to day/night changes in dry deposition velocities; yet yearly average deposition may be as well or as poorly reproduced by a model which does not incorporate such changes, and the added complexity in the model might not be relevant to some other question in another context.

Air quality models can be classified by their treatment of the following: [CARP A-9.1]

- Frame of Reference
- Temporal and spatial scale
- Treatment of turbulent wind motion
- Transport
- Chemical transformation
- Removal mechanisms

Frame of Reference. Most long range transport models are written either using a coordinate system (frame of reference) that is fixed on the surface of the Earth--such models are called Eulerian models--or using a coordinate system fixed on the moving air parcel as it moves downwind from a source or as its history is traced upwind from a receptor--these models are called Lagrangian models. Lagrangian models at the present stage of model development and verification are more practical for estimating single source/multiple receptor (type II) and multiple source/single receptor (type III) source/receptor relationships. Eulerian models require much more extensive computation; however, once the difficulties of extracting source/receptor information from these models has been resolved, they may ultimately be better suited for providing these answers because they provide a natural framework for taking into account non-linearities and topography, and because the input meteorological information is necessarily measured in the Earth's reference frame.

Spatial/Temporal Scales. The spatial scales in acid deposition are conventionally defined as short-range (less than 100 km), intermediate range (100 km to 500 km) and long-range (greater than 500 km), although different authors often choose different boundaries. Models developed specifically for application to acid deposition generally cover deposition over the scale of interest in this problem, namely both intermediate and long-range transport. Occasionally models developed for other purposes may be used to answer specific questions. Thus, short-range transport models extended to intermediate distances may provide information about effects of detailed meteorology or complexity of terrain. Continental or global-scale climatological models may provide information about the effect of large scale weather patterns. Both short duration (one day to one week) and long-term average deposition patterns are of interest, and models have been specifically designed for each, or both. Questions about long-term averages may be more interesting for effects; short-term predictions may be more readily tested experimentally.

Turbulence. Random fluctuations in wind speed and direction are responsible for dilution and mixing of pollutants in air. The amount of turbulence to be



expected will depend on season and time of day, on terrain, and on other meteorological variables. Models may account for fluctuations either implicitly through defining a well-mixed volume or through one of various parameterizations of turbulent diffusion.

Transport. Pollutants travel with the wind. The available information on wind speed and direction is the network of ground level weather stations plus a sparse network of upper air measuring stations. The models differ in how they cope with the problem of estimating wind shear (variation of wind direction and speed with height) and how they interpolate between wind observations. An important difference is the role of the weather data themselves (this applies to other aspects, wet deposition especially): one use of models is to simulate actual weather conditions over some period of time (for which there might be deposition data); another possibility is to use synthetic weather, based on historical weather measurements, to estimate the deposition to be expected on the average or to determine the sensitivity of deposition patterns to variation in weather conditions for a particular year.

Chemical Transformations. In the simplest models, the complexity described in Section A.2.5 is boiled down to a single number, an average rate of conversion of SO<sub>2</sub> to sulfate. A more elaborate treatment allows for the dependence of this rate on time of day, and on meteorological conditions such as cloud cover. In principle the role of nitrogen oxides and other species can also be taken into account. In practice, even the modeling of simple nitrogen oxide transformations has lagged, and treatment of complex systems is practically nonexistent.

Removal Mechanisms. Dry deposition is most simply parameterized by average deposition velocities for SO<sub>2</sub> and sulfate. Complexities such as variation with time of day or season and dependence on region or terrain have been modeled. None of these approaches can resolve the large uncertainties discussed in Sections A.2.1.7 and A.2.3.

Wet deposition may be parameterized by either a scavenging rate and/or a washout ratio--a single parameter relating the amount of pollutant in rain to the concentration in the air. A major problem in the use of such parameterizations, aside from the fact that the parameters are very poorly known (see Section 2.4), is that the amount scavenged depends on the nature of the storm and that storm type is a function of other variables such as wind affecting transport, and season and cloud cover affecting oxidation rates.

#### B.1.4 WHAT IS THE RELATIVE IMPORTANCE OF DISTANT AND SHORT-RANGE SOURCES TO DEPOSITION IN SENSITIVE REGIONS? [CARP A-3.5]

For the effects of most concern--harm to forests or to aquatic ecosystems--most of the sensitive areas, forest stands or lakes and streams are spread out in remote areas. Consequently, local sources at distances less than 50 km are not significant except in isolated cases. Answering the question, which are more important, intermediate range sources (50-500 km away) or distant sources (>500 km), is more difficult and requires further specification. When considering a representative source in the eastern United

States, for most locations, we know the source can contribute to deposition at sensitive receptor areas that are both at distant and intermediate range. Contributions in these two categories, when averaged over many sources, are likely to be comparable since a typical net travel distance for an emitted sulfur atom is roughly 500 km [CARP A-3.3.3]. Of the three broad regions identified as of most concern, the Adirondack and New England Mountains receive roughly equal amounts from distant and intermediate-range sources, the southern Appalachians receive most deposition from intermediate-range sources, and Maine and eastern Canada receive most deposition from distant sources.

It is interesting to look at the basis for these conclusions. Thus, the following items need to be considered:

Relative Density of Sources-If there are practically no sources within 500 km of the sensitive region, only distant sources will be important. The emissions map (Figure III.22) shows substantial concentrations of sources centered around the Ohio Valley and around the mid-Atlantic urban areas. Close to those regions these sources surely dominate; downwind more than 500 km, they will still be important.

Geometry and Plume Dispersion-If one considers a single receptor point in a sensitive region (type III source/receptor relationship), then a nearby source will contribute more than a distant source of the same emission strength, just because the nearby plume will encounter the receptor point in a less depleted state. That does not mean, however, that the distant source necessarily contributes less to all sensitive areas (type II source/receptor relationship); it may contribute smaller amounts to each of more areas.

Dry Deposition-The crucial parameters determining how much of the sulfur from a source is deposited relatively close to the source are the rate of dry deposition of  $\text{SO}_2$ , the rate for the competing process of oxidation to sulfate, and the amount of vertical mixing. As we have seen these rates are highly variable and not well known. If most of the plume sulfur is dry deposited within the first 24 h then there won't be very much sulfur available for transport distances greater than 500 km. Model calculations for a St. Louis Power Plant Plume [CARP A-3.4] suggest that "perhaps more than half of the sulfur released from a 200 m stack may be deposited, wet and dry, within 500 km of the source in the summer." In the Ohio River Valley with less frequent nocturnal jets and generally lighter winds, the effective transport ranges are likely to be shorter. Winter residence times and distances traveled are likely to be substantially greater than summer ones.

The numerical values in these calculations depend on the specific nature of the model and the choice of dry deposition and oxidation rate parameters. The qualitative result that long-range and intermediate-range deposition are roughly comparable on an annual basis for emissions from a typical source is not sensitive to most typical choices of the model and its parameters. This result is also consistent with the estimate (Section B.2.3) that the average atmospheric residence time for a sulfur atom is 1 to 3 days.

The effect of the actual distribution of emissions strengths can be included in model calculations as well. The results for the ASTRAP model [CARP A-3.5] using current emission data and summer 1980 meteorological data are that the boundary where distant and intermediate-range sources contribute equal amounts to total sulfur deposition is a line running roughly southeast from the northwest corner of New England. The precise location of the boundary line is very sensitive to the choice of model and model parameters; however, the qualitative conclusion that over much of the Northeast distant and intermediate-range sources contribute comparable amounts seems reasonably secure. Of the sensitive regions, distant and intermediate-range sources appear to be of comparable importance to the Adirondack and New England mountain areas; distant sources, more important to remote areas in eastern Canada and Maine; and intermediate range sources, more important to the southern Appalachians.

#### B.1.5 HOW DO THE DEPOSITION PATTERNS PRODUCED BY TALL STACKS DIFFER FROM THOSE PRODUCED BY LOW LEVEL (URBAN) RELEASES? [CARP A-3.4]

The single source modeling discussed on the previous page was for the power plant emissions from a 200 m stack located in St. Louis. One striking change in the nature of U.S. SO<sub>2</sub> emissions has been the large increase in the proportion of emissions released from stacks 200 m or higher (see Figure III.24). What is the effect of stack height on the amount of sulfur transported long distances?

It seems surprising that a difference of a few hundred meters in the height of release could make a difference when we are considering transport over more than one hundred or even one thousand kilometers. However, there is a mechanism that can separate emissions from short and tall stacks--the variation in height of the mixing layer, the lower layer of the atmosphere in which there is essentially unlimited mixing of substances in the air. On a summer day the mixing layer is one to two kilometers thick; air mixes rapidly within that layer, so even plumes released several hundred meters up will not differ significantly in their contact with the ground from plumes emitted lower. In winter, however, the mixing layer may be considerably shallower; much or all of the release from a tall stack may be above that layer and travel many hundreds of kilometers before coming into contact with the ground. In addition, shallow nocturnal inversions may completely decouple elevated plumes from surfaces, so there will be essentially no dry deposition until the inversion is dissipated the next day. Even though nighttime and winter oxidation rates are lower than those on a summer day, the ratio of sulfate produced to SO<sub>2</sub> dry deposited can be appreciably greater since the limited contact of the plume with the ground means there will be much less dry deposition. This mechanism is confirmed in field observation of power plant plumes.

To estimate the magnitude of this effect, the amount of additional sulfate that will be deposited and the reduction in SO<sub>2</sub> dry deposition as stack height is increased, it is necessary to know: 1) the distribution of mixing heights over time and space, 2) oxidation rates over time and space, and 3) dry deposition rates over time and space. There is a considerable amount of data on the temporal distribution of mixing heights. Oxidation rates and dry

deposition rates, largely uncertain, are parameterized in the models. Information for the St. Louis area has been used to model tall stacks and low level (urban) plumes over the year. The prediction is that the amount of sulfur carried long distances by tall stack emissions is enhanced nearly 25 to 50 percent compared to urban plumes. Modeling of Ohio River Valley sources gives similar results. [CARP A-3.4]

#### B.1.6 HOW IMPORTANT IS THE EMISSION OF PRIMARY SULFATE?

It is unimportant. The previous discussion (Sections B.1.1.2, B.1.1.4, B.1.1.5) has indicated that sulfate has a privileged role in the long-range transport of sulfur compounds because it is less readily dry deposited near its source. Typical model calculations [CARP A-3.4] suggest that on average only 20 to 40 percent of  $\text{SO}_2$  is oxidized to sulfate. This has prompted suggestions that even comparatively small amounts of primary sulfate emissions might be important in acidic deposition, especially since for some oil-fired boilers, as much as 15 percent of the sulfur is released as primary sulfate, and that is a percentage comparable to the percentage of secondary sulfate produced from the  $\text{SO}_2$  emissions of these sources.

The amounts of primary sulfate released, however, are too small for primary sulfate to merit special attention. Sulfate does not predominate in short- or intermediate-range deposition;  $\text{SO}_2$  is more important. For long-range transport it is necessary to consider many sources; primary sulfates represent less than 3 percent of sulfur emission and are thus a small fraction of a regional sulfate budget.

#### B.1.7 HOW DO SOURCE/RECEPTOR RELATIONS FOR NITROGEN OXIDES COMPARE WITH THOSE FOR SULFUR OXIDES?

Several important differences affect the analysis of the long range transport of nitrogen oxides. Most important is that much less is known about the key parameters for nitrogen oxides. Emissions, for which motor vehicles are an important component, are less well determined. Wet deposition has been less extensively studied. Dry deposition rates are at least as poorly known as those for  $\text{SO}_2$  and sulfate, and the chemical reactions in the atmosphere and their dependence on secondary species are both more complex and less thoroughly studied than those that lead to the oxidation of  $\text{SO}_2$ .

Even amidst this ignorance a few generalizations are possible. A substantially higher percentage of  $\text{NO}_x$  emissions are from low-level urban sources, especially motor vehicles (see Section A.2.7.3). Oxidation of  $\text{NO}_2$  is faster than oxidation of  $\text{SO}_2$ . Dry deposition velocities for  $\text{HNO}_3$  are higher than those for  $\text{SO}_2$  and  $\text{NO}_2$ , which are probably roughly comparable. The combined effect of these two differences is likely to be that source/receptor relationships for nitrogen oxides are likely to be similar to those for sulfur oxides but to have a higher percentage of short-range deposition.

#### B.1.8 HAS THE INSTALLATION OF PARTICULATE CONTROLS ON POWER PLANTS AND OTHER SOURCES CONTRIBUTED TO ACIDIFICATION?

No. It has been suggested that fly ash from coal burning is a significant source of neutralizing material. Calcium oxide, in particular, can form a significant fraction of the fly ash content. It is now becoming routine to install particulate controls that capture most of those emissions. Even if such controls were not in place, the amount of CaO and other potentially neutralizing compounds transported significant distances from the source would be small, since most of the mass is in large particles with a short atmospheric residence time. Those compounds are not sufficiently reactive to scavenge an appreciable fraction of the emitted sulfur while they remain in the plume.

#### B.1.9. HOW WELL CAN ACIDITY BE PREDICTED, KNOWING EMISSIONS?

Not very well. The acidity is even more difficult to predict than sulfate or nitrate concentrations in precipitation. The acidity depends on the amounts of both sulfate and nitrate ions present. It also depends on the amount of neutralizing material present, and it is clear from field studies of aqueous-phase oxidation that neutralization plays an important role in determining acidity. Neutralizing substances have different sources and transport properties from sulfate and nitrate. At present, the patterns for acidity, sulfate deposition, and nitrate deposition appear quite similar (compare Figures III.4, III.5, III.7) in the eastern United States while they appear largely uncorrelated in the West.

#### B.2 WHAT ARE THE OVERALL BUDGETS FOR ACIDIFYING SUBSTANCES?

To complete our review of the atmospheric sciences aspects of the acid deposition problem we summarize in the next subsection what is known about the total amounts of sulfur and nitrogen emitted, carried in the air, and wet or dry deposited. Based on these totals and the information developed in parts A and B.1, we go on to consider how present deposition amounts compare with the deposition expected from natural sources, with deposition in the recent past, and with other deposition changes. Information on emissions provides insight for determining what constitutes a significant increase or decrease in emissions and for determining what source categories are most important. Information on atmospheric concentrations can be used to estimate atmospheric residence times for the substances of interests. Residence times are directly linked to the important processes of deposition, chemical transformations, and transport from one region to another. Information on amounts deposited is essential for establishing what is a significant input to a "sensitive" system, and for determining appropriate time scales for changes in affected systems.

#### B.2.1 WHAT ARE THE BEST ESTIMATES OF SULFUR AND NITROGEN OXIDE BUDGETS FOR THE EASTERN UNITED STATES?

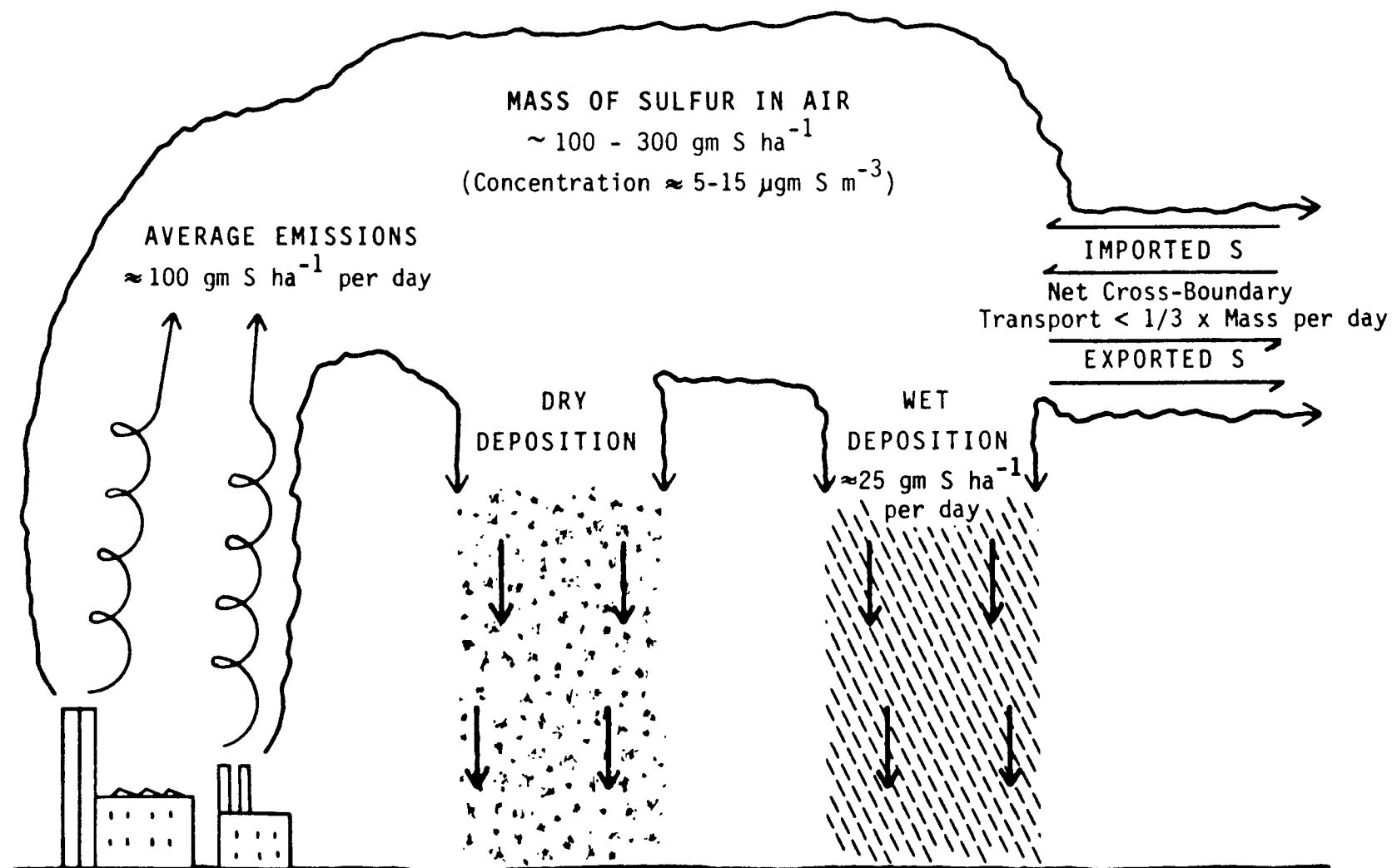
Sulfur. Three fates are possible for a sulfur atom emitted in the eastern United States. It can be wet deposited in the eastern United States; it can be dry deposited in the eastern United States; or it can be blown across a

boundary, the Mississippi River, the Canadian Border, the Atlantic Ocean, or the Gulf of Mexico, and subsequently wet or dry deposited. At present it is not possible to say that any of these three fates is more likely than another, and various models estimate each contribution to be between 15 and 50 percent of the sulfur emitted.

Even with limited data, some further generalizations are possible. Because there is no significant long-term build up of sulfur in the atmosphere, the average amount of sulfur emitted in the eastern United States per day will, in general, equal the sum of the average amounts of sulfur wet deposited and dry deposited in the eastern United States and the net average amount of sulfur exported across boundaries. Note that because measurements of sulfur atoms deposited or in the air do not include labels locating the source of the sulfur, to have the sum come out right, we must use the net amount transported, the amount of eastern U.S. sulfur exported minus the amount of non-eastern U.S. sulfur imported. Since emissions from the states just west of the Mississippi, and Canadian emissions across the eastern U.S. border are each only about 20 percent of Eastern emissions, and since the concentrations across these borders are lower than the concentrations over much of the eastern United States, the net transport summed over all borders appears to be dominated by eastern U.S. exports.

The equality between emissions and the sum of deposition and transport provides a simple picture of the sulfur budget, shown in Figure III.30. Sulfur is released into the atmosphere, spends an average amount of time in the 2 km of air directly above the eastern United States and then is wet or dry deposited or carried across a boundary. Reasonably certain (+ 30%) data are available to document emissions and wet deposition; poor data (+ 300% uncertainty) exist for concentrations; and no monitoring data exist for dry deposition and net transport. Although scant direct information on cross-boundary transport exists, observations that the average transport wind velocity (the average distance per day an air parcel travels) is roughly 500 km per day and that no concentration build ups occur at borders imply that net transboundary transport per day from the eastern United States is less than 1/3 the mass of sulfur in the atmosphere above the eastern United States. (Note: The eastern United States is very approximately a square, 1500 km to a side. Thus, 500 km/day/1500 km  $\approx$  1 per 3 days.) This information has been used to fill in the amounts shown in Figure III.30. For a more detailed budget for the eastern North American continent based on additional assumptions, including a closer look at transport into the Atlantic, see Galloway et al. (1984). Since the average residence time in the air of a given sulfur atom is 1 to 3 days, average amounts emitted and deposited per day are convenient for considering atmospheric processes, while for effects, yearly amounts are probably more interesting. In Table III.10, we show the conversion from amounts per day to amounts per year--thus 100 gm S per ha per day corresponds approximately to 40 kg S per ha per year.

Further information on sulfur concentrations in the atmosphere offers the possibility of refining these estimates considerably and should be a high priority for future research. If, for example, the average concentration of sulfur in air turns out to be at the low end of the observed range, near 5  $\mu\text{g S m}^{-3}$ , then the average mass of sulfur above the Earth's surface will



$$\text{AVERAGE EMISSIONS PER DAY} = \text{AVERAGE} [\text{MASS IN AIR} / \text{RESIDENCE TIME}] =$$

$$\text{AVERAGE} [\text{DRY DEPOSITION} + \text{WET DEPOSITION} + \text{NET CROSS-BOUNDARY}] \text{ PER DAY}$$

Figure III.30 Illustration of sulfur mass balance for the Eastern United States.

TABLE III.10 COMPARISON OF DAILY AND ANNUAL  
EMISSIONS AND DEPOSITION ESTIMATES

	Eastern U.S. Total Annual	Annual ha <sup>-1</sup>	Daily ha <sup>-1</sup>
S Emissions	9 Tg $\pm$ 30%	40 kg $\pm$ 30%	100 g $\pm$ 30%
S Wet Deposition	2.2 Tg $\pm$ 30%	10 kg $\pm$ 30%	25 g $\pm$ 30%
N Emissions	4 Tg $\pm$ 40%	18 kg $\pm$ 40%	40 g $\pm$ 40%
N Wet Deposition	1 Tg $\pm$ 30%	4.5 kg $\pm$ 30%	10 g $\pm$ 90%



be approximately  $100 \text{ g S ha}^{-1}$ . Transboundary transport can account for at most a third of the sulfur emitted; therefore, dry deposition would have to account for at least a third of the sulfur.

We may call this Case I. The mass balance equation then is

$$\begin{aligned}\text{Case I: Average Emissions} &= \text{Average [Mass in Air/Residence Time]} \\ &= \text{Average [Dry Dep. + Wet Dep. + Net Cross Bds]}\end{aligned}$$

$$100 \text{ g S/day} = [100 \text{ g S/1 day}] = [>30 \text{ g} + 20\text{--}35 \text{ g} + <35 \text{ g}] \text{ per day.}$$

If concentrations of S in air are higher at the upper end of the observed range, say  $15 \mu\text{g S m}^{-3}$  or  $300 \text{ g S ha}^{-1}$ , which we call Case II, the mass balance becomes

Case II:

$$100 \text{ g S/day} = [300 \text{ g S/3 days}] = [>0 + 20\text{--}35 \text{ g} + <100 \text{ g}] \text{ per day.}$$

In Case II, no immediate generalization about the relative amounts of dry deposition and net transboundary transport can be made. The two observations, (1) the average time between rainstorms is greater than 3 days, and (2) wet deposition accounts for at least 20 percent of the emitted sulfur, provide a lower limit for the average concentration of S in air of  $3 \mu\text{g m}^{-3}$ , independent of the (limited) direct measurements of concentration.

Nitrogen Oxides. Budget estimates for nitrogen oxides are even cruder than those for sulfur oxides. The amounts emitted are more uncertain, and the concentrations in air are even more poorly determined than sulfur concentrations; in particular no counterpart to Figure III.10 exists. Annual emissions of nitrogen oxides for the eastern United States in 1980 were approximately  $4 \pm 1.5 \text{ Tg N yr}^{-1}$  or  $18 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , or  $50 \text{ g N ha}^{-1} \text{ day}^{-1}$ . The average amount wet deposited in 1980 was approximately  $5 \pm 2 \text{ kg N ha}^{-1}$ . Since the ratio of nitrogen in nitrate to sulfur in sulfate wet deposited appears similar to the ratio of emitted nitrogen to emitted sulfur (See Figure III.8), it is likely that the proportions dry deposited and carried across boundaries will also be similar. However, higher proportions of sulfur at remote areas suggest that dry deposition may be a slightly larger fraction of the total for nitrogen oxides.

It is important to recognize that the apparent similarity between S and N emission and deposition ratios holds only for annual averages. Pronounced seasonal differences, previously illustrated in Figure III.9, must be accounted for in any more detailed analysis.

#### B.2.2 WHAT IS THE RELATIVE IMPORTANCE OF NATURAL AND ANTHROPOGENIC SOURCES TO DEPOSITION IN SENSITIVE REGIONS?

Sulfur. Most of the sulfur oxides deposited in eastern North America have an anthropogenic origin. Anthropogenic sources of sulfur oxides exceed natural sources in eastern North America by roughly a factor of 20 (Section A.2.7.5).

While there may not be a strict linear relationship between emitted sulfur dioxide and distant deposition, most emitted sulfur is transported substantial distances and is deposited in broad regional patterns (Sections A.2.3-A.2.6).

The contribution of various sources to regional deposition is roughly proportional to the amount of sulfur emitted (though location and stack height matter); thus electric utility power plant emissions probably account for slightly more than half of eastern sulfur deposition. Other major source categories are industrial boilers and metal smelting and processing.

In the western United States, anthropogenic emissions are at least 3 to 5 times natural sulfur emissions and contribute proportionately to deposition.

Nitrogen. Similar conclusions may be drawn for nitrogen oxides, with, however, greater uncertainties in the estimated level of natural emissions.

Acidity. Sulfate and nitrate account for practically all of the anions in precipitation in eastern North America. Since production of these ions from their precursors, almost entirely derived from anthropogenic sources, results in production of hydrogen ions, the acidity in precipitation must be largely attributable to human activities.

#### B.2.3 WHAT CAN BE CONCLUDED ABOUT DEPOSITION TRENDS FROM EMISSIONS TRENDS?

We have seen that there are not enough network data to support an estimate of historical trends in acid deposition. Although emissions estimates are markedly uncertain, the uncertainty in the relative amounts of emissions from one year to another should be substantially less than the uncertainty in overall emission amounts. Furthermore, projections of future emissions trends can be plausibly based on economic projections, fuel mix, and assumptions about regulatory impact. The question, then, concerns to what extent it is feasible to extrapolate from current deposition information to estimate deposition under different emissions conditions. There are two problems: one is establishing what current deposition is; the second is making the extrapolation.

As discussed in Section A.2.1, the observed year-to-year variation in wet deposition rates appears to be as much as 30 percent, so several years of network data will be needed to provide an adequate base estimate of current wet deposition rates. Also, dry deposition rates are very poorly known.

Although the relationship between emission and deposition appears roughly linear, provided background oxidant levels are kept unchanged, several changes in historical emissions cast doubt on the assumption that deposition in the past was the same percentage of emissions that it is at present. One is the trend toward the use of tall stacks (see Section A.2.7.4) which has probably increased the proportion of sulfate and the amount of long range transport. A second is the increase in nitrogen oxide emission which has had an undetermined effect on the availability of oxidants. A third is the change in the relative emission rates of different regions.

Emission of sulfur oxides has increased substantially in the southeastern United States; it has declined in the northeastern United States (see Figure III.23). At current levels of uncertainty in deposition amounts, it appears justifiable to extrapolate emissions trends in a broad region upwind, in estimating deposition trends; but high confidence should not be placed in such extrapolation, and it is likely that some non-linearity will appear when (and if) deposition data are known with greater precision.

#### B.2.4 HOW PREDICTABLE ARE REDUCTIONS IN DEPOSITION RESULTING FROM REDUCTIONS IN EMISSIONS?

This question cannot be answered generally with confidence. One can begin with a constrained version of this question and afterwards consider relaxing various constraints.

Simple case. A uniform X percent reduction of sulfur emissions over a broad region upwind of a receptor area will lead to approximately an X percent reduction in total deposition over the receptor area, provided that the deposition amounts compared are averages over several years and over a moderately large spatial area and provided that the amounts of co-emitted oxidants are not appreciably altered.

We can now try to relax each of the constraining assumptions.

Temporal averaging. The year to year variation in wet deposition at a point is substantial, perhaps 30 percent, so several years' averaging will be needed to be certain a reduction has occurred.

Spatial averaging. The averaging over the receptor region probably is unimportant provided that the temporal averaging has been done, that the region is relatively homogenous, and that it is small compared to the distance from most of the sources.

Co-emitted oxidants. Changes in the amounts of co-emitted oxidants may alter the predicted equality between the percentage reduction in emissions and the percentage reduction in average deposition. However, a substantial reduction in emissions will still lead to substantial reduction in average deposition.

Uniformity of reduction. A sulfur atom deposited at a receptor site will, typically, have traveled a substantial distance and will arrive at the receptor site in an air parcel containing sulfur atoms from many sources, many quite distant from the source of the first atom. When considering averages over several years, then, we would see a reduction in sulfur emissions at one source is likely to be very approximately equivalent to the same size of reduction at another source. As with the case of co-emitted species one cannot expect strict proportionality: an X percent emissions reduction that changes the mix of tall-stack and low sources or that changes the mix of intermediate and distant sources may not produce an X percent reduction in average deposition at a site. However, substantial reductions in emissions will lead to substantial reduction in deposition.

#### IV. INTEGRATION AND SUMMARY

##### 1. ARE THE SULFUR AND NITROGEN COMPOUNDS FOUND IN THE AIR, IN SOILS, AND IN WATER PRIMARILY FROM ANTHROPOGENIC SOURCES?

Yes, for air. Perhaps, for soils and water. For the eastern United States, anthropogenic sources account for at least 90 percent of the sulfur compounds found in air and at least 80 percent of the nitrogen compounds (ammonia and its salts, and nitrogen oxides). In soil and water systems, both anthropogenically derived and naturally derived sulfur compounds are important; the percentages cannot be readily established. Biological production of nitrogen compounds may about equal amounts from anthropogenic sources in many soil and water systems, however.

For concentrations of sulfur and nitrogen compounds in air, the argument is simple [see Sections III.A.2.7.5 and III.B.2.2.2]. No appreciable storage of these compounds occurs in the atmosphere (molecules remain in the air at most a few days), so the relative proportion of anthropogenically derived sulfur in the air directly reflects the proportion of current emissions into the air.

Aquatic and terrestrial sulfur flows will reflect atmospheric proportions of anthropogenic to non-anthropogenic sources, but because sulfur can be stored in these systems for substantial periods of time, it is necessary to ask whether the proportion more closely approximates that of the present, that of a decade or so ago or that of a century or more ago. Sulfur enters a soil system through several pathways: mineral weathering, precipitation, dry deposition on the soil, washout of material dry deposited on other surfaces (the forest canopy, for instance), and the fall and decomposition of biological material that has taken up sulfur either from the soil or the air. Two mechanisms of storage exist: storage in vegetation, (just alluded to) and storage of sulfur in the soil (adsorption of sulfur to soil particle surfaces or chemically combined in organic matter). Biological storage times are relatively short, a few years to perhaps decades. Adsorption of most sulfate deposited on soils can continue as long as several decades especially in the Ultisols of the Southeast. Much of the organically-bound sulfur in soils has accumulated over the centuries. Since by 1950 in the eastern United States sulfur compounds in the air were already at least 80 percent anthropogenically derived, even in soils with high adsorption of sulfate, there will be a substantial excess flow of sulfur over that to be expected with only naturally derived inputs.

Sulfur enters aquatic systems through all the same pathways it enters soils; in addition, water passing through soils may account for much of the sulfur entering an aquatic system. Like the soil system, the reservoir of water and sediments can also store sulfur. Because the average residence time for water is seldom longer than a decade, in most lakes only the sediments provide significant sulfur storage.

The case of nitrogen compounds is in one respect simpler, because nitrogen adsorption does not appear significant in soils. Complications arise,

however, because there are two important families of nitrogen compounds, ammonia with its salts, and nitrogen oxides. Biological activity can affect either family and convert between them, and nitrogen is frequently the limiting nutrient for many ecosystems. Furthermore, the biological process of nitrogen fixation of nitrogen gas from the air can act as another source of nitrogen compounds for soil and aquatic systems. Deposition of nitrogen compounds from the atmosphere (primarily anthropogenically derived in the eastern United States) dominates biological nitrogen fixation.

2. HAVE THERE BEEN ADVERSE EFFECTS THAT CAN RELIABLY BE ATTRIBUTED TO ACIDIC DEPOSITION?

Yes. Some lakes and streams have been made sufficiently acidic that their fish populations have been lost.

The earliest concerns about acid deposition in Europe and in North America were about harmful effects on aquatic systems. Although numerous difficulties deter obtaining reliable historical data on aquatic chemistry, enough studies have been done at enough different locations to provide a clear scientific consensus. pH or alkalinity declines have occurred in some surface waters over broadly distributed regions in Europe and North America; the only plausible explanation for these changes is acid deposition from anthropogenic sources. The changes in aquatic chemistry have in some cases led to those in fish populations; historical field evidence from the Adirondacks, Canada, and Scandinavia, as well as confirmation from laboratory and field studies show mechanisms through which changes in aquatic chemistry can harm both adult fish and fish reproduction.

Sufficient data do not exist to support a consensus on how many lakes and streams have been significantly altered or how many will change, for better or worse for fish, at current deposition levels.

Harmful effects of acidic deposition or its gaseous precursors on materials exposed to the air are well documented. How much damage can be attributed to broad regional background levels of acidifying substances (the acidic deposition phenomena that are the subject of this report), and how much is to be viewed as the result of local urban air pollution is still in question.

3. ARE THERE OTHER POTENTIALLY SERIOUS BUT NOT DEMONSTRATED ADVERSE EFFECTS OF ACID DEPOSITION?

Yes. Acidic deposition might be implicated in recently reported regional forest declines.

Over broad areas of the eastern United States and northern Europe substantial declines in coniferous forest growth and diebacks of forest areas have been observed (Section III.A.2.2.5). The declines or dieback appeared approximately 25 years ago, a period of time when emissions of acid precursors increased substantially (Section III.A.2.7). A number of mechanisms have been proposed relating forest declines to acidic deposition; however, more detailed observations attempting to establish the connection between declines and deposition have provided mixed evidence. Some support but also some

contrary evidence exists for each mechanism. The evidence for and against other mechanisms for forest decline, not involving acidic deposition, is similarly mixed (Section II.B.2).

#### 4. WHERE ARE THE AREAS WITHIN THE UNITED STATES IN WHICH ADVERSE EFFECTS ARE OCCURRING OR MAY OCCUR?

For acid deposition to cause adverse effects it is necessary both that the environmental system of concern be sensitive to deposition and that it actually receive substantial amounts of deposition. Except for comparatively small areas it appears that the combination of sensitivity and high deposition is found only in the northeastern and southeastern United States, especially in mountainous areas.

The environmental systems of most concern are aquatic systems--lakes and streams--and forests. An aquatic system appears to be vulnerable to acid deposition if it can provide only a limited amount of basic cations and if the terrestrial system within the watershed passes sulfur and/or nitrogen compounds through while adding only a limited amount of basic cations. High mountain terrain, where there are steep slopes and very little soil, passes sulfur and nitrogen compounds essentially unaltered. The same is true of areas where the predominant soil type is Spodosol--acid soils that provide limited amounts of basic material and do not adsorb sulfate. Spodosols are the predominant soil type over much of the northeastern United States.

Other soil types in which future effects on aquatic systems may occur are Ultisols together with certain Inceptisols. These also do not provide many basic cations; however, they do adsorb sulfate, thus slowing the response of the aquatic system to increased acid deposition. These soils predominate in the Southeast, and it is quite possible that at many locations the time before response would be between one and several decades. Since deposition in the Southeast probably increased one to two decades ago (based on changes in emissions; see Gschwandtner et al. 1985), these soil regions might be the locations where new adverse effects would be seen in the relatively near future.

In Figure II.5, we showed the regions whose terrain and soil type--mountainous terrain and Spodosols--give most concern for prompt response to acid deposition; and Ultisols and Inceptisols for delayed responses. Using the pH isopleths of wet deposition from Figure III.7 as representative contours for high deposition areas, we show in Figure IV.1 the deposition contours superimposed upon the terrain and soil regions of concern. Finally, we show in Figure IV.2 the deposition contours superimposed upon regions where extensive areas of low surface water alkalinity are found (portions of the regions identified  $< 200 \mu\text{eq l}^{-1}$ ). If deposition does not change appreciably in the next decades, the prompt response regions, mainly the Northeast and mountainous West, should have little change in alkalinity. As noted before, the alkalinity in delayed response regions, mainly southeastern water systems, may decrease.

Diebacks and declines have been observed in high elevation conifer forests in the Northeast; however, this distribution may reflect more the distribution

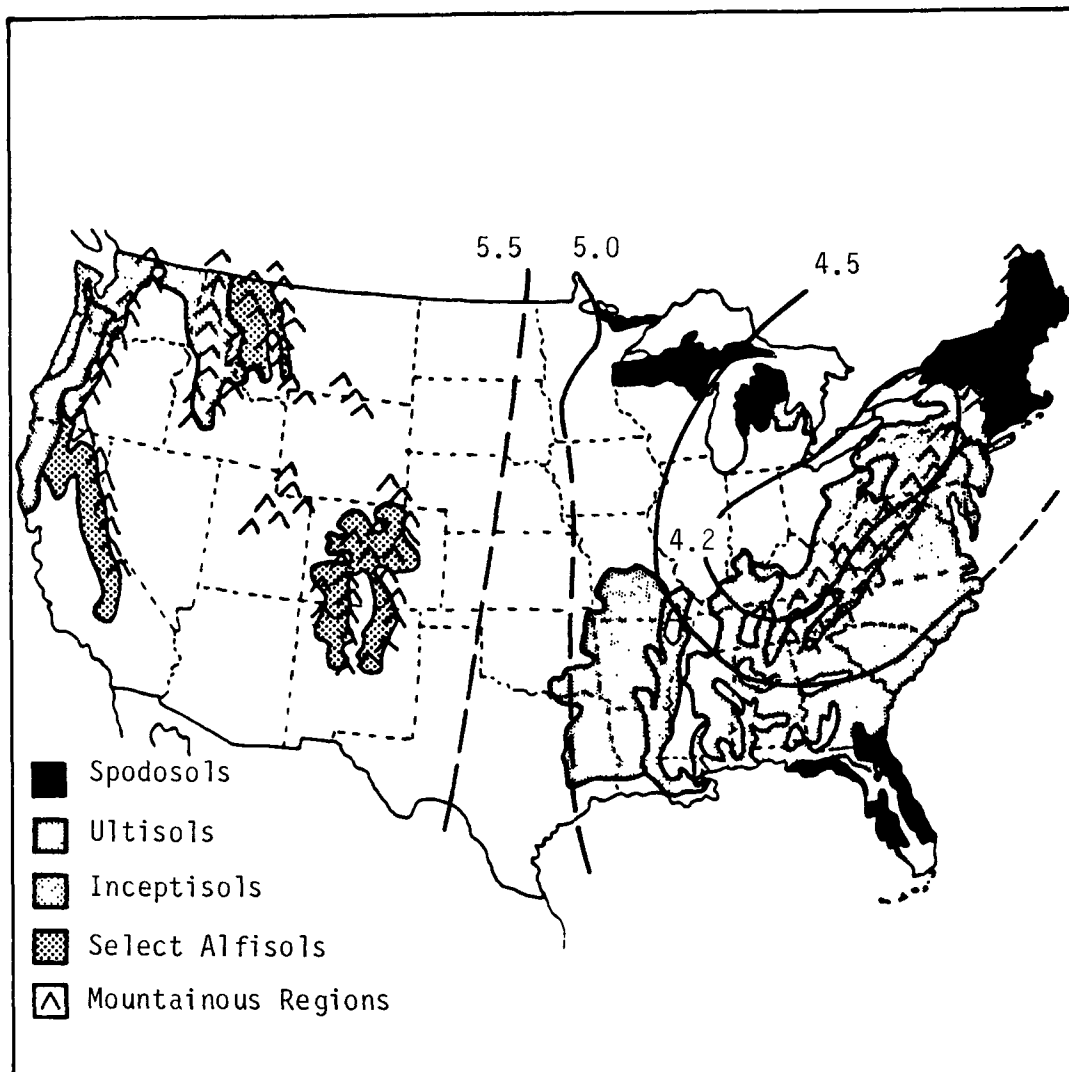


Figure IV.1 pH contour lines (Figure III.7) and soil regions of concern in the United States (Figure II.5).

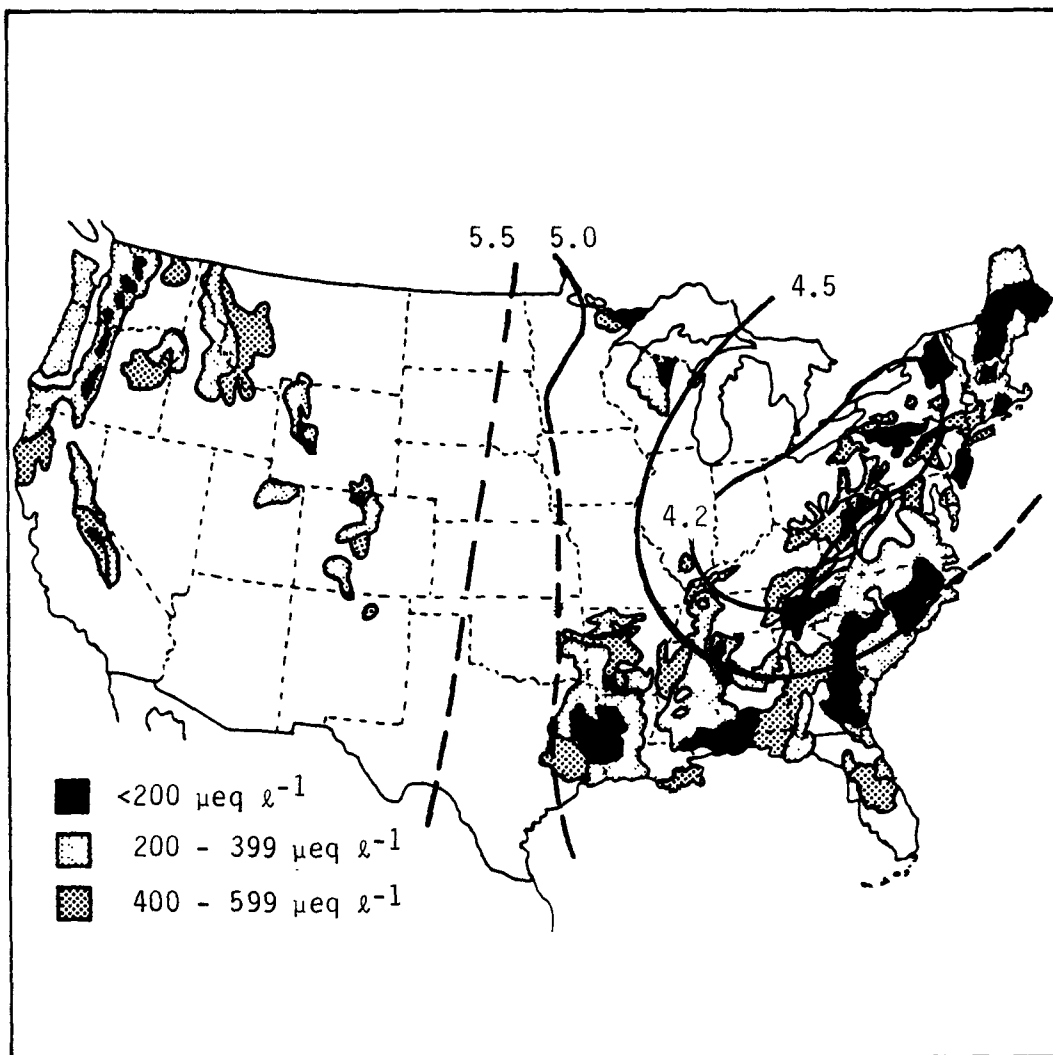


Figure IV.2 pH contour lines (Figure III.7) and low alkalinity surface waters in the United States (Figure II.10).



of observations than the actual distribution of impacted forests. We show in Figure IV.3 deposition contours and the distribution of high-elevation coniferous forests. To the extent that acidic deposition were to affect forests through changes in aluminum mobilization in soils, the most sensitive regions would be those having vulnerable trees where Spodosols predominate, with future impacts possible in Ultisol and Inceptisol regions. To the extent that acidic deposition directly affects foliage, the most sensitive regions would be found where deposition is heavy and vulnerable species of trees exist. Neither effect may prove to be important.

5. IS IT FEASIBLE TO IDENTIFY SOURCES RESPONSIBLE FOR THE DEPOSITION THAT PRODUCES ADVERSE EFFECTS?

All sources of sulfur and nitrogen compounds in the eastern United States and Canada contribute some acidic deposition to affected and sensitive areas. Emissions from these sources go into the atmosphere, are mixed, transformed over time by oxidizing agents, and eventually wet or dry deposited. A substantial fraction of the emissions will be transported well over 500 km from the source, and the deposition pattern from any source averaged over a year or so will be spread over a very large area. As noted in Section II.A.2.3.7, locales in eastern North America where acidic deposition appears to have decreased the pH or alkalinity of surface waters are scattered over a number of broad regions--New England, New York, New Jersey, Ontario, Nova Scotia. If acidic deposition were found to affect forests adversely, declines and diebacks would be expected to be similarly widespread, at least over high elevations.

To what extent is it feasible to apportion among sources the deposition causing adverse effects? One measure is the strength of the source, the number of tons of sulfur and nitrogen compounds emitted per year. This is not a bad first approximation to the relative importance of sources over a broad region, given that 1) sensitive areas are widely distributed, 2) a substantial amount of the emitted material is transported long distances, 3) there is considerable uncertainty in our knowledge of the determinants of long-range transport.

Some refinement in assessing the relative importance of sources is feasible. A source close to a sensitive region will contribute relatively larger amounts of sulfur or nitrogen than will a source farther away. Furthermore, prevailing weather patterns exist, at least in broad terms: on the average the wind blows more often from the Southwest to the Northeast; hence sources upwind will contribute relatively more to deposition in sensitive regions than sources downwind from them. These two effects can be seen by comparing deposition patterns with emission patterns. We show in Figure IV.4 emissions of sulfur within grids (EPRI-1983) for the eastern United States together with interpolated (CARP A-8) deposition lines for sulfur in rainfall. Deposition appears shifted north and east as expected. The reader should note that the deposition pattern here is slightly different from that in Figures IV.1, IV.2, IV.3 because it is sulfur compounds not pH measured. Also only wet deposition is shown, because we do not have adequate data on dry deposition to determine patterns. One further refinement is that sources

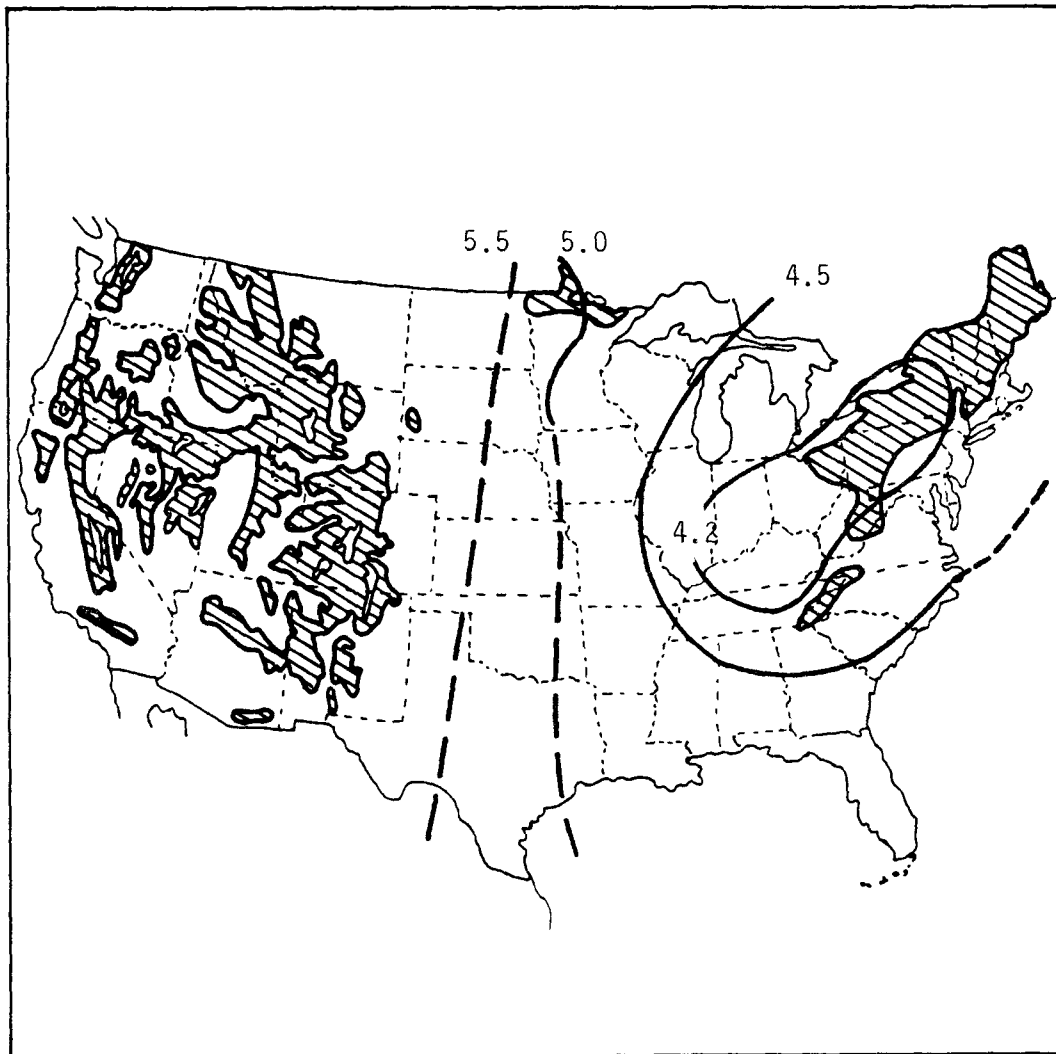


Figure IV.3 pH contour lines (Figure III.7) and high-elevation forests in the United States (Figure II.9).

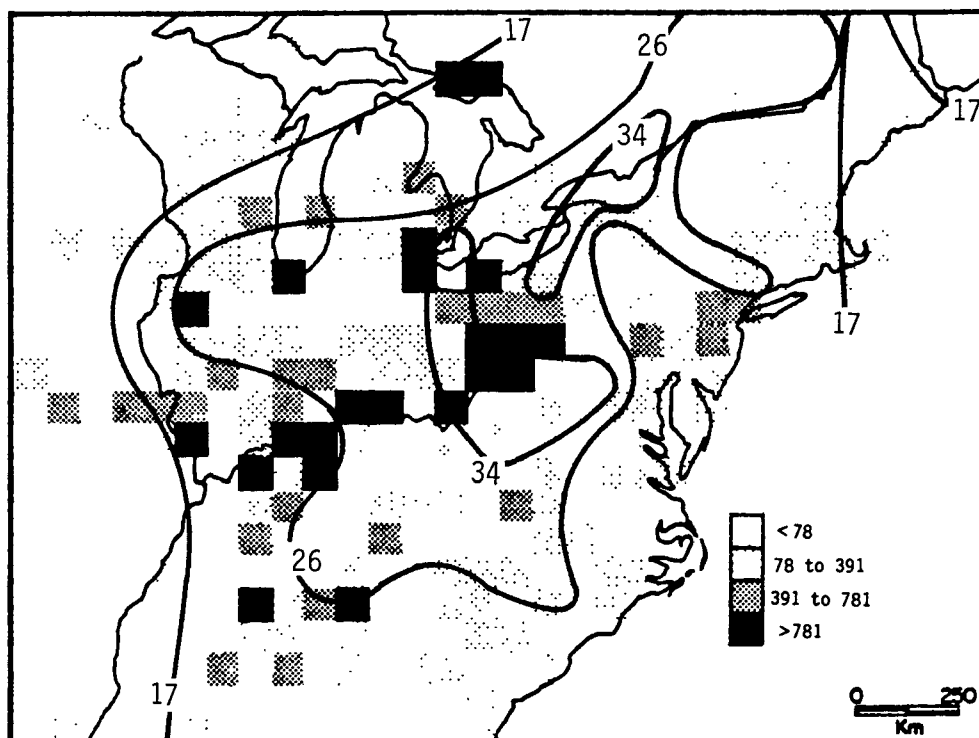


Figure IV.4 Distribution of sulfur emissions (calculated from  $\text{SO}_2$ ) in the SURE area (80 x 80 km grids) for summer 1977 and sulfur deposition contour lines from Figure III.4. Data are in g S ha<sup>-1</sup> day<sup>-1</sup>.

with tall stacks will have a somewhat greater proportion of their emissions transported long distances.

If, instead of considering the relative importance of sources to deposition at all sensitive and affected localities, we ask for the relative importance of sources to a specific region (though still a broad region), the data summarized in Figure IV.4, also permit some simple generalizations. We can consider three sensitive regions: the watersheds and forests of eastern New England and eastern Canada, the northeastern mountains (in New York and New England), and the southeastern mountains. For each region, Figure IV.4 shows the density of emissions from sources near and far upwind ("upwind" determined from the deposition pattern). Eastern New England is sufficiently far from most sources that most deposition comes from sources more than 500 km away. The northeastern mountains probably receive roughly equal amounts of deposition from sources farther than 500 km and nearer than 500 km. The southeastern mountains probably receive most of their deposition from sources within 500 km. These simple observations are supported by more detailed modeling (see III.B.1.4).

The presently available capability and supporting data are insufficient to give reliable predictions for the contribution of a localized source region to a localized receptor or to predict impacts of localized emission reductions, when the source is far from the receptor.

#### 6. WHAT EFFECTS CAN BE EXPECTED FROM CONTINUING PRESENT TRENDS IN SULFUR AND NITROGEN EMISSIONS?

In the absence of new efforts at regulating the emission of acid precursors, the best prediction appears to be that sulfur emissions will remain relatively constant in the next decade, while nitrogen oxide emissions will increase slightly both regionally and nationally. Total emissions of acid precursors are unlikely to change more than 10 percent. The prediction is based on continuing implementation of new source performance standards, which will tend gradually to reduce emissions as new sources replace old ones, and a moderate increase in economic activity, which will tend to increase emissions. These assumptions have operated over the past decade and emissions trends have satisfied the predictions, but other effects have been important: the enactment and implementation of the Clean Air Act amendments of 1970, which led to a substantial reduction of sulfur emissions in the early 1970's; fuel switching from oil to coal in response to the energy crisis, which increased sulfur emissions during the 1970's; and the economic recession which reduced emissions in the years beginning about 1980.

If emissions were to remain within 10 percent of their present values, then deposition amounts also would, although there might be some regional differences as patterns of emissions change. Thus deposition would be more likely to decline slightly in the Northeast and to increase slightly in the Southeast, judging from emissions trends in the recent past. Changes of 10 percent or less in average deposition are smaller than the year to year fluctuations in deposition amounts and thus would not likely produce noticeable changes in the response of either aquatic systems or forests.

The real question is whether future harm would show up as a result of the accumulation of acidifying substances at present levels of deposition. For the case of aquatic systems, the most important storage mechanism appears to be sulfate adsorption in soils; this would likely be important only in the Southeast. Thus, a continuation of deposition in today's amount would not likely change by very much the numbers of northeastern lakes and streams adversely affected, though some future change in individual lakes or streams, perhaps as a result of episodic fluctuations in deposition, could not be ruled out. In the Southeast it is possible that more lakes and streams would be adversely affected as the accumulation of sulfate made sulfate adsorption less of a barrier to the passage of sulfate into the aquatic system.

Because the mechanisms, if any, through which acid deposition might harm forests are not understood, and, in particular, forest response times are not known, it is impossible to say at present whether continued deposition would produce any adverse effects. Since forest growing times are as long or longer than the two decades or so that deposition has approximated its present values, accumulating damage would have to be considered possible.

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